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Oligomeric liquid crystals: Viscoelastic properties and surface interactions

DiLisi, Gregory Anthony, Ph.D.
Case Western Reserve University, 1992

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OLIGOMERIC LIQUID CRYSTALS: 
VISCOELASTIC PROPERTIES 
AND 
SURFACE INTERACTIONS 

by 

GREGORY ANTHONY DILISI 

Submitted in partial fulfillment of the requirements for 
the Degree of Doctor of Philosophy 

Thesis Advisor: Charles S. Rosenblatt 

Department of Physics 
Case Western Reserve University 
May 1992
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We hereby approve the thesis of
Gregory Anthony DiLisi
candidate for the Ph. D.
degree. *

Signed: [Signature]
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OLIGOMERIC LIQUID CRYSTALS:
VISCOELASTIC PROPERTIES
AND
SURFACE INTERACTIONS

ABSTRACT
by
GREGORY ANTHONY DI LISI

Liquid crystalline systems display some very unique and unusual qualities: they represent states of matter "caught" between a conventional liquid and solid. Liquid crystals flow and assume the shape of their container, as would be expected of a typical liquid, yet microscopically, they possess certain long-range order more common to a typical solid. Liquid crystals, therefore, are essentially identified by this assortment of intermediate, or mesomorphic, phases which they can assume.

Inherent to the discussion of liquid crystals is an understanding of the molecular building blocks, or components, of these mesomorphic systems. Traditionally, the constituent components are either one of two extremes. On one hand, the system is comprised of small, monomeric, organic molecules. The monomeric molecule is regarded as a short, stiff central core with possible flexible end-chains attached to each end. On the other hand lie the polymeric liquid crystals. These systems are comprised of many hundreds or thousands of monomers linked together to form a massive polymer backbone,
ultimately assuming the shape of a main-chain or side chain polymer liquid crystal. Both the monomeric and polymeric liquid crystals have attracted their own individual schools of thought in an effort to explain their unique characteristics. However, often overlooked in this spectrum of liquid crystalline building blocks is the oligomeric system. Here, the constituent components are molecular units of only a few (i.e. two-to-several tens) linked monomeric segments. Clearly, the oligomeric liquid crystal represents a crossover regime between typical monomeric samples and the those constructed from main-chain or side-chain polymers. In addition, not only can oligomeric specimens be synthesized of varying lengths, but of varying molecular shapes as well. For example, a dimer version of a particular species can be constructed by linking together two monomer units along a relatively straight conformation. Likewise, however, the two monomer units can be linked with an intrinsic rigid or flexible kink between the two successive monomer mesogens. Hence, oligomers offer an excellent opportunity to study liquid crystalline systems comprised of bent, or “banana-shaped”, molecules.

Oligomeric liquid crystalline systems, in addition to displaying many structural phase transitions, exhibit a variety of fascinating optical, magnetic, electrical, and mechanical properties which are sensitive to several experimental measuring techniques. In particular, as with any liquid crystalline sample, the oligomeric nematic phases, defined by their average orientational order parallel to the direction of the nematic director $\hat{n}$, are capable of experiencing three dimensional bulk deformations referred to as either splay, bend, or twist distortions. These distortions are easily quantified
via optical or magnetic probes. Crucial to these bulk deformations however, is the surface interaction between the nematic molecules and the external medium which contains the liquid crystalline sample. For example, not only does the nematic surface alignment ultimately determine which types of distortions occur within the bulk sample, but such surface considerations play an integral role in characterizing the sample response to possible applied external fields.

With this in mind, a battery of experiments was developed to study the viscoelastic properties and surface interactions of a dialkoxyphenylbenzoate monomer and its associated oligomers while in their respective nematic phases. These properties were determined as a function of temperature and were examined to determine their dependence on both molecular length, using the straight-dimer version of the series, and molecular shape, using the bent-dimer version of the series.

The quasi-elastic light scattering measurements are reported for three oligomeric samples. The splay and twist elastic moduli of the even-dimer are found to be nearly the same as that of the monomer. The even-dimer's bend modulus, however, shows an anomalous increase with decreasing temperature well below the nematic-isotropic phase transition. Monomer viscosities are consistent with typical literature values, although $\gamma_1 / \eta_{\text{splay}}$ and $\eta_{\text{bend}}$ seem to be larger than expected for the even-dimer, where $\gamma_1$ is the twist viscosity. The results are discussed in terms of viscoelastic properties of rigid and semi-flexible rods. Despite the apparently large population of fully extended even-dimers, neither the viscosities nor the elasticities are well described by past models, except for the possible exception of the bend
modulus. In this light, the recently-developed model of Petschek and Terentjev is discussed and found to be in good agreement with the elastic properties. Concerning the bent-dimer conformation, the ratio of the twist-to-splay elastic modulus is nearly the same as for the straight-dimer conformation. However, the ratio of the dimer's bend-to-splay modulus is considerably smaller in the bent conformation than in the straight conformation.

The anchoring strength coefficient $W$, for the oligomers are reported for different surface alignments as a function of reduced temperature. Utilizing the Freedericksz splay geometry, the monomer and even-dimer were aligned parallel to a buffered polyimide-coated glass substrate. A magnetically-induced Freedericksz transition in both thick and thin cells was used in conjunction with a capacitance technique to determine the anchoring strength coefficient as a function of temperature in the nematic phase. The results show $W$ increasing with decreasing temperature. The anchoring coefficient for the even-dimer, moreover, was found to be an order of magnitude larger than for the monomer at comparable reduced temperatures. While in this geometry, the splay elastic moduli were also determined for both species, and found to be of comparable magnitude, consistent with previous results.

Finally, utilizing the Freedericksz bend geometry, the monomer was aligned with its nematic director perpendicular to a lecithin-treated glass substrate. Again using the Freedericksz transition technique, the anchoring energy and bend modulus was obtained versus reduced temperature. The results show $W$ rapidly decreasing as the temperature is reduced. The bend elastic modulus was found to be entirely consistent with the result obtained in
the light scattering data analysis. The results of the surface anchoring measurements are meant to contribute to a wider body of data from which a complete microscopic understanding of surface effects might emerge.
This thesis is dedicated to my grandparents, Tommaso and Carmela Frate.
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# Table of Contents

Abstract ................................................................................................................................. ii

Acknowledgements .................................................................................................................. viii

List of Figures ........................................................................................................................... xvii

Chapter 1: Introduction

1.1 Overview .......................................................................................................................... 1
1.2 Possible Mesophases ......................................................................................................... 3
1.3 Liquid Crystal Components ............................................................................................... 7
1.4 Liquid Crystal Phases ........................................................................................................ 12
1.5 Polymer Liquid Crystals .................................................................................................... 26
1.6 Oligomeric Liquid Crystals ............................................................................................... 30
1.7 Motivation of Thesis and Experiments .............................................................................. 33
1.8 The Oligomeric System Under Investigation .................................................................. 36
1.9 Outline of Experiment ...................................................................................................... 39

Chapter 2: Theory

2.1 The Continuum Theory ..................................................................................................... 43
2.2 Remarks ............................................................................................................................ 49
2.3 Boundary Effects ............................................................................................................ 50
2.4 Effects of Bulk Distortions on Surface States ................................................................. 54
2.5 Concluding Remarks ........................................................................................................ 60
2.6 Magnetic Field Effects ..................................................................................................... 61
2.7 Magnetic Diamagnetism .................................................................................................. 62
2.8 The Freedericksz Effect ................................................................................................... 66
2.9 Calculation of the Magnetic Freedericksz Threshold Field ............................................. 73
2.10 Magnetic Coherence Length .......................................................................................... 78
2.11 Response Time of the Freedericksz Transition ............................................................... 81
2.12 The Case of Weak (or Finite) Surface Anchoring ........................................................... 84

xiii
2.13 Calculation of the Critical Field in the Case of 
Finite Surface Anchoring .......................................... 93
2.14 Fluctuations in Nematic Alignment ...................... 96
2.15 Orientation Fluctuations and Correlations in 
Nematic Liquid Crystals ......................................... 98
2.16 Scattering of Light by Orientation 
Fluctuations .......................................................... 102

Chapter 3: Experimental: Light—Scattering
3.1 Quasi—Elastic Light Scattering .............................. 110
3.2 Configuration A — Homogeneous Alignment 
Splay/Twist Geometry ............................................. 113
3.3 Configuration B — Homogeneous Alignment 
Bend/Twist Geometry .............................................. 121
3.4 Configuration C — Homeotropic Alignment 
Bend/Twist Geometry .............................................. 128
3.5 Light Scattering Techniques ................................. 134
3.6 Filter Methods .................................................... 135
3.7 Optical Mixing Techniques ................................. 136
3.8 Homodyne Scattering .......................................... 138
3.9 Heterodyne Scattering ......................................... 141
3.10 Experimental Homodyne Autocorrelation 
Function ............................................................. 145
3.11 Sample Preparation and 
Experimental Apparatus .......................................... 149
3.12 Experimental Caveats .......................................... 154
3.13 Refractive Indices .............................................. 156
3.14 Measuring the Average (Isotropic) 
Refractive Index .................................................... 158
3.15 Measuring the Birefringence ................................. 162
3.16 Measuring the Ordinary Refractive Index ............ 165
3.17 Materials Summary ............................................ 167
3.18 Normalized Intensity Measurements .................... 172
3.19 Experimental Angular Calibration 
Verification ......................................................... 181
3.20 Freedericksz and Angular Calibration 
Verification ......................................................... 181
3.21 Data Analysis ................................................... 185
3.22 Error Contributions and Analysis ......................... 189
3.23 Error Summary .................................................. 201
3.24 Analysis Parameters ............................................. 203

Chapter 4: Experimental: Fredericksz
4.1 Anchoring Strength Coefficient:
   Infinite and Finite Anchoring ................................... 228
4.2 Experimental Procedure .......................................... 231
4.3 Homogeneous Alignment:
   Sample Preparation ................................................. 233
4.4 Homogeneous Alignment:
   Results ................................................................. 239
4.5 Homeotropic Alignment:
   Sample Preparation ................................................. 247
4.6 Homeotropic Alignment:
   Results ................................................................. 253
4.7 Error Contributions and Analysis ......................... 259

Chapter 5: Results
5.1 Homeotropically-Aligned Anchoring Results .... 267
5.2 Homogeneously-Aligned Anchoring Results .... 271
5.3 Light Scattering Results: Characterizing the
   Viscoelastic Properties as a Function of the
   Molecular Length-to-Diameter Ratio by
   Comparing the Monomer and Even-Dimer
   Light Scattering Results ........................................... 276
5.4 Light Scattering Results: Characterizing the
   Viscoelastic Properties as a Function of the
   Molecular Shape by Comparing the Even-Dimer
   and Odd-Dimer Light Scattering Results .............. 283
5.5 Future Work ........................................................... 290
Appendix A: Interferometric Scheme for Determining the Sample Thickness ........................................ 297
Appendix B: Eigen-Equation for Determining the Effective Refractive Index of a Uniaxial and Biaxial Crystal .... 302
Appendix C: Autocorrelator Counting Routine ................................. 312
Appendix D: Distortions Associated with Motion along the Unit Vectors \( \hat{e}_1 \) and \( \hat{e}_2 \) .................................................. 318

Bibliography ........................................................................... 327
# List of Figures

## Chapter 1

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-1</td>
<td>Typical Liquid Crystalline Molecular Core</td>
<td>7</td>
</tr>
<tr>
<td>1-2</td>
<td>Amphiphilic Tubule or Leaflet</td>
<td>11</td>
</tr>
<tr>
<td>1-3</td>
<td>Isotropic Phase</td>
<td>13</td>
</tr>
<tr>
<td>1-4</td>
<td>Nematic Phase</td>
<td>16</td>
</tr>
<tr>
<td>1-5</td>
<td>Representation of a Chiral Molecule</td>
<td>19</td>
</tr>
<tr>
<td>1-6</td>
<td>Cholesteric Phase</td>
<td>20</td>
</tr>
<tr>
<td>1-7</td>
<td>Smectic A Phase</td>
<td>21</td>
</tr>
<tr>
<td>1-8</td>
<td>Smectic C Phase</td>
<td>23</td>
</tr>
<tr>
<td>1-9</td>
<td>Thermotropic Liquid Crystalline Phases</td>
<td>25</td>
</tr>
<tr>
<td>1-10</td>
<td>Main-Chain Polymer Liquid Crystal</td>
<td>27</td>
</tr>
<tr>
<td>1-11</td>
<td>Side-Chain Polymer Liquid Crystal</td>
<td>28</td>
</tr>
<tr>
<td>1-12</td>
<td>Even/Odd Effect</td>
<td>31</td>
</tr>
<tr>
<td>1-13</td>
<td>&quot;Crossover&quot; Behavior of Oligomers</td>
<td>32</td>
</tr>
<tr>
<td>1-14</td>
<td>Molecular Length-to-Diameter Ratio</td>
<td>34</td>
</tr>
<tr>
<td>1-15</td>
<td>Molecular Shape</td>
<td>35</td>
</tr>
<tr>
<td>1-16</td>
<td>Molecules Used in Study</td>
<td>38</td>
</tr>
</tbody>
</table>

## Chapter 2

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-1</td>
<td>Nematic Distortions</td>
<td>44</td>
</tr>
<tr>
<td>2-2</td>
<td>Nematic Distortion Coordinate System</td>
<td>47</td>
</tr>
<tr>
<td>2-3</td>
<td>Molecular Alignment at a Rubbed Surface Interface</td>
<td>52</td>
</tr>
<tr>
<td>2-4</td>
<td>Comparison of Homeotropic and Homogeneous Alignment</td>
<td>53</td>
</tr>
<tr>
<td>2-5</td>
<td>Nematic Twist Distortion Geometry</td>
<td>54</td>
</tr>
<tr>
<td>2-6</td>
<td>Nematic Profile Near a Surface Interface</td>
<td>56</td>
</tr>
<tr>
<td>2-7</td>
<td>Magnetic Orientation of a Benzene Ring</td>
<td>62</td>
</tr>
<tr>
<td>2-8</td>
<td>Freedericksz Geometries</td>
<td>68</td>
</tr>
<tr>
<td>2-9</td>
<td>Dielectric Constant Versus Magnetic Field</td>
<td>70</td>
</tr>
<tr>
<td>2-10</td>
<td>Detector Intensity Versus Magnetic Field</td>
<td>72</td>
</tr>
<tr>
<td>2-11</td>
<td>Freedericksz Splay Geometry</td>
<td>74</td>
</tr>
<tr>
<td>2-12</td>
<td>Minimum Freedericksz Distortion</td>
<td>76</td>
</tr>
<tr>
<td>2-13</td>
<td>Typical Light Scattering Geometries</td>
<td>96</td>
</tr>
<tr>
<td>2-14</td>
<td>Geometry for Dipole Radiation</td>
<td>103</td>
</tr>
</tbody>
</table>
Chapter 4

Figure 4–1: Magnetically–Induced Splay Distortion 236
Figure 4–2: Oven and Sample Holder for Homogeneous Alignment 237
Figure 4–3: Block Diagram of Capacitance Technique 238
Figure 4–4: Experimental Dielectric Constant Versus Magnetic Field 242
Figure 4–5: Threshold Fields for Monomer – Homogeneous Alignment 243
Figure 4–6: Threshold Fields for Even–Dimer – Homogeneous Alignment 244
Figure 4–7: Splay Elastic Constant for Monomer and Even–Dimer 245
Figure 4–8: Anchoring Strength Coefficient for Homogeneous Alignment 246
Figure 4–9: Magnetically–Induced Bend Distortion 250
Figure 4–10: Oven and Sample Holder for Homeotropic Alignment 251
Figure 4–11: Block Diagram of Birefringence Technique 252
Figure 4–12: Experimental Detector Intensity Versus Magnetic Field 255
Figure 4–13: Threshold Fields for Monomer – Homeotropic Alignment 256
Figure 4–14: Bend Elastic Constant for Monomer 257
Figure 4–15: Anchoring Strength Coefficient for Homeotropic Alignment 258

Chapter 5

Figure 5–1: Monomer Homeotropically–Aligned Anchoring Coefficient 267
Figure 5–2: Monomer and Even–Dimer Homogeneously–Aligned Anchoring Coefficients 271
Figure 5–3: Monomer and Even–Dimer Splay Elastic Constants 272
1. INTRODUCTION

1.1 – Overview

Liquid crystals were first observed in the late nineteenth century by F. Reinitzer and O. Lehman. In 1888, Reinitzer, an Austrian botanist, wrote a letter to Lehman describing the discovery of a substance with two melting points. Reinitzer continued by saying that at 145.5 °C, the substance appeared to be a cloudy, fully liquid melt, while at 178.5 °C, the unknown substance became completely clear. Lehman, also working on materials with similar behavior, responded by labeling the substances as “liquid crystals”. Since that time, thousands of organic compounds have likewise been found to exhibit this same type of behavior[1].

The term “liquid crystal” might at first appear to be an oxymoron. Typically, matter is viewed as existing in three states: solid, liquid, or gas. The existence of a substance labeled as both a liquid and a solid may appear, initially, to be counter-intuitive. However, as described above, certain organic materials do not demonstrate a simple transition from solid to liquid, but rather display intermediate phases characteristic of both a liquid and a solid. Liquid crystals, as the name suggests, are states of matter between a conventional liquid and solid: they flow and take on the external shape of their container, as in a traditional liquid; however, they also display the anisotropic properties, such as orientational or translational order, that are more characteristic of a
solid. The mechanical and symmetry properties of these materials are intermediate between those of a liquid and those of a crystal. For this reason, liquid crystals are also commonly referred to as exhibiting or possessing "mesomorphic phases"[2].
1.2 – Possible Mesophases:

For a given material, the differences between the solid and liquid phase are most accurately described by the degree of order with which the component molecules arrange themselves. Inherent to the crystalline structure is the three dimensional regularity of the components: the centers of mass of the various molecules, or groups of molecules, are regularly stacked; occupying positions on a periodic three dimensional lattice. In a liquid, on the other hand, the centers of mass of the constituent components are generally regarded as not having any three dimensional periodicity. The question which then arises is in what ways can these “mesophases” possibly exist. The answer is twofold:

(i) One Dimensional Ordering
An interesting mesophase can be established by imposing positional order in one, rather than three, dimensions. In this light, the mesophase is viewed as a system of two dimensional layers stacked on top of each other, separated by a quasi-long range spacing. Clearly the layers themselves act as a conventional liquid, while the overall system has some periodic structure more common to a crystal. This type of mesophase is called a smectic phase, a term coined after the Greek word for “soap”[2].
(ii.) **Positional or Orientational Order in Anisotropic Molecules**

Mesophases of crystalline solids can occur by either losing orientational order in the molecular distribution while maintaining translational order or by losing translational order while maintaining orientational order\[^{[2]}\):

(a.) **Maintaining Positional Order**

Many crystals show a transition from a strongly-ordered state to a phase where each molecule commutes between several equivalent orientations, thus positional order is kept while orientational ordering is sacrificed. These crystals are commonly referred to as *plastic crystals* and include such examples as solid hydrogen and ammonium halides.

(b.) **Maintaining Orientational Order**

Most liquid crystals, having a phase which falls into this category, demonstrate a phase where the molecules are preferentially aligned along one direction. This phase, labeled the *nematic phase*, involves molecules which are orientationally ordered, but positionally disordered. The word nematic translates from the Greek word for “thread”, since thread-like disclination lines commonly occur in most nematic specimens.
At this point, the different types of mesophases must be classified, so as to clarify the commonly-used nuances associated with the field. The designation “liquid crystals” is generally used to describe materials possessing a nematic and/or smectic phase. As described above, for such phases to exist, the component molecules must be anisotropic, either elongated or disk-like, in shape. Conversely, the “plastic crystals” are comprised of constituents which are nearly (but not perfectly) spherical in shape; hence permitting positional order at the cost of orientational order.

The bulk of this thesis focuses on materials characterized as “liquid crystals” and, more specifically, on the viscoelastic properties and surface interactions occurring in the nematic phase of these materials. However, in the interest of cultural and historical review, the generalities of liquid crystalline phases are discussed; the field of plastic crystals is considered to be very distinct from that of liquid crystals and will not be discussed further. Also, to facilitate the discussion of various systems in this, and subsequent chapters, some of the more common molecular compound groups are summarized on the following page:
Table 1 - 1: Summary of Common Molecular Components of Liquid Crystals
1.3 – Liquid Crystal Components

Liquid crystalline systems which are capable of forming either nematic and/or smectic phases are typically comprised of one of three types of elongated molecular components:

(i.) **Small Organic Molecules**

The majority of liquid crystals are those whose components come from a broad class of small organic molecules. These organic molecules typically share the characteristics of the general pattern given below:

![Diagram of typical liquid crystalline molecular core]

**Figure 1 – 1: Typical Liquid Crystalline Molecular Core**

The rigid core of the molecule is composed of two benzene rings linked together directly or by an intermediate group (such as a Schiff base) represented schematically by the \( (A=B) \) pair.
Attached to the core are partly flexible end-chains varying in length; often the chains are alkyl groups, linked directly to the benzene rings, or by an intermediate oxygen or ester. Since the end-chains are generally flexible, their conformations depend on a variety of factors. However, in many applications, the flexibility of the end-chain may be neglected and the entire molecule is viewed as a single cylindrical rigid rod. These end-chains, which need not be symmetric about the core, are represented in (Figure 1 – 1) by the (R) and (R') chains. Also in the liquid crystalline systems described above, the phase transitions are almost always induced by temperature changes and hence are denoted as thermotropic systems.

The elongated organic molecules traditionally associated with liquid crystals widely vary in a number of parameters. The viscosities vary between 0.1 to 1.0 Poise; the optical birefringence for liquid crystals typically range from 0.05 to 0.25, which is comparable to the optical birefringence of most uniaxial crystals; and the length of the components vary from 20 Å for monomeric specimens to tens of microns for polymeric materials[3].

As will be described shortly, the system studied in this thesis is a thermotropic, oligomeric (this term will likewise be defined later) system, comprised of small organic molecules of varying length. The exact molecular structure of the system under investigation will be described later.
(ii.) **Rods in a Liquid Substrate**

Most rod-like structures in a suitable solvent will likewise form the various phases associated with liquid crystals[^2]. For example, a system of synthetic polypeptides, in concentrated solutions, will give rise to liquid crystalline mesophases. Similar phases also occur in the more common systems of deoxyribonucleic acids (DNA), tobacco mosaic viruses (TMV), and glass or plastic fibers suspended in water. Typically, when dealing with these systems, one must consider the poly-dispersity of size of the rod-like structure. Fortunately, for such examples as the TMV system, the rods from one virus species are almost exactly the same, having the values: length $= 3000 \text{ Å}$ and width $= 200 \text{ Å}$. In these systems, contrary to the thermotropic systems, the various phases are induced by changes in the concentration of the rods. Hence, these systems are referred to as *lyotropic* liquid crystals.
(iii.) **Amphiphilic Compounds and Associated Structures**

An amphiphilic compound is a chain consisting of an anion head (e.g. \( \text{CO}_3^- \)) and a tail containing a positive ion (e.g. \( \text{NH}_4^+ \)). Thus an amphiphile is a compound that both "likes" and "hates" water; the polar head of the acid, the aliphatic ion, tends to favor proximity to water molecules while the remaining apolar chain avoids water\(^3\). Obviously, a single unit of these amphiphilic compounds in water cannot satisfy the preferences of both the polar head and apolar chain. However, a cluster of these compounds, when immersed in water, forms rods or leaflets which can satisfy the conflicting preferences of the head and tail chain. These leaflets, in turn, form the elongated or disk-shaped structures (called *micelles*) necessary for liquid crystal mesophases. A schematic of such a leaflet is shown below:
Figure 1 – 2: Depiction of Amphiphilic Tubule or Leaflet

These amphiphilic leaflet-structures may form mesophases which are induced either thermotropically or lyotropically.

As stated earlier, this thesis extensively investigates the viscoelastic properties and surface interactions of a thermotropic oligomeric liquid crystalline system in the nematic phase. Although the entire body of data soon to be presented was obtained while in the nematic phase, the most common liquid crystal phases will be described.
1.4 – Liquid Crystal Phases

Probably the most interesting property of liquid crystals is the variety of phase transitions which they often experience. As mentioned earlier, two quantities are responsible for driving the transitions: changes in either temperature (thermotropic) or concentration (lyotropic). Because this thesis deals exclusively with thermotropic materials, the most common phases and the associated parameters of a common thermotropic system will be discussed. Although the types of transitions and order in which they occur, vary for different materials, the discussion below represents a typical thermotropic liquid crystalline material:
(i.) **Isotropic Phase**

At high enough temperatures, the liquid crystalline material exists in its isotropic phase. The isotropic phase of a such a system is characterized as a true liquid phase. The optical, mechanical, electrical, and magnetic properties of the system are totally independent of coordinate choice[^4]. Being optically isotropic, the birefringence $\Delta n$, of the sample is ideally zero, and the material appears totally dark under crossed-polarizers. Note that for a material centered between crossed-polarizers, the transmitted intensity is proportional to $\sin^2(\phi / 2)$, where $\phi = 2\pi d(\Delta n)/\lambda$. is the total sample phase shift and $d$ is the sample thickness[^5]. At this point, the molecular “director” is defined as a unit vector $\hat{n}(\vec{r})$, which is oriented along the long axis of the molecule whose center of mass is located at point $\vec{r}$.

**Figure 1-3: Schematic Representation of the Isotropic Phase**
In the isotropic phase, the spatial average of $\hat{A}(\vec{r})$ is zero. The system has no long range order and the correlation function $G(\vec{r}) = \langle S(0)S(\vec{r}) \rangle$ is proportional to $e^{-r/\xi}$, where $\xi$ is the isotropic correlation length and $S$ is the scalar nematic order parameter which will be discussed in greater detail in the next section\textsuperscript{[5]}. As the temperature decreases, the molecules begin to register themselves over long length scales. Suddenly and discontinuously, as the nematic-isotropic phase transition temperature (denoted by $T_{NI}$) is crossed, $G(\vec{r})$ approaches some finite value as $\vec{r}$ approaches infinity: a first order phase transition brings the system into an anisotropic state and is considered to be in its nematic phase.
(ii.) **Nematic Phase**

Below $T_{NI}$, long range orientational order is established between the molecules. Each molecule's director $\hat{n}(\vec{r})$ is, on the average, pointing along some particular direction $\hat{n}$. This direction $\hat{n}$ describes the alignment of the nematic sample and is called the "nematic director". The optical, mechanical, electrical, and magnetic properties of the nematic system are anisotropic and usually characterized as uniaxial. Several other interesting properties characterize the nematic phase:\[2\]:

(a.) The centers of mass of the molecules have no long range order. In other words, the centers of the molecules act, for the most part, as a conventional liquid.

(b.) The direction of $\hat{n}$ is arbitrary in space; usually determined by boundary forces imposed at the surface interfaces of the sample. The various techniques used to establish the desired direction of $\hat{n}$ are discussed in detail in Chapter 2.

(c.) The states $+\hat{n}$ and $-\hat{n}$ are indistinguishable. For example, if each molecule had an electric dipole parallel to $+\hat{n}$, and all molecules preferentially aligned along the $+\hat{n}$ direction, then the system would be ferroelectric. To prevent this, an equal number of molecules are directed along $+\hat{n}$ as are along $-\hat{n}$, and the states are considered identical.

(d.) The nematic phase does not distinguish "handedness". In other words, each molecule must be identical to its mirror image, or, if a chiral molecule is present (i.e. a right- or left-handed molecule which is different from its mirror image), the sample must be racemic (i.e. containing a 1-to-1 mixture of right- and left-handed molecules). The cholesteric phase, which will be discussed briefly, describes systems whose molecules are chiral and are mixed in a non-racemic ratio.
The nematic phase is most easily described by a parameter denoted as the "scalar nematic order parameter". If $\theta(\vec{r})$ represents the angular deviation of a particular molecule's orientation $\hat{n}(\vec{r})$ from the nematic director $\hat{n}$, then clearly the spatial average of $\theta(\vec{r})$, in a crude sense, represents a measure of how well the entire sample is aligned.

**Nematic Phase**

$\theta(\vec{r})$ is the angular deviation of $\hat{n}(\vec{r})$ from $\hat{n}$.

**Figure 1 – 4: Schematic Representation of the Nematic Phase**

Thus, the nematic tensor order parameter is introduced which, for uniaxial systems, has the form:

$$Q_{ab} = S \left( n_a n_b - \frac{1}{2} \delta_{ab} \right) \quad \text{Eq. 1.1}$$

where $S$ is referred to as the scalar nematic order parameter and is defined as:
\[ S = \frac{1}{2} \langle (3 \cos^2 \theta(\vec{r}) - 1) \rangle. \]  

Eq. 1.2

As usual, the braket notation represents a statistical spatial averaging. Clearly, for an ideal, perfectly ordered solid, \( S = 1 \); while for a typical liquid, \( S = 0 \). Most liquid crystals, across their entire nematic temperature range, have an intermediate value of the scalar nematic order parameter of about \( S = 0.5 \) to 0.7, but this is highly dependent on temperature, especially when near a phase transition temperature.\[d\]
(iii.) **Cholesteric or Helical Phase**

As just noted, the cholesteric phase is very similar to the nematic phase; the primary difference being that the molecular components are chiral in the cholesteric phase. In fact, the cholesteric phase is often referred to as the Nematic\* or N* phase. As in the nematic phase, the cholesteric phase is characterized by a lack of positional order in the centers of mass of the constituent molecules and also by the preferential alignment of the molecules along the direction of an axis labeled as \( \hat{n} \). When a chiral molecule is introduced as the nematic component, the system forfeits a mirror plane of symmetry\(^6\); the following argument depicts the handedness of the chiral molecule by a pen possessing a single inscription on its upper half. The handedness of the molecule is determined by the orientation of the inscription relative to some symmetric surface:
Figure 1 – 5: Schematic Representation of a Chiral Molecule – Upon reflection, the pen loses a mirror plane of symmetry due to the inscription on its upper-half.

The loss of the mirror symmetry operation causes \( \hat{n} \) not to be a constant in space; instead, the preferred conformation is helical. While in the cholesteric phase, the molecular director twists as the sample thickness is traversed. The pitch of this helical twist is determined by the chemical composition of the molecule as well as the temperature. The cholesteric phase is schematically represented on the following page:
$\hat{n}(\tilde{r})$ changes as a function of $z$ according to:

$$\hat{n}(z) = (\cos(q_o z + \phi_o), \sin(q_o z + \phi_o), 0)$$

typically, the pitch is large on the molecular scale,

$q_o a = 10^{-2}$.

Figure 1 – 6: Schematic Representation of the Cholesteric Phase
(iv.) **Smectic Phases**

The final phase which will be examined is the smectic phase. As the temperature is lowered still, the nematic liquid crystal sample enters into one of several layered phases, the most common of which are the smectic A and smectic C phases. Note that the smectic phases, which are more ordered than the nematic phase, always occur at temperatures below the nematic temperature range. The smectic A and C phases will be discussed separately:

**Smectic A Phase**

A schematic of the smectic A phase is shown below:

![Smectic A Phase Diagram](image)

**Figure 1 – 7: Schematic Representation of the Smectic A Phase**

In the smectic A phase, a degree of translational order has been introduced which was absent in the higher temperature nematic phase. The molecules are still preferentially oriented along the
direction denoted by \( \hat{n} \), however, the molecules are now arranged in layers whose normal is parallel to \( \hat{n} \). For the most part, the molecules are confined to motion within a layer. The nematic-smectic A phase transition, occurring at the transition temperature \( T_{NA} \), is usually a second order transition, although some materials display a transition which is clearly first order. The smectic A phase is characterized by the following properties\[^{22}\]:

(a.) The layered structure is typically the length of the constituent molecule although several materials have smectic layer spacings ranging between one and two molecular lengths.

(b.) Inside each layer, the molecules show no long range order. Each layer acts as a two dimensional liquid.

(c.) The system is optically uniaxial with the optical axis being the normal to the layers (i.e. along \( \hat{n} \)).

(d.) The directions \( +\hat{z} \) and \( -\hat{z} \) are totally equivalent, where \( \hat{z} \) is the layer normal.
Smectic C Phase

A schematic of the smectic C phase is shown below:

Figure 1 – 8: Schematic Representation of the Smectic C Phase

As the temperature is lowered below $T_{AC}$, a phase transition occurs in which the smectic A layered structure is retained, yet the molecules experience a tilt $\theta_T$ with respect to the layer normal. The material is now in the smectic C phase. Presently, several theories have been formulated to explain the mechanics of this phase transition. The smectic C phase is characterized by the following properties:

(a.) As in the smectic A phase, inside each layer, the molecules show no long range order. Each layer acts as a two dimensional liquid.

(b.) The system is optically biaxial as opposed to the smectic A phase's optical uniaxiality.

As a final note concerning the smectic C phase, recall that if the
constituent chiral molecule is substituted for a non-chiral species in the nematic phase, the cholesteric, or N*, phase results. Likewise for the smectic C phase, the aforementioned smectic C structure is obtained only when the constituent molecules are optically-inactive, or chiral but in a racemic mixture. If, in fact, optically-active molecules are present in the smectic C phase, the structure will distort in a fashion similar to that occurring in the nematic phase. The direction of the tilt given by $\theta_T$ precesses around the z-axis (the axis normal to the layers) and the helical configuration smectic C* is obtained$^{[2,4]}$. 
In addition to the phases just described, many other fascinating liquid crystalline phases are known to exist. For example, the smectic C* phase was only briefly mentioned above, yet this phase, which allows for the existence of a spontaneous electric dipole moment, is worthy of its own dissertation. Other phases include the smectic B phase, which contains order within the smectic layers and thus makes it the most ordered of the smectic phases, as well as the "exotic" smectic phases which range in denomination from smectic D through smectic O. Regardless of the specific material under investigation, the typical thermotropic liquid crystalline specimen has behavior which can be diagrammatically summarized below:

![Diagram of liquid crystalline phases](image)

**Figure 1 – 9: Summary of Typical Thermotropic Liquid Crystalline Phases**
1.5 – Polymer Liquid Crystals

The systems previously described emphasized the formation of liquid crystalline phases which were driven by thermotropic processes and whose constituent components were generally regarded as small organic molecules. However, recent developments in macromolecular science have shown that certain polymer systems also display the various mesophases more commonly associated with liquid crystalline systems. Such polymer systems have been coined “polymer liquid crystals” or PLC’s. Not only do polymer liquid crystals provide new insight into conventional liquid crystalline and polymeric systems, but they have significant technological importance in their own right. The generalities of polymer liquid crystalline materials will now be discussed. Traditionally, two methods are available to synthesize polymer liquid crystals:
(i.) **Main-Chain Polymer Liquid Crystals**

Recall that the most common liquid crystal components are the small organic molecules typically comprised of a rigid benzene–spacer–benzene core, with semi-flexible end-chains of varying length attached to each end of the core. Such a structure is referred to as the "monomeric unit" or "monomeric mesogen", since the polymeric systems will ultimately be built by linking together many of these single units. Main-chain polymer liquid crystals are constructed by linking together appropriate monomer mesogens into a polymer backbone. If the single mesogen end-chains are suitable, they may link together and, in turn, couple the mesogenic cores into a polymer "chain" or "backbone":

![Schematic Representation of a Main-Chain Polymer](image)

**Figure 1 – 10: Schematic Representation of a Main-Chain Polymer**

The chain may be many hundreds or even thousands of units in length and the end-chain linkage may cause the backbone to be either rigid, flexible, or both: depending on the constituent monomers, the backbone may be formed of alternating rigid and flexible segments.
(ii.) **Side-Chain Polymer Liquid Crystal**

Another method of synthesizing polymer liquid crystals results in a structure appropriately described as a side-chain polymer liquid crystal. If the mesogenic monomers contain end-chains which themselves can polymerize, a backbone can be formed which results in the mesogenic cores dangling from the backbone as a side chain. A schematic representation of this type of polymerization closely resembles a household pocket-comb and for this reason, these materials are also called "comb polymers"[^1]:

![Diagram of a side-chain polymer liquid crystal](image)

**Figure 1 – 11: Schematic Representation of a Side-Chain Polymer**

The crucial consideration in predicting the properties of a side-chain polymer liquid crystalline material is the rigidity of the core linkage to the backbone. Direct, or rigid, linkage hinders the formation of liquid crystalline phases and in general only an uninteresting anisotropic structure results, which vanishes at the
glass transition. However, if a flexible spacer or linkage group is used, the backbone motions do not prevent the side-chain cores from arranging themselves anisotropically. Hence, the polymer exhibits typical liquid crystal phases. The object is to retain the desired mesomorphic properties of small molecules in the side chains, while gaining the mechanical properties of a polymer in the backbone\cite{8}. In this light, most side-chain polymer liquid crystals are comprised of sufficiently flexible spacer groups. Although the side-chain liquid crystal polymers behave as liquid crystals and display all the interesting properties of liquid crystals such as mesophases and transition behavior, this thesis will focus most of its motivation on the main-chain polymer specimens.
1.6 – Oligomeric Liquid Crystals

The discussion on main-chain polymer liquid crystals and conventional (i.e. small, organic, monomeric molecular components) liquid crystals presents an interesting dichotomy. On one hand, the system is comprised of relatively short, rigid molecular segments with possible flexible end-chains. On the other hand, these same monomers are linked together to form a polymeric system which, although possessing similar mesophases and transitions, behaves very differently from its monomeric counterpart. Both systems, for the most part, appear to be quite well-understood and individually, these systems have their own self-consistent models and rules by which their properties may be predicted; technologically, both the polymeric and monomeric liquid crystal industries have flourished. However, an obvious question which now arises is: what can be said about the “crossover” regime between monomers and main-chain polymers? In other words, if monomers and main-chain polymers behave differently, and if main-chain polymers are roughly viewed as many monomers linked together end-to-end, then perhaps an intermediate region, consisting of two or three molecular segments must be explored. This intermediate region has been dubbed “oligomers”, from the Greek word “olig” which translates into “few”.

The oligomers studied in this thesis have been nick-named “dimers”, “trimers” and “tetramers”; consisting of two, three, and four linked monomer segments respectively. Inherent to oligomeric systems is the possibility of “kinked” or “bent” molecules. Thus, the effects of molecular shape on the liquid crystalline properties can be studied. For example, the kinked version
of a dimer allows one to quantify the behavior of a molecular system comprised of “banana-shaped” molecules. The shape of the molecule can be understood by examining, for example, the number of methylene groups in the spacer unit\textsuperscript{[9]}. In the all-trans conformation, a molecule with an even number of methylene groups in the spacer will be relatively straight while a molecule with an odd number of methylene groups in the spacer will be bent with some characteristic angle (this characteristic angle will, for an idealized isolated molecule, be determined by the appropriate bond geometry). This effect is depicted diagrammatically below:

![Diagram showing molecular shape in even and odd number of methylene groups](image)

Even number of methylene groups in spacer

Odd number of methylene groups in spacer

Figure 1 – 12: Illustration of the Straight Versus Bent Conformations in a Typical Dimeric Oligomer – For an even number of methylene units in the spacer group, the overall molecular shape is comparatively straight. Conversely, for an odd number of methylene units in the spacer group, the molecule is inherently kinked.

The crossover feature of the oligomeric regime is schematically represented on the following page:
Figure 1 – 13: Depiction of the "Crossover" Behavior of Oligomeric Liquid Crystals
1.7 – Motivation of Thesis and Experiments

The motivation behind this thesis is to study the viscoelastic properties of an oligomeric system of liquid crystals utilizing the technique of quasi-elastic light-scattering. More specifically, the ultimate goal is to measure and understand the elastic moduli and rheological characteristics (i.e. the viscosity coefficients) of the oligomeric system, associated with the splay, twist, and bend deformations of the nematic director. These three types of distortions will be described later. The elastic and rheological properties are characterized as a function of reduced temperature (presently defined as: $T - T_{NI}$), since the oligomeric system under investigation is thermotropic. In addition, in a series of magnetic experiments, the surface interactions of the various oligomeric species are measured and quantified. The anchoring strength interaction coefficient, another term which will be well-defined in a later section, is measured for the different species for a variety of alignment orientations.

As just noted, these oligomers lie in an interesting crossover regime from monomeric liquid crystalline behavior to that of a many-mesogen main-chain polymer. Obviously, single-segment systems and many-segment polymers are expected to react differently to the various distortions, measured via light scattering and magnetic techniques, occurring within the nematic sample. The experiments attempt to determine where the models used to describe monomeric or polymer properties break-down. In other words, how many molecular segments can be treated as a monomer and at what number can the mesogenic-chain be expected to behave as a polymer?
The experiments attempt to isolate the dependence of these properties on two quantities:

(i.) **The Molecular Length-to-Diameter Ratio:**
In oligomeric systems, one can easily double or triple the molecular length simply by examining other members within the oligomeric family; thus, the splay, twist, and bend distortions are measured as the molecular length is changed. Experimentally, this will be accomplished by comparing the viscoelastic properties of the monomer and even-dimer systems:

![Diagram of molecular length-to-diameter ratio](image)

**Figure 1 – 14: The Molecular Length-to-Diameter Ratio**
(ii.) The Molecular Shape:
Fortunately, the dimer species of the molecular system under investigation has a "kinked" or "bent" version of the mesogen, as well as one in a relatively straight conformation. Again, the three nematic distortions are measured for a system comprised of "banana-shaped" molecules. Experimentally, this effect will be examined by measuring the viscoelastic properties of the even- and odd-dimers:

![kinked-dimer](image)

Figure 1 – 15: The Molecular Shape
1.8 – The Oligomeric System Under Investigation

The light scattering data and surface interaction coefficients in the nematic phase are reported for an oligomeric system of liquid crystals based on the 4,4'-dipentylxyloxyphenylbenzoate monomer. Specifically, results for the monomer, “even-dimer”, and “odd-dimer” are presented. Experiments concerning the future investigation of the trimer and tetramer versions of this system are discussed in the last chapter.

The monomeric system is comprised of nearly symmetric 4,4'-dipentylxyloxyphenylbenzoate molecules having the molecular structure $\text{C}_5\text{H}_{11}\text{OC}_6\text{H}_4\text{COOC}_6\text{H}_4\text{OC}_5\text{H}_{11}$, and has been nicknamed the “5-00-5” liquid crystalline monomer. One dimer version (i.e. the “even-dimer”) of this group, called the “5-10-5” dimer, consists of two monomers (minus one hydrogen each) attached end-to-end, thus having ten methylene units in the spacer and thereby being approximately straight in the all-trans conformation. The other dimer version (i.e. the “odd-dimer”) of this species, called the “5-9-5” dimer, contains an odd number (nine) of methylene units in the spacer group and is inherently kinked in the all-trans conformation with some characteristic angle between the two mesogenic groups. For an isolated odd-dimer molecule, one might expect the characteristic angle $\theta_0$ to be approximately 73°, characteristic of carbon tetrahedral bonding. Interactions between other molecules, however, might diminish this angle somewhat, although it is still expected to be several tens of degrees$^{10-13}$.

Some relevant properties of this oligomeric system are summarized in the following table, while schematically, the system is represented by the
<table>
<thead>
<tr>
<th>System</th>
<th>$T_{NI}$ (°C)</th>
<th>$T_{Cryst}$ (°C)</th>
<th>Spacer Group</th>
<th>Molecular Length (Å)</th>
<th>Molecular Diameter (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monomer</td>
<td>80.97</td>
<td>61</td>
<td></td>
<td>27.6</td>
<td>4.6</td>
</tr>
<tr>
<td>Even-Dimer</td>
<td>149.70</td>
<td>125</td>
<td>$\text{OC}<em>{10}\text{H}</em>{20}\text{O}^-$</td>
<td>53.7</td>
<td>4.6</td>
</tr>
<tr>
<td>Odd-Dimer</td>
<td>133.80</td>
<td>109</td>
<td>$\text{OC}<em>9\text{H}</em>{18}\text{O}^-$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
MOLECULAR STRUCTURE
OF THE MONOMER AND ITS DIMERS

MONOMER:
C_5H_{11}O

EVEN-DIMER:
C_5H_{11}O

ODD-DIMER:

Figure 1 - 16: Molecules Used in Study
1.9 – Outline of Experiment

Having outlined the basic concepts and terminology involved with liquid crystal research, and detailing the more relevant topics in later sections, this section briefly discusses the major highlights of the experiments presented herein. Essentially, four projects were undertaken:

(i.) **Optical Characterization of Oligomers**
Before any of the light scattering measurements can be obtained, the optical properties of the three oligomers have to be determined. The refractive indices for light polarized parallel to the optical axis \( n_{\text{extraordinary}} \), and that for light polarized perpendicular to the optical axis \( n_{\text{ordinary}} \), are an absolute necessity in order for the light scattering experiments to proceed. These refractive indices are obtained, as a function of temperature, in a series of experiments whereby the average refractive index (i.e. the index while in the isotropic phase) and the optical birefringence (i.e. \( \Delta n = n_e - n_o \)) of the material is measured.

(ii.) **Surface Anchoring Coefficient for Perpendicular Alignment**
Using the Freedericksz threshold field technique, a technique whereby nematic distortions are induced by a variety of appropriately applied magnetic field geometries, the surface anchoring energy of the monomer is measured. Using a well-known surface treatment, the nematic director is aligned *perpendicular* to the glass substrate which in turn allows the bend elastic constant, as well as the surface energy, to be measured as a function of temperature. This measurement is not performed on either version of the dimer mesogen since the necessary alignment can not be obtained.

(iii.) **Surface Anchoring Coefficient for Parallel Alignment**
Again using the Freedericksz technique, the surface anchoring energy for the monomer and even-dimer are determined by aligning the nematic director *parallel* to the glass substrate. This geometry allows one to extract the splay elastic constant for the oligomers as a function of reduced temperature.
(iv.) **Light Scattering Measurements**

Culminating the experimental project is the determination of the viscoelastic and rheological properties of the oligomeric system. Initially, the Freedericksz technique is once again employed in an independent set of experiments to verify the previously-obtained splay elastic constant measurements. The separately-measured splay elastic constants are found to be in perfect agreement with those obtained while measuring the anchoring energy. From this point, the absolute splay elastic moduli are used in conjunction with light scattering results to determine the remaining distortion elastic moduli and viscosities. As will be discussed shortly, light scattering techniques can only provide elastic constant ratios; hence, the Freedericksz determination of the splay elastic moduli is a prerequisite to any absolute light scattering measurements.
References


2. THEORY

2.1 – The Continuum Theory

The continuum approach is currently the best theory for describing the response of a nematic liquid crystal to distortions occurring within the sample as a result of an applied external field. The theory was first suggested by C. W. Oseen\[1\] and H. Zocher\[2\] in 1933 and was extensively developed by F. C. Frank\[3\] and J. L. Ericksen\[4\] in the late 1950s and early 1960s. In his book, The Physics of Liquid Crystals, P. G. de Gennes summarizes the assumptions and important results of the continuum theory\[5\]. An outline of his arguments is presented as an overview.

In an ideal, nematic single crystal, the molecules are, on the average, aligned along one common direction ± \( \hat{n} \). The system is uniaxial, and the tensor order parameter has the form:

\[
Q_{\alpha\beta} = \mathcal{O}(T) \left( n_\alpha n_\beta - \frac{1}{3} \delta_{\alpha\beta} \right)
\]

Eq. 2.1

However, in most practical circumstances, this ideal conformation will not be compatible with the constraints which are imposed by the limiting surfaces of the sample (i.e. the walls of the sample holder) or by external fields (magnetic, electric, etc.) acting on the molecules. Thus the
deformations of the nematic director require the tensor order parameter $Q_{\alpha\beta}$ to vary from point to point. The three types of deformations possible in a nematic sample, the splay, twist, and bend distortions, are depicted below:

Figure 2 – 1: Distortions of the Nematic Director

For situations of practical interest, variations in $\hat{n}$, due to distorting external fields or boundary constraints, occur over a distance denoted by $\ell$. This distance $\ell$, over which significant variations in $Q_{\alpha\beta}$ occur, is typically
greater than one micron, while molecular dimensions, denoted by the distance \( a \), are typically of the order 20 Å. Since the length scale over which variation in the nematic order occurs is much greater than the typical molecular dimension, the system may be treated by a \textit{continuum theory} --- the nematic liquid crystal is viewed as a continuous medium in which the deformations are described disregarding the details of the structure on the molecular scale.

The theory proceeds using the following assumption: the system under investigation is sufficiently weakly-distorted such that the ratio \( (a / \ell) \ll 1 \). Consequently, local optical properties remain equivalent to a uniaxial crystal; the only effect of the distortion is to reorient the optical axis \( \hat{n} \) by rotation. With the optic axis varying according to position, the tensor order parameter likewise becomes a function of position \( \vec{r} \):

\[
Q_{\alpha\beta}(\vec{r}) = Q(T) \left( n_{\alpha}(\vec{r}) n_{\beta}(\vec{r}) - \frac{1}{3} \delta_{\alpha\beta} \right) + \text{terms of higher order in } \left( \frac{a}{\ell} \right).
\]

\textbf{Eq. 2.2}

The nematic director is still of unit length but may vary in orientation. Thus the distorted state is described entirely in terms of a vector field \( \hat{n}(\vec{r}) \) which is assumed to vary smoothly and slowly with respect to \( \vec{r} \), with the possible exception of singular points and singular lines.

The free energy, per unit volume of nematic material, due to the distortion of \( \hat{n} \) is denoted by \( F_d \). This distorted free energy may be expanded in powers of \( \nabla \hat{n} \) provided certain conditions apply; a few assumptions
concerning the distorted system must be made:\(^5\):

(i.) The variations in \(\hat{n}\) are large on the molecular scale: 
\[ a \nabla \hat{n} \ll 1. \]

(ii.) The only forces of importance between molecules are short range.

(iii.) \(F_d\) must be an even function of \(\hat{n}\) since the nematic states \(+\hat{n}\) and \(-\hat{n}\) are generally indistinguishable.

(iv.) There are no terms linear in \(\nabla \hat{n}\); such terms change sign under rotation which would violate condition (iii.).

(v.) All terms involving \(\nabla \cdot \vec{u}\), where \(\vec{u}(\vec{r})\) is an arbitrary vector field, may be discarded. By invoking the divergence theorem (i.e. \(\int_V (\nabla \cdot \vec{u}) dV = \int_S (\vec{u} \cdot \vec{n}) dS\), where \(\vec{n}\) is the surface normal), one can show that such terms contribute only to surface energies, and not to volume energies. For the present case of bulk properties, these terms may be omitted. However, such terms must be included when considering surface interactions.

Thus \(F_d\) must contain all possible terms of order \((\nabla \hat{n})^2\). The remaining arguments used by de Gennes in his development of \(F_d\) are somewhat tectious and are not presented here (de Gennes himself admits that because of the subtle nature of the various terms used to compute \(F_d\), the distortion free-energy took almost thirty years to define unambiguously). Instead, a more geometrical interpretation is provided in order to describe the different types of nematic deformations. Consider \(\hat{n}\) to be slightly distorted from its unstressed orientation (along the z-axis), using a right-handed Cartesian
coordinate system as shown below:

![Nematic Distortion Coordinate System](image)

**Figure 2 – 2: Nematic Distortion Coordinate System**

Recalling the three basic types of nematic distortions, splay, twist, and bend, a simple argument can be constructed to determine the connection between the various geometrical distortions and the possible terms in $F_d$ of order $(\nabla \hat{n})^2$. Geometrically, the splay distortion is described by changes in $n_x$ and $n_y$ with respect to changes in $x$ and $y$ respectively; the twist deformation is described by changes in $n_x$ and $n_y$ with respect to changes in $y$ and $x$ respectively; while the bend distortion is described by changes in $n_x$ and $n_y$ with respect to change in $z$. These distortions, can therefore be represented mathematically as:

- **Splay:** \( \frac{\partial n_x}{\partial x} \) and \( \frac{\partial n_y}{\partial y} \)
- **Twist:** \( \frac{\partial n_x}{\partial y} \) and \( \frac{\partial n_y}{\partial x} \)
- **Bend:** \( \frac{\partial n_x}{\partial z} \) and \( \frac{\partial n_y}{\partial z} \)
Hence, the free energy density $F_d$, representing the static deformation of the nematic director in the bulk liquid crystal, ignoring surface energies occurring at the sample cell's boundaries, is written as:

$$F_d = \frac{1}{2} K_{11} (\nabla \cdot \hat{n})^2 + \frac{1}{2} K_{22} (\hat{n} \cdot (\nabla \times \hat{n}))^2 + \frac{1}{2} K_{33} (\hat{n} \times (\nabla \times \hat{n}))^2 , \quad \text{Eq. 2.3}$$

where $K_{11}$, $K_{22}$, and $K_{33}$ represent the splay, twist, and bend elastic moduli respectively. Note that $F_d$ is defined as having units of energy per unit volume.
2.2 – Remarks

From (Eq. 2.3) alone, several useful remarks can be made about the elastic moduli\cite{5}: each elastic constant must be positive; otherwise the undistorted nematic conformation would not represent a minimum in the free energy $F_d$. Also, $F_d$ is an energy per unit volume (erg/cm$^3$), $\hat{n}$ is dimensionless; thus the elastic constants $K_{ii}$ have dimensions of energy per unit length (erg/cm $\equiv$ dynes). By purely dimensional argument, the $K_{ii}$'s are expected to be of order $U/a$, where $U$ is a typical interaction energy between molecules, while $a$ is a molecular dimension. Thus, using $U = 0.1$ eV and $a = 14$ Å, the $K_{ii}$'s are expected to be of magnitude $10^{-6}$ dynes ($\equiv 1.4 \times 10^{-13}$ erg / $1.4 \times 10^{-7}$ cm). Indeed, for the oligomeric system soon to be discussed, the splay, bend, and twist elastic constants are all of this order of magnitude.

Furthermore, the magnitude of the distortion energy $F_d$, can also be estimated based on dimensional arguments. For a typical distortion, taking place over a distance $\ell$, $F_d$ (per molecule) will roughly be: $F_d a^3 = (K / \ell^2) a^3 = U (a / \ell)^2$. Thus, in the continuum limit where $(a / \ell) << 1$, the distortion energy, per molecule, represents only a small fraction of the total energy.
2.3 – Boundary Effects

As mentioned earlier, the complete picture of nematic distortions must include not only the energies associated with deformations occurring in the bulk, but also the energies associated with the surface of the sample. Fortunately, because of the phenomenon known as “strong anchoring”, the surface forces, in almost all practical circumstances, are strong enough to impose a well-defined direction to the nematic director \( \hat{n} \), at the surface boundary. In light of this effect, instead of minimizing a free-energy comprised of the sum of bulk and surface energies, only the bulk free-energy need be minimized — with the constraint that fixed boundary conditions are imposed on \( \hat{n} \) at the surface\(^{[5,8]} \).

To further illuminate the effect of strong anchoring, consider the following situation: a plane surface separates a nematic liquid crystal from an external medium. Initially, the bulk nematic is undistorted, with a well-defined, constant, nematic director \( \hat{n} \). The “easy axis” or “easy direction” is now defined as the direction of \( \hat{n} \) which will minimize the surface interaction energies. The direction of the easy axis will obviously depend upon the nature of the external medium, the most common cases of which are discussed below:
(i.) **Single Crystal**

If the external medium is a single crystal, and the interface corresponds to a well-defined crystallographic plane, it often happens that the easy directions are parallel to some simple crystallographic axes.

(ii.) **Homogeneous Alignment due to Rubbing**

If a glass surface (or polymer-coated glass surface) is carefully rubbed *unidirectionally*, the nematic molecules of certain materials will tend to align themselves along this direction[7]. A true microscopic understanding of this effect is still lacking, although it is easy to imagine that the rubbed surface forms a mechanical template within which the molecules prefer to lie, perhaps due to their shape (see below). An alternative explanation for the homogeneous alignment phenomenon is that, for the case of a rubbed polymer-coated glass surface, the rubbed polymer acts as a layer of aligned liquid crystalline material[8]. Thus, the bulk nematic molecules orient themselves according to the orientation established by the surface molecules (i.e. "epitaxial growth" of the preferred orientation). In any case, the rubbing technique indeed creates one easy direction perpendicular to the glass normal. This type of alignment is referred to as "homogeneous" or "planar".
(iii.) **Homeotropic Alignment due to Surfactant**

For several years now, it has been known that suitable detergents, when added in small amounts to a nematic liquid crystalline material, tend to attach their polar head on a glass surface. The detergent, or surfactant, forms a comb-like template within which the nematic molecules can intercalate. With such a treatment performed on two glass slides, liquid crystal samples, sandwiched between the slides, will align themselves with their director parallel to the normal of the interface. This “homeotropic” alignment is also possible using surface treatments of polyamides or certain lipids, such as lecithin\(^{9-13}\). The two types of surface alignment techniques are
compared below:

![Diagram showing Homeotropic and Homogeneous Alignment](image)

**Figure 2 – 4: Comparison of Homeotropic and Homogeneous Alignment Techniques**
2.4 – Effects of Bulk Distortions on Surface States

The next step in considering surface interactions is to examine a distortion in the bulk nematic sample and to investigate the effects of this distortion on the surface properties. Consider the following arrangement, specifically displaying a pure twist deformation, but which can be generalized later: the surface boundary is a plane (the y=0 plane) and has one easy axis at an angle $\theta(0)$ relative to the $+\hat{z}$ direction; for simplicity $\theta(0) = 0$, such that $\hat{n}$ lies along the $+\hat{z}$ direction. At a distance $y$ from the surface, the nematic director $\hat{n}$ is twisted at an angle $\theta(y)$, relative to the easy axis. Finally, at the second surface, a distance $y=L$ away from the first surface, the nematic director lies at the angle $\theta(L)$ relative to the $z$-axis.

![Diagram of Nematic Twist Distortion Geometry](image)

Figure 2 – 5: Nematic Twist Distortion Geometry
The bulk distortion energy, per unit area in the $y=0$ plane, is easily obtained by integrating $F_d$, which is the free-energy per unit volume, across the sample thickness. The geometry dictates that only pure twist distortions need to be included:

$$
\mathcal{S}_{\text{bulk}} = \int_0^L F_d \, dy = \int_0^L \frac{1}{2} K_{22} \left( \hat{n} \cdot (\nabla \times \hat{n}) \right)^2 \, dy.
$$

**Eq. 2.4**

However, taking $\hat{n} = [n_x = \sin \theta(y), n_y = 0, n_z = \cos \theta(y)]$, the bulk distortion energy reduces to:

$$
\mathcal{S}_{\text{bulk}} = \int_0^L \frac{1}{2} K_{22} \left( \frac{d\theta}{dy} \right)^2 \, dy.
$$

**Eq. 2.5**

Minimizing $\mathcal{S}_{\text{bulk}}$, by writing $\delta \mathcal{S}_{\text{bulk}} = 0$, for an arbitrary variation in the form of the twist $\delta \theta(y)$ gives:

$$
0 = \delta \mathcal{S}_{\text{bulk}} = K_{22} \int_0^L \delta \left( \frac{d\theta}{dy} \right)^2 \, dy = K_{22} \int_0^L 2 \left( \frac{\partial \theta}{\partial y} \right) \left( \frac{d\theta}{dy} \right) \, dy = 2 K_{22} \int_0^L \frac{\partial \theta}{\partial y} \frac{\partial}{\partial y} \frac{\partial}{\partial y} \theta \, dx.
$$

**Eq. 2.6**

Integrating by parts, results in:

$$
0 = K_{22} \frac{d\theta}{dy} \left. \frac{\partial^2 \theta}{\partial y^2} \right|_0^L - K_{22} \int_0^L \frac{\partial^2 \theta}{\partial y^2} \frac{\partial}{\partial y} \theta \, dx.
$$

**Eq. 2.7**

Thus, temporarily ignoring the surface terms (i.e. the evaluated terms), the condition for local bulk equilibrium is:
\[ K_{22} \frac{\partial^2 \theta}{\partial y^2} = 0 \quad \text{or} \quad \frac{\partial \theta}{\partial y} = \text{constant.} \quad \text{Eq. 2.8} \]

However, near the surface, this solution no longer holds since the surface contributions to the integral must be incorporated. Instead, an angular profile \( \theta(y) \), is assumed to hold throughout the sample. A possible curve for such a profile may look like:

**NEMATIC PROFILE, \( \theta(y) \)**

![Diagram showing the nematic profile with labels](image)

**Figure 2 – 6: Nematic Profile of the Director Orientation Near a Surface Interface**
An exact calculation of the profile $\theta(y)$ near the surface is not necessary. Provided that throughout the surface region $\theta$ is small, the profile for $\theta(y)$ will be governed by linear behavior. Any change in the value of $\theta(L)$ will merely scale the entire profile up or down. Hence, the "extrapolation length" $b$ is independent of $\theta(L)$ and contains all the necessary information relevant to the continuum theory.

The magnitude of $b$ can be estimated based upon simple argument. Assuming that the condition for local bulk equilibrium holds even at the surface, the term necessary to compute the bulk free-energy can be approximated by:

$$\frac{\partial \theta}{\partial y} = \frac{\theta(L) - \theta(0)}{L}.$$  \hspace{1cm} \text{Eq. 2. 9}

Also, at the surface itself, there is a surface contribution to the free-energy which, in the absence of an elastic torque, requires $\theta(0)=0$ as a boundary condition:

$$\mathcal{S}_{\text{surface}} = \frac{1}{2} W(\theta(0))^2.$$ \hspace{1cm} \text{Eq. 2. 10}

where $W$ is a positive constant with units of energy per unit area (erg/cm$^2$). Thus the total free-energy per unit area at the surface boundary can be written:

$$\mathcal{S}_{\text{total}} = \mathcal{S}_{\text{bulk}} + \mathcal{S}_{\text{surface}} = \frac{1}{2} K_{22} L \left( \frac{\theta(L) - \theta(0)}{L} \right)^2 + \frac{1}{2} W(\theta(0))^2.$$ \hspace{1cm} \text{Eq. 2. 11}
Minimizing this expression with respect to $\theta(0)$ gives:

$$\theta(0) = \frac{K_{22}}{W} \frac{\partial \theta}{\partial y}.$$  \hspace{1cm} \text{Eq. 2.12}

which, when substituted into the free-energy expression, results in the following expression for the total energy per unit area at the surface:

$$\Sigma_{\text{total}} = \Sigma_{\text{bulk}} + \frac{1}{2} \frac{K_{22}}{W} \left( \frac{\partial \theta}{\partial y} \right)^2.$$ \hspace{1cm} \text{Eq. 2.13}

Finally, the expression for $\theta(0)$, combined with the previous depiction of the extrapolation length, suggests that $b$ is given by:

$$\frac{\partial \theta}{\partial y} = \frac{\theta(0)}{b} = \frac{\theta(0)}{(K_{22}/W)} \rightarrow b = \frac{K_{22}}{W}.$$ \hspace{1cm} \text{Eq. 2.14}

The anchoring strength coefficient $W$, is of the order $(U_{WN}a^2)$ where $U_{WN}$ is the interaction between the wall and one nematic molecule lying against the wall, and $a$ is a typical molecular dimension. Previously, $K_{22}$ was estimated to be of the order $U/a$, where $U$ is a nematic-nematic interaction. Thus the extrapolation length is of the order, $b = a (U/U_{WN})$. Obviously, the magnitude of $b$ has two possibilities:
(i.) **Strong Anchoring**

If $U_{WN}$ is larger than $U$, the extrapolation length is comparable to a molecular dimension. Also, the ratio of surface-to-bulk energies, given by (assuming $b = a$ or $U_{WN} >> U$):

$$\frac{S_{surface}}{S_{bulk}} = \frac{K_{22}}{WL} = \frac{b}{L} = \frac{a}{L},$$

Eq. 2. 15

implies that in the continuum limit, where $(a / L) << 1$, the surface energy is negligible compared to the bulk contribution. Thus, the extrapolation length may be set as $b=0$ and the boundary condition $\theta(0)=0$ used at the surface. This situation is called "strong anchoring".

(ii.) **Weak Anchoring**

In the case where $U_{WN} << U$, the extrapolation length becomes much larger than the average molecular dimension. The angle of rotation of the molecules at the surface may be large; external constraints can significantly affect the surface alignment. This case is commonly referred to as "weak anchoring" and will be discussed in greater detail when external magnetic field effects are considered.
2.5 – Concluding Remarks

The effects of boundary restrictions presented above were derived for the special case of a pure twist deformation and a planar surface boundary. Also not considered was the possibility of a degenerate system of easy directions (i.e. the surface has more than one easy axis). However, the results can be generalized without significant alteration, and are meaningful inasmuch as they produce the following formulation for the case of strong anchoring:

In all cases where $U_{WN}$ is comparable in magnitude to $U$ (strong anchoring), the effect of the surface is simply to impose certain easy directions to $\hat{n}$. All $\hat{n}$-dependent contributions to the surface energy may be omitted.

As will be discussed shortly, strong anchoring conditions are generally assumed to hold in most experimental situations. Thus, the formulation of an easy axis at the surface is a common and quite useful approach. However, the considerations of weak anchoring become important when external field contributions are included. Experimentally, determining the anchoring wall-to-nematic interaction energy $U_{WN}$ is possible only when strong anchoring conditions are removed. This will be treated in the latter sections of this chapter.
2.6 – Magnetic Field Effects

The next step in the analysis of nematic deformations is to determine the effect of an external field on the sample. In particular, attention is given to the response of the sample to an externally-applied magnetic field; ultimately the magnetic Freedericksz transition technique will be developed, along with the derivation of an expression for the critical Freedericksz field, $H_{\text{critical}}$ or $H_{\text{threshold}}$. Once again, the treatment offered by P. G. de Gennes is presented as an overview of magnetic field effects, including discussion of the Freedericksz technique$^5$. However, for the calculation of the critical Freedericksz field, the more descriptive arguments used by S. Chandrasekhar, in his text *Liquid Crystals*, are presented$^6$. 
2.7 – Magnetic Diamagnetism

Most organic molecules are diamagnetic. They usually do not possess natural ferromagnetic poles, yet dipole magnetic moments can be induced along the molecule by external magnetic fields. The diamagnetism associated with organic molecules is particularly strong for aromatic (containing a benzene ring) specimens. A benzene molecule, as shown below, tends to choose an orientation in which the external field \( \vec{H} \), is parallel to the plane of the ring:

![Diagram of benzene molecule orientation](image)

The benzene rings lie perpendicular to the page. \( \hat{n} \) represents the normal to the ring.

**Figure 2-7: Orientation of a Benzene Ring in an Externally-Applied Magnetic Field**
To explain the response of the benzene ring to the applied magnetic field, one could correctly argue that the preferred orientation of the benzene ring is simply due to the magnitude of the magnetic susceptibility anisotropies. If \( \chi_{\text{parallel to the plane}} \) is greater than \( \chi_{\text{perpendicular to the plane}} \), then the magnetic energy term \( F_{\text{magnetic}} = - (\chi || - \chi \perp) H^2 \) is minimized when the benzene ring is parallel to the applied field. For most liquid crystals, which contain a pair of aromatic rings along the optic axis, the lowest energy is achieved when the optical axis is parallel to the field.

Although the coupling strength between a single molecule and the applied field (assuming nominal achievable fields) is not strong enough to overcome typical thermal energies, for a macroscopic nematic sample, containing on the order of \( 10^{22} \) molecules (all of which can rotate in unison), the coupling energy between the molecules and the applied field is indeed strong enough to rotate the nematic director such that the optical axis is parallel to \( \vec{H} \). Hence, for sufficiently narrow samples, an energetic competition arises between the orientation preferred by the surface boundary and that preferred by the magnetic field. This competition gives rise to deformations called curved conformations with which one may extract information concerning the elastic constants. To quantify these curved conformations, the effect of the magnetic field on the direction of the nematic director must be examined. The applied field \( \vec{H} \), induces a magnetization \( \vec{M} \) on each molecule according to:

\[
\vec{M} = \chi_0 \vec{H} ; \text{ for } \vec{H} \text{ parallel to } \vec{n},
\]

\[
\vec{M} = \chi_\perp \vec{H} ; \text{ for } \vec{H} \text{ perpendicular to } \vec{n},
\]

Eq. 2.16

Eq. 2.17
where $\chi_\parallel$ and $\chi_\perp$ are the diamagnetic susceptibilities per unit volume, parallel and perpendicular to the director respectively. For an arbitrary angle between $\vec{H}$ and $\vec{n}$, the total magnetization is given by:

$$\vec{M} = \chi_\perp \vec{H} + (\chi_\parallel - \chi_\perp)(\vec{H} \cdot \vec{n})\vec{n}. \quad \text{Eq. 2.18}$$

For convenience (and in accordance with common convention), the difference in diamagnetic susceptibilities is defined to be:

$$\chi_a = \chi_\parallel - \chi_\perp, \quad \text{Eq. 2.19}$$

which is a positive quantity in most rod-like liquid crystals. An example of an instance where $\chi_a < 0$ is discussed below.

An expression for the free-energy per unit volume, including a contribution from the applied external magnetic field, can then be calculated using the previous form of the distorted free-energy density, minus the integral of the total magnetization:

$$F = F_d - \int_0^H \vec{M} \cdot d\vec{H} = F_d - \frac{1}{2} \chi_\perp H^2 - \frac{1}{2} \chi_a (\vec{n} \cdot \vec{H})^2. \quad \text{Eq. 2.20}$$

The term $\frac{1}{2} \chi_\perp H^2$ is independent of $\vec{n}$ and lends no contribution to subsequent calculations; hence it will be omitted from consideration. Note that provided $\chi_a > 0$, the last term is minimized when $\vec{H}$ and $\vec{n}$ are parallel, as desired. As a caveat, note that contrary to the example of rod-like nematic molecules in
which $\chi_a > 0$, for disk-shaped liquid crystal samples (where $\chi_a < 0$), the aromatic
group is in the plane of the disk; hence the disk orients perpendicular to the
applied field\(^{[14]}\). At this point, de Gennes discusses the distorted state in
terms of torques, rather than energies. Writing perturbations to the nematic
director in terms of a Fourier series, he then proceeds to derive the
expression for the critical Freedericksz field. However, as noted earlier, the
development used by Chandrasekhar is a bit more lucid, though still
somewhat cloudy for the liquid crystal novice, and is outlined below.
2.8 – The Freedericksz Effect

To generalize the technique of a Freedericksz phase transition, imagine a nematic sample, of nominal thickness 25 μm, well-aligned between two glass slides. The molecules are assumed to be strongly anchored to the two external substrates. The surface alignment may be either homeotropic (perpendicular) or homogeneous (planar); specific details for the various possible geometries will be discussed later. Regardless of the alignment, the Freedericksz method mandates that the external magnetic field be applied normal to the easy axis. Initially, for a very weak applied field, the surface alignment will determine the nematic conformation throughout the sample. However, it is clear that for large $\vec{H}$, the energetically-favored state will correspond to a different conformation (recall the field is applied perpendicular to the easy axis), with the molecules aligned along $\vec{H}$ in most of the sample, except for two thin transition regions near each wall where strong anchoring still holds. This transition region is characterized by a parameter $\xi$, called the “magnetic coherence length”, which will be discussed in more detail in a later section. Thus, a transition will occur at some critical applied magnetic field $H_c$ (or $H_{th}$) between the unperturbed and the distorted conformations$^{[5,6]}$.

This type of phase transition was first observed by V. Freedericksz in 1927$^{[15]}$ [coincidentally the same year, the New York Yankees assembled what is considered the greatest baseball team in the modern era. While the 1927 Yankees were without the services of some of baseball’s greatest players: Stan Musial, Hank Greenberg, Bob Feller, and yes, Ted Williams, the
Yankee starting rotation consisted of five would-be Hall-of-Famers: Waite Hoyt, Earl Combs, Tony "poosh 'em up, Tony" Lazzeri, Babe "the Bambino" Ruth, and of course, Lou "Iron Horse" Gehrig \[^{[16]}\]. Freedericksz also showed that the critical field $H_c$ was inversely proportional to the sample thickness, $d$:

$$H_c d = \text{constant.}$$  \hspace{1cm} \text{Eq. 2.21}

Soon after Freedericksz's experimental observations, H. Zocher showed that Freedericksz's relation was a direct result of the continuum theory and that the technique could be used to relate the nematic elastic constants to the critical field\[^{[2]}\]. The experimental set-up required to observe such a transition and to determine the three elastic constants is well-established and relatively easy to achieve. Given the two possible types of strong anchoring alignments, homeotropic and homogeneous, the three Freedericksz deformations geometries are summarized in the following table and more intuitively, by the schematic that follows:

<table>
<thead>
<tr>
<th>Name</th>
<th>Director Distortion</th>
<th>Elastic Constant</th>
<th>Surface Alignment</th>
<th>Field Direction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Splay</td>
<td>$\nabla \cdot \hat{n} \neq 0$</td>
<td>$K_{11}$</td>
<td>Homogeneous</td>
<td>$\hat{z}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$(\hat{n} = \hat{x})$</td>
<td></td>
</tr>
<tr>
<td>Twist</td>
<td>$(\nabla \times \hat{n}) \parallel \hat{n}$</td>
<td>$K_{22}$</td>
<td>Homogeneous</td>
<td>$\hat{y}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$(\hat{n} = \hat{x})$</td>
<td></td>
</tr>
<tr>
<td>Bend</td>
<td>$(\nabla \times \hat{n}) \perp \hat{n}$</td>
<td>$K_{33}$</td>
<td>Homeotropic</td>
<td>$\hat{x}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$(\hat{n} = \hat{z})$</td>
<td></td>
</tr>
</tbody>
</table>
The Splay, Twist, and Bend Freedericksz Deformations

Figure 2 – 8: Three Possible Freedericksz Geometries
Modern applications of the Freedericksz technique fall into two categories: macroscopic measurements and optical measurements\textsuperscript{[5]}. Both types of measurements were necessary to obtain the data presented in this study. Only the relevant examples are discussed below:
(i.) **Macroscopic Measurements:**

Any anisotropic property, such as the dielectric constant or thermal conductivity, may be used as a probe of the average state of alignment of the system. This type of measurement is extremely useful for determining the splay elastic constant and in fact, was the method by which the absolute splay elastic constant was determined for the monomer and even-dimer as a function of reduced temperature\(^{17}\). Initially, while surface interactions dominate, the effective dielectric constant \(\varepsilon_{\text{eff}}\), is relatively unaffected by the applied magnetic field. However, once \(H_c\) (or \(H_{th}\)) is reached, the value of \(\varepsilon_{\text{eff}}\) quickly saturates (to some value \(\bar{\varepsilon}\)) as nearly all of the sample is aligned along \(\vec{H}\), typically at \(H \geq (2 \text{ or } 3) H_c\). A typical trace of \(\varepsilon_{\text{eff}}\) versus applied field is shown below:

![Graph showing \(\varepsilon_{\text{effective}}\) versus \(H_{applied}\)](image)

**Figure 2-9:** Typical Trace of Effective Dielectric Constant Versus Applied Magnetic Field – The sample is in the Freedericksz splay geometry.
(ii.) **Optical Measurements:**

Verification of the bend elastic constant for the monomer was determined using an optical measurement of the bend Freedericksz distortion\(^{13}\). Such a verification was impossible for the even-dimer since this material could not be homeotropically-aligned, an obvious requisite for the technique. For this type of measurement, a laser is directed along the direction of the undistorted nematic director; for a homeotropically-aligned sample, the sample's refractive index would correspond to the ordinary index, regardless of the laser's polarization. The beam passes through a polarizer rotated 45° to the field, the sample, a second analyzer crossed relative to the first polarizer, and finally into a photo-diode detector. Unless the nematic director changes its orientation, the measured intensity at the photo-diode will ideally be zero, due to the crossed polarizers. However, once the bend distortion begins to occur, the sample's birefringence, due to its anisotropic optical properties, will allow some light to enter the detector. At the critical field \( H_c \), a trace of the detector's intensity versus the applied magnetic field will abruptly change; in fact \((dI/dH)\) will jump in a discontinuous fashion at \( H_c \).
Figure 2 - 10: Typical Trace of Detector Intensity Versus Applied Magnetic Field – The sample is in the Freedericksz bend geometry.

The specific experimental procedures will be discussed later. In the next section, continuing the discussion of magnetic distortions in nematic liquid crystals, the calculation of the critical Freedericksz field, as developed by S. Chandrasekhar, is presented[6].
2.9 – Calculation of the Magnetic Freedericksz Threshold Field

The determination of $H_C$ by S. Chandrasekhar is a simple application of the distorted free-energy expression, including the external magnetic field coupling term:

$$ F = F_d - \frac{1}{2} \chi_d H^2 - \frac{1}{2} \chi_d (\hat{n} \cdot \vec{H})^2, \quad \text{where} \quad \text{Eq. 2.20} $$

$$ F_d = \frac{1}{2} K_{11} (\nabla \cdot \hat{n})^2 + \frac{1}{2} K_{22} (\hat{n} \cdot (\nabla \times \hat{n}))^2 + \frac{1}{2} K_{33} (\hat{n} \times (\nabla \times \hat{n}))^2. \quad \text{Eq. 2.3} $$

The simplest case (splay geometry) is outlined as an example, and the result generalized for the remaining Freedericksz geometries. Consider a nematic sample, aligned along the $\hat{x}$-direction, in which the initial undisturbed orientation of the director is parallel to the glass holder. The magnetic field $\vec{H}$ is now applied perpendicular to the plates, along the $+z$ direction, corresponding to the splay Freedericksz geometry. $\theta(z)$ is the angle between the molecule located at $z$, and the undisturbed alignment along the $x$-axis. The set-up is represented schematically below:
Mathematically, the geometry is described as:

\[ \hat{n} = (\cos \theta, 0, \sin \theta), \quad \text{and} \quad \vec{H} = (0, 0, H). \]  
\[ \text{Eq. 2.22} \]

Noting the following relations, which hold for this particular geometry:

\[ \nabla \cdot \hat{n} = \cos \theta \left( \frac{d \theta}{dz} \right), \quad \nabla \times \hat{n} = (0, -\sin \theta \frac{d \theta}{dz}, 0), \]

\[ \hat{n} \cdot (\nabla \times \hat{n}) = 0, \quad \hat{n} \times (\nabla \times \hat{n}) = (d \theta / dz) \left( -\sin^2 \theta, 0, -\sin \theta \cos \theta \right), \quad \text{and} \]

\[ \hat{n} \cdot \vec{H} = H \sin \theta, \]  
\[ \text{Eq. 2.23} \]

the equation for the free-energy density (Eq. 2.20 and Eq. 2.3) reduces to:
\[
F = \frac{1}{2} \left[ \left( K_{11} \cos^2 \theta + K_{13} \sin^2 \theta \right) \left( \frac{d\theta}{dz} \right)^2 - \chi_s H^2 \sin^2 \theta \right].
\]

Eq. 2. 24

Near the threshold, where \( \theta(z) \) is small (i.e. \( \theta(z) \ll 1 \)), the free-energy density reduces to:

\[
F = \frac{1}{2} \left[ K_{11} \left( \frac{d\theta}{dz} \right)^2 - \chi_s H^2 \theta^2 \right].
\]

Eq. 2. 25

At this point, it is convenient to Fourier transform \( \theta(\bar{r}) \) into \( \theta(\bar{q}) \). In order to maintain the same units on all transformed quantities, the Fourier transformation is performed according to the conventional prescription:

**forward transform:** \( \rightarrow \theta(\bar{r}) = \sqrt{V} \int \theta(\bar{q}) e^{-i\bar{q}\cdot\bar{r}} d\bar{q} \) and

Eq. 2. 26

**reverse transform:** \( \rightarrow \theta(\bar{q}) = \frac{1}{\sqrt{V}} \int \theta(\bar{r}) e^{i\bar{q}\cdot\bar{r}} d\bar{r} \)

Eq. 2. 27

Also noting that \((d\theta/dz)^2\) transforms into \((-i\theta_q)(-i\theta_q)^*\), this transformation converts the energy-density (Eq. 2. 20 and Eq. 2. 3) into the form:

\[
F_q = \frac{1}{2} K_{11} \theta_q^2 q^2 - \frac{1}{2} \chi_s H^2 \theta_q^2,
\]

Eq. 2. 28

where \( \theta_q \) is the Fourier-transformed angular displacement and \( F_q \) is the free-energy per unit volume for a particular \( q \) component. Obviously, in order to minimize \( F_q \), the lowest possible value of \( q \) that matches the boundary
conditions must be determined. Physically, the lowest allowed value of \( q \) occurs when the sample thickness corresponds to a half-wavelength oscillation of the distortion; or, where \( q=(\pi/d) \):

![Figure 2-12: Minimum Freedericksz Distortion](image)

Hence, \( F_q \) further simplifies to:

\[
F_q = \frac{1}{2} K_{11} \theta_i^3 \left( \frac{\pi}{d} \right)^2 - \frac{1}{2} \chi_s H^2 \theta_i^2. 
\]  

Eq. 2.29

Finally, notice that the sign of \( F_q \) depends on the magnitude of the applied field \( \vec{H} \). This demonstrates the true nature of the Freedericksz phenomenon: an energetic competition between magnetic deformation terms and elastic restoration forces. Clearly, for small enough \( H \), \( F_q \) is a positive quantity; but at some point, as \( H \) increases, \( F_q \) will change sign and become negative. Thus a transition must occur at the critical value of \( H \) which changes the sign of \( F_q \). Solving for this critical field gives:
\[ H_c = \frac{\pi}{d} \sqrt{\frac{K_{11}}{\chi_a}} \]  

\textbf{Eq. 2.30}

This is the expression for the Freedericksz magnetic threshold field, used to determine the elastic moduli for a particular threshold configuration. This result was derived using the splay geometry, however, the essential result remains the same for all three set-ups. The previous table, summarizing the various Freedericksz geometries, can now be made more explicit:

**FREEDERICKSZ DEFORMATION SUMMARY**

<table>
<thead>
<tr>
<th>Name</th>
<th>Director Distortion</th>
<th>K</th>
<th>Surface Alignment</th>
<th>Field Direction</th>
<th>Critical Field</th>
</tr>
</thead>
<tbody>
<tr>
<td>Splay</td>
<td>$\nabla \cdot \hat{n} \neq 0$</td>
<td>$K_{11}$</td>
<td>Homogeneous</td>
<td>$\vec{H} = (0,0,H)$</td>
<td>$H_c = \pi/d \sqrt{K_{11}/\chi_a}$</td>
</tr>
<tr>
<td></td>
<td>$\hat{n} = (\cos \theta, 0, \sin \theta)$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Twist</td>
<td>$(\nabla \times \hat{n}) \parallel \hat{n}$</td>
<td>$K_{22}$</td>
<td>Homogeneous</td>
<td>$\vec{H} = (0,H,0)$</td>
<td>$H_c = \pi/d \sqrt{K_{22}/\chi_a}$</td>
</tr>
<tr>
<td></td>
<td>$\hat{n} = (\cos \theta, \sin \theta, 0)$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bend</td>
<td>$(\nabla \times \hat{n}) \perp \hat{n}$</td>
<td>$K_{33}$</td>
<td>Homeotropic</td>
<td>$\vec{H} = (H,0,0)$</td>
<td>$H_c = \pi/d \sqrt{K_{33}/\chi_a}$</td>
</tr>
<tr>
<td></td>
<td>$\hat{n} = (\sin \theta, 0, \cos \theta)$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
2.10 – Magnetic Coherence Length

P. G. de Gennes has introduced a very useful parameter, called the magnetic coherence length \( \xi \), which physically represents the thickness of the transition region near the boundary\(^6\). Consider the Freedericksz twist geometry: the nematic liquid crystal occupies the half space \( z>0 \); the boundary is the xy-plane at \( z=0 \), imposing a planar orientation along the x-axis; and the magnetic field is applied along +\( \hat{y} \) direction. The angle \( \varphi \), made between the field and the director, is given by \( \varphi = (\pi/2 - \theta) \), where \( \theta \) is, as before, the angle between the director and the x-axis (the x-axis represents the ideal undisturbed planar director orientation). Using the particular relations given below:

\[
\begin{align*}
\hat{n} &= (\cos \theta, \sin \theta, 0) = (\sin \varphi, \cos \varphi, 0), \\
\hat{H} &= (0, H, 0), \\
\nabla \cdot \hat{n} &= \hat{n} \times (\nabla \times \hat{n}) = 0, \\
\hat{n} \cdot (\nabla \times \hat{n}) &= (d\varphi/dz), \text{ and} \\
\hat{n} \cdot \hat{H} &= H \cos \varphi.
\end{align*}
\]

Eq. 2.31

the free-energy density (Eq. 2.20 and Eq. 2.3) trivially converts into the expression:

\[
f = \frac{F}{\chi_a H^2} = \frac{1}{2} \left[ \xi^2 \left( \frac{d\varphi}{dz} \right)^2 + \cos^2 \varphi \right].
\]

Eq. 2.32

where the magnetic coherence length \( \xi \), is given by:
\[ \xi = \frac{\sqrt{(K_{12}/\chi_s)}}{H}. \]  \hspace{1cm} \text{Eq. 2.33}

In order to solve for \( \phi \), the calculus of variations (i.e. Euler’s equation) is formulated using the free-energy density expression for \( f(\phi, d\phi/dz) \) (Eq. 2.32). Namely, using the Euler equation,

\[ \frac{\partial f}{\partial \phi} - \frac{d}{dz} \left( \frac{\partial f}{\partial (\phi)} \right) = 0, \]  \hspace{1cm} \text{Eq. 2.34}

the differential equation for \( \phi \) simply becomes:

\[ \frac{d^2 \phi}{dz^2} = \frac{\sin(2\phi)}{2\xi^2}. \]  \hspace{1cm} \text{Eq. 2.35}

This differential equation can be integrated and solved, somewhat tediously, subject to the boundary conditions: \( \phi \rightarrow 0 \) and \( (d\phi/dz) \rightarrow 0 \) at \( z \rightarrow \infty \):

\[ \tan \left( \frac{\phi}{2} \right) = \exp \left( \frac{z}{\xi} \right). \]  \hspace{1cm} \text{Eq. 2.36}

Notice that the magnetic coherence length increases with diminishing magnetic field. Thus, if the sample thickness \( d \), is much larger than the magnetic coherence length, the sample will align almost entirely along the direction of the field. Usually, for a typical applied field of 10^4 Gauss, the magnetic coherence length is roughly one micron\(^5\). As will be discussed shortly, samples whose thickness is between five and ten microns (in which
case $d \equiv \xi$) will experience a significant energetic competition between field and surface effects. Therefore, a significant difference in threshold field will result depending on whether strong or weak anchoring is established. However, for a sample whose thickness is many tens of microns ($d >> \xi$), the bulk, or field effects will dominate and the threshold field will be relatively independent of surface conditions. These differences will later be explored in detail when the anchoring strength coefficient is explicitly measured.
2.11 – Response Time of the Freedericksz Transition

The purpose of this section is to develop a qualitative understanding of
the response time of the Freedericksz transition with respect to the applied
field. Although this question is probably better discussed in a section
dedicated to the dynamical properties of nematic liquid crystals, the final
result is indeed relevant at this point in the development.

The Freedericksz effect represents a direct energetic competition
between the magnetic field-induced alignment of the nematic sample, and the
elastic resistance to this externally driven orientation. In general, near the
threshold field, where the angle between the distorted director and the easy
axis is small, the two competing terms in the free energy will have the form:

\[ F_{\text{total}} = F_{\text{elastic}} + F_{\text{magnetic}} = \frac{1}{2} K_\| \left( \frac{d\theta}{dz} \right)^2 - \frac{1}{2} \chi_s H^2 \theta^2. \]

Eq. 2.25

Again, Fourier-transforming \( \theta(\vec{r}) \) into \( \theta(\vec{q}) \) as before, [i.e. according to the
usual prescription given by (Eq. 2.26 and Eq. 2.27): \( \theta(\vec{r}) = V \int \theta(\vec{q}) e^{-i\vec{q} \cdot \vec{r}} d\vec{q} \)],
converts this equation into the form:

\[ F_q = \frac{1}{2} K_\| \theta_q^2 q^2 - \frac{1}{2} \chi_s H^2 \theta_q^2. \]

Eq. 2.28

where \( \theta_q \) is the transformed angular displacement and \( F_q \) is the free-energy
per unit volume for a particular \( q \) component. Since \( \theta_q \) is the generalized
displacement in this system, the derivative of \( F_q \) with respect to \( \theta_q \) represents
a generalized force (although the resulting expression will not have the usual
units of force since the displacement variable \( \theta_q \) is unitless), expressed as:

\[
\frac{dF_q}{d\theta_q} = K_q \theta_q q^2 - \chi_a H^2 \theta_q = \eta - \frac{d\theta_q}{dt},
\]

Eq. 2.37

where \( \eta \) is the viscosity (measured in the cgs unit of Poise, Poise = erg * sec/cm\(^3\)) of the nematic sample. To derive this equation, note that the generalized force is equated to a damping term which is, as is the usual procedure, set proportional to a generalized velocity\(^{[5,6,18]}\). Evaluating the differential equation gives the solution:

\[
\theta(t) = \theta_e \exp\left(\frac{K_q q^2 - \chi_a H^2}{\eta} t\right) = \theta_e \exp\left(-\frac{t}{\tau}\right),
\]

Eq. 2.38

where

\[
\tau = \frac{-\eta}{K_q q^2 - \chi_a H^2},
\]

Eq. 2.39

is the response time of the Freedericksz transition with respect to the applied field.

An important question which will arise during the analysis of surface interactions, is how does this response time scale with sample thickness? Recall that the Freedericksz threshold field is given by the expression,

\[
H_c = \left(\frac{\pi d}{\lambda}\right) \left| \frac{K_q \eta}{\chi_a} \right| \quad \text{(Eq. 2.30)}.
\]

In practice however, the field threshold can only be measured to within some experimental resolution which, for the present case, is represented by the expression:
\[ H_{\text{measured}} = H_n = \frac{\pi}{d} \sqrt{\frac{K_{ii}}{\chi_s(1 + \varepsilon)}}, \]
\[ \text{Eq. 2. 40} \]

with \( \varepsilon \ll 1 \). Hence, near the threshold field, again assuming \( q = (\pi/d) \), the response time will scale as:

\[ \tau = \frac{-\eta}{K_{ii}q^3 - \chi_s \left( \frac{\pi}{d} \sqrt{\frac{K_{ii}}{\chi_s(1 + \varepsilon)}} \right)^3} \approx \frac{\eta}{(\frac{\pi}{d})^3 K_{ii} \varepsilon}. \]
\[ \text{Eq. 2. 41} \]

Note that the above expression correctly indicates that if the experimentalist could measure the threshold field to perfect accuracy \( (\varepsilon \to 0) \), the response time diverges \( (\tau \to \infty) \). At a fixed temperature, as the sample size increases, the response time of the Freedericksz field likewise increases, meaning that the system itself is responding more slowly to the applied field. In addition to the result for the critical field, this is an important experimental result to keep in mind when measuring Freedericksz fields. Namely, although the Freedericksz threshold field scales at \( H_c \propto d \), the response time of the transition scales as \( \tau \propto d^2 \). Hence, if a sample thickness is reduced by a factor of ten, the threshold field will increase by a factor of ten, while the transition itself will occur one hundred times as fast. This is a crucial point to remember when setting the magnetic field sweep rate while using the Freedericksz technique[8].
2.12 – The Case of Weak (or Finite) Surface Anchoring

To conclude this theoretical discussion on the magnetic effects in nematic liquid crystals, the case of weak, or finite, anchoring interactions is discussed. The results are particularly useful for determining the anchoring strength coefficient at the surface boundaries. In fact, for sufficiently narrow samples \( (d \equiv \xi) \), the weak anchoring results are a necessity. The following is an overview as presented by A. Rapini and M. Papoular\(^{[19]} \) and as further discussed by K. H. Yang and C. S. Rosenblatt\(^{[20]} \). Since the results in this section are somewhat difficult to derive, the equations are developed in excruciatingly painful detail.

As before, consider a nematic liquid crystal sample of thickness \( d \), sandwiched between surfaces at \( z=0 \) and \( z=d \). The magnetic field is applied along the \( x \)-axis and the undisturbed nematic director is assumed to be everywhere parallel to the \( z \)-axis. The angle \( \theta(z) \) denotes the tilt angle between the distorted director and its undisturbed orientation along the \( z \)-axis. The configuration corresponds to the Freedericksz bend geometry. Again, in order to determine the equilibrium condition, the free-energy per unit area at the surface must be calculated using the equation:

\[
\mathcal{S} = \int_0^d F(z) dz. \tag{2.4}
\]

The expression for \( F(z) \), as in the previous examples, must include:

(i.) The distorted bulk contribution.

(ii.) The magnetic coupling term.

(iii.) The liquid crystal-wall interaction term, comparable to the
previous surface term $\mathcal{S}_\text{surface} = (1/2)W\theta^2(0)$ (i.e. Eq. 2.10), but presently assuming a somewhat more general form.

Thus, the free-energy per unit volume is written as:

$$F(z)_{\text{wall}} = \frac{1}{2} \left( K_{33} \cos^2 \theta + K_{11} \sin^2 \theta \right) \left( \frac{d\theta}{dz} \right)^2 - \frac{1}{2} \chi_s H^2 \sin^2 \theta$$

$$- \frac{1}{2} I(\theta) \delta(z) + \delta(z - d) \right] \,.$$

Eq. 2.42

where $\delta(z)$ is a Dirac delta function (with units of length$^{-1}$), and the last term corresponds to the anisotropic liquid crystal-wall interfacial energy per unit area. Assuming inversion symmetry of the nematic medium at the surface interface, a possible form of $I(\theta)$ can be formulated as:

$$I(\theta) = \sum_{n=1}^{\infty} A_2 \cos \theta = C \cos^2 \theta + \left( \sum_{n=2}^{\infty} C_{2n} \cos^{2n} \theta \right) \right) \,.$$

Eq. 2.43

where $P_{2n}(\cos \theta)$ are the Legendre polynomials; $A_2$, $C$, $C_{2n}$, and $C$ are constants. As will be shown shortly, the actual form of $I(\theta)$ is irrelevant to the final result; all that matters is that to lowest order $I(\theta)$ scales at $\theta^2$.

Now that the free-energy expression has been established, the threshold field for weak anchoring can be calculated. First, however, two results must be derived from the free-energy expression:
1. Balance of Torque at z=0

The first equation necessary for the development of the finite anchoring threshold field is derived from the balance of torque at the z=0 surface. The generalized torque is obtained from the equation:

\[
\left[ \frac{\partial}{\partial \theta} (S) \right]_{z=0} = \lim_{\epsilon \to 0} \left[ \frac{\partial}{\partial \theta} \left( \int_{z=0}^{z=\epsilon} F(z) dz \right) \right] = \lim_{\epsilon \to 0} \left[ \int_{z=0}^{z=\epsilon} \left( \frac{\partial}{\partial \theta} F(z) \right) dz \right] = 0, \quad \text{Eq. 2.44}
\]

where \(\epsilon\) is some small distance which will eventually be made to vanish; hence the equation will ultimately be evaluated at the z=0 surface. Plugging the free-energy density \(F(z)\) (Eq. 2.42), into the torque equation (Eq. 2.44) gives:

\[
\int_{z=0}^{z=\epsilon} \frac{d}{d\theta} \left[ \left( K_{33} \cos^2 \theta + K_{11} \sin^2 \theta \right) \left( \frac{d\theta}{dz} \right)^2 \right] - \chi_s H^2 \sin \theta \cos \theta - l(\theta) \delta(z) \right] dz = 0.
\]

\quad \text{Eq. 2.45}

which upon differentiation with respect to \(\theta\), becomes:

\[
2 \int_{z=0}^{z=\epsilon} \left( K_{33} \cos^2 \theta + K_{11} \sin^2 \theta \right) \left( \frac{d\theta}{dz} \right)^2 + (K_{11} - K_{33}) \sin \theta \cos \theta \left( \frac{d\theta}{dz} \right)^2 dz
\]

\[-\int_{z=0}^{z=\epsilon} \left( 2 \chi_s H^2 \sin \theta \cos \theta \right) + \left( \frac{dl(\theta)}{d\theta} \delta(z) \right) \right] dz = 0.
\]

or upon further simplification reduces to:
\[ \int_{z=0}^{z=a} \left[ (K_{33} \cos^2 \theta + K_{11} \sin^2 \theta) \left( \frac{d^2 \theta}{dz^2} \right) + \left( K_{11} - K_{33} \right) \sin \theta \cos \theta \left( \frac{d \theta}{dz} \right)^2 \right] dz \]

\[ - \int_{z=0}^{z=d} \left[ \chi_s H^2 \sin \theta \cos \theta \left( \frac{1}{2} \frac{df(\theta)}{d\theta} \delta(z) \right) \right] dz = 0. \]

Eq. 2. 46

The first term, the \((d^2 \theta/dz^2)\) term, can be integrated by parts (i.e.
\[ \int_a^b uv = [uv]_a^b - \int_a^b vu' \]
using the substitutions:

\[ u = \left( K_{11} \sin^2 \theta + K_{33} \cos^2 \theta \right), \quad du = 2 \cos \theta \sin \theta \left( K_{11} - K_{33} \right) \left( \frac{d \theta}{dz} \right) dz, \]

\[ v = \frac{d \theta}{dz}, \quad dv = \left( \frac{d^2 \theta}{dz^2} \right) dz. \]

Hence, noting that the terms in \((d \theta/dz)^2\) cancel each other, the torque equation (Eq. 2. 44 or Eq. 2. 46) becomes:

\[ \left( K_{11} \cos^2 \theta + K_{33} \sin^2 \theta \right) \frac{d \theta}{dz} \bigg|_{z=a}^{z=b} - \chi_s H^2 \sin \theta \cos \theta \frac{df(\theta)}{d\theta} \bigg|_{z=a}^{z=b} - \frac{1}{2} \frac{df(\theta)}{d\theta} \left( \frac{d \theta}{dz} \right) \bigg|_{z=a}^{z=b} = 0. \]

Eq. 2. 47

As a further simplification, recall that for a typical nematic profile
(Figure 2 – 6), \((d \theta/dz)\) has a finite value for \(z>0\) and is zero for \(z<0\). Thus the evaluated term, containing the elastic constants, contributes a finite value only as zero is approached from the \(z>0\) region (i.e. \(z \to 0^+\)). Also, note that the field term can be ignored provided \(\varepsilon\) is made vanishingly small. In this limit, the field term is only integrated over a small layer of surface molecules.
Thus, as \( \varepsilon \) decreases, the field couples to a decreasing layer of molecules and, in the limit of \( \varepsilon \to 0 \), the field term vanishes. Hence, letting the integration thickness vanish, the torque equation reduces to:

\[
(K_{33} \cos^2 \theta + K_1 \sin^2 \theta) \left. \frac{d\theta}{dz} \right|_{z=0} - \frac{1}{2} \left. \frac{dI(\theta)}{d\theta} \right|_{z=0} = 0.
\]  

Eq. 2. 48

The final form of the torque equation, however, is most useful near the threshold when \( \theta(z) \) is small. Near the threshold field, in the limit \( \theta(z) \ll 1 \), the torque equation simplifies to:

\[
K_{33} \frac{d\theta}{dz} = \frac{1}{2} \frac{dI(\theta)}{d\theta}.
\]  

Eq. 2. 49

This form of the torque equation, when combined with the result of the Euler equation (derived in the next section), will provide the expression for the finite surface anchoring threshold field.
II. Applying Euler’s Equation on the Free-Energy Density

Euler’s equation (Eq. 2.34), written explicitly for the present case as:

$$\frac{\partial f}{\partial \theta} - \frac{d}{dz} \left( \frac{\partial f}{\partial (\theta/z)} \right) = 0,$$

Eq. 2.50

allows the calculus of variations to be applied to the free-energy density.

Remembering that the term \((d\theta/dz)\) is treated as a separate variable, the relevant Euler terms are:

$$\frac{\partial f}{\partial \theta} = \sin \theta \cos \theta \left[ K_{11} \left( \frac{d\theta}{dz} \right)^2 - K_{33} \left( \frac{d\theta}{dz} \right)^2 - \chi_s H^2 \right],$$

Eq. 2.51

$$\frac{d}{dz} \frac{\partial f}{\partial (\theta/z)} = 2 \cos \theta \sin \theta \left( \frac{d\theta}{dz} \right)^2 \left\{ K_{11} - K_{33} \right\} + \left( K_{11} \sin^2 \theta + K_{33} \cos^2 \theta \right) \left( \frac{d^2 \theta}{dz^2} \right).$$

Eq. 2.52

Substituting into the Euler equation gives:

$$\sin \theta \cos \theta \left[ (K_{33} - K_{11}) \left( \frac{d\theta}{dz} \right)^2 - \chi_s H^2 \right] - \left( K_{11} \sin^2 \theta + K_{33} \cos^2 \theta \right) \frac{d^2 \theta}{dz^2} = 0.$$

Eq. 2.53

Note that the wall-liquid crystal interaction term \(I(\theta)\) is omitted from the Euler
equation since it only has a contribution at the wall surfaces and the Euler equation is presently being applied to the bulk. The Euler equation can be significantly simplified by multiplying each term by \((d\theta/dz)\) and integrating over \(dz\) from \(z\) to \(z=d/2\). Specifically, the last term in the integrated Euler equation,

\[
\int_z^{z=d/2} \left(K_{11} \sin^2 \theta + K_{33} \cos^2 \theta\right) \frac{d^2 \theta}{dz^2} \frac{d\theta}{dz} \, dz.
\]

Eq. 2.54

can be evaluated by parts (i.e. \(\int_a^b uv = uv\big|_a^b - \int_a^b vu\)), making the following substitutions:

\[
u = \left(K_{11} \sin^2 \theta + K_{33} \cos^2 \theta\right), \quad \frac{dv}{dz} = \frac{d^2 \theta}{dz^2}
\]

\[
u = \frac{1}{2} \left(\frac{d\theta}{dz}\right)^2, \quad du = 2 \cos \theta \sin \theta \left(K_{11} - K_{33}\right) \left(\frac{d\theta}{dz}\right) \, dz.
\]

Hence, this last term becomes:

\[
\int_z^{z=d/2} \left(K_{11} \sin^2 \theta + K_{33} \cos^2 \theta\right) \frac{d^2 \theta}{dz^2} \frac{d\theta}{dz} \, dz
\]

\[
= \frac{1}{2} \left(K_{11} \sin^2 \theta + K_{33} \cos^2 \theta\right) \left(\frac{d\theta}{dz}\right)^3 \bigg|_z^{z=d/2} - \int_z^{z=d/2} \sin \theta \cos \theta \left(K_{11} - K_{33}\right) \left(\frac{d\theta}{dz}\right)^3 \, dz.
\]

Eq. 2.55

The last term is further reduced by noting that \((d\theta/dz)=0\) at \(z=d/2\), giving the result:
\[
\int_z^{z=d/2} (K_{11} \sin^2 \theta + K_{33} \cos^2 \theta) \frac{d^2 \theta}{dz^2} \frac{d \theta}{dz} dz
\]

\[= -\frac{1}{2} \left( K_{11} \sin^2 \theta + K_{33} \cos^2 \theta \right) \left( \frac{d \theta}{dz} \right)^2 \bigg|_z^{z=d/2} \sin \theta \cos \theta (K_{11} - K_{33}) \left( \frac{d \theta}{dz} \right)^3 dz.\]

Eq. 2. 56

Putting this last result back into the integrated Euler equation, and noting that terms in \((d \theta/dz)^3\) cancel, gives:

\[\frac{1}{2} \left( K_{11} \sin^2 \theta + K_{33} \cos^2 \theta \right) \left( \frac{d \theta}{dz} \right)^2 \bigg|_z^{z=d/2} \sin \theta \cos \theta \frac{d \theta}{dz} dz.\]  

Eq. 2. 57

which can be integrated trivially to produce:

\[\frac{1}{2} \left( K_{11} \sin^2 \theta + K_{33} \cos^2 \theta \right) \left( \frac{d \theta}{dz} \right)^2 \bigg|_z^{z=d/2} = -\frac{\chi_c H^2}{2} (\cos^2 \theta |_{z=d/2} - \cos^2 \theta).\]  

Eq. 2. 58

Thus, the expression obtained from the application of the Euler equation to the free-energy density reduces (for \(0 < z < d/2\)) to:

\[\left( \frac{d \theta}{dz} \right)^2 = \chi_c H^2 \frac{\cos^2 \theta - \cos^2 \theta |_{z=d/2}}{(K_{33} \cos^2 \theta - K_{11} \sin^2 \theta)}.\]  

Eq. 2. 59

Solving this equation for \(H\) gives:
\[ H = \frac{1}{\sqrt{\chi_a}} \sqrt{\frac{(K_{33} \cos^2 \theta + K_{11} \sin^2 \theta)}{(\cos^2 \theta - \cos^2 \theta|_{z=d/2})}} \frac{d\theta}{dz}. \]  

Eq. 2.60

which, by integrating both sides over \( dz \) from \( z=0 \) to \( z=d/2 \), gives:

\[ H = \frac{2}{d\sqrt{\chi_a}} \int_{\theta|_{z=0}}^{\theta|_{z=d/2}} \left( \frac{K_{33} \cos^2 \theta + K_{11} \sin^2 \theta}{\cos^2 \theta - \cos^2 \theta|_{z=d/2}} \right)^{\frac{1}{2}} d\theta. \]  

Eq. 2.61

This is the final form of the free-energy expression needed to calculate the finite anchoring threshold field. The expression for \( H \), as well as the boundary condition obtained by balancing torques at \( z=0 \), made no assumptions concerning the magnitude of the anchoring strength. From this point, the procedure is to calculate the Fredericksz threshold field for the more general case of finite surface anchoring.
2.13 – Calculation of the Critical Field in the Case of Finite Surface

**Anchoring**

Near the threshold, the angles \( \theta(z) \), \( \theta(z=0) \), and \( \theta(z=d/2) \) will be small\(^{[20]} \), and the previous field equation simplifies to:

\[
H = \frac{2}{d \sqrt{\chi_a}} \int_{\theta(z=0)}^{\theta(z=d/2)} \left( \frac{K_{33}}{\theta^2_{z=d/2} - \theta^2} \right)^{\frac{1}{2}} \ d\theta. \tag{Eq. 2.62}
\]

By gathering some terms and solving the integral, the equation takes the form:

\[
\frac{Hd}{2} \sqrt{\frac{\chi_a}{K_{33}}} = \int_{\theta(z=0)}^{\theta(z=d/2)} \left( \frac{1}{\theta^2_{z=d/2} - \theta^2} \right)^{\frac{1}{2}} d\theta = \arcsin \left( \frac{\theta}{\theta(z=d/2)} \right) \bigg|_{\theta(z=0)}^{\theta(z=d/2)} \tag{Eq. 2.63}
\]

or

\[
\frac{Hd}{2} \sqrt{\frac{\chi_a}{K_{33}}} = \frac{\pi}{2} - \arcsin \left( \frac{\theta}{\theta(z=d/2)} \right) \tag{Eq. 2.64}
\]

However, defining \( U \) as the threshold field for the case of strong (or infinite) anchoring, \( U = (\pi/d) \sqrt{K_{33}/\chi_a} \), the left-hand side of the equation simplifies and the entire equation becomes:
where U now explicitly represents the threshold field in the presence of strong surface anchoring. Rewriting the equilibrium condition as:

\[
\frac{\theta}{\theta|_{z=d/2}} = \sin\left(\frac{\pi}{2} - \frac{\pi H}{2 U}\right) = \cos\left(\frac{\pi H}{2 U}\right),
\]

Eq. 2.66

allows the original differential equation (Eq. 2.59), for small angles \(\theta(z)\), \(\theta(z=0)\), and \(\theta(z=d/2)\), to be written as:

\[
\left(\frac{d\theta}{dz}\right) = \sqrt{\frac{\chi_s H}{K_{33}} (\theta^2|_{z=d/2} - \theta^2)^{1/2}} = \sqrt{\frac{\chi_s H}{K_{33}} \cos^2\left(\frac{\pi H}{2 U}\right) - \theta^2^{1/2}}.
\]

Eq. 2.67

or, after some manipulations, as:

\[
\left(\frac{d\theta}{dz}\right) = \left(\frac{\chi_s H}{K_{33}}\right) \tan\left(\frac{\pi H}{2 U}\right).
\]

Eq. 2.68

However, recall that the boundary condition, near \(\theta(z)=0\), reduces to:

\[
K_{33} \frac{d\theta}{dz} = \frac{1}{2} \frac{dI}{d\theta} \quad \text{or} \quad K_{33} \frac{d\theta}{dz} = W\theta.
\]

Eq. 2.49

since \(I = W\theta^2\) to lowest order. Note that until now, the form of \(I(\theta)\) had been
entirely general; the final result requires only that $I(\theta)$ be proportional to $\theta^2$ for small $\theta$. Hence, equating expressions for $(d\theta/dz)$ produces:

$$\frac{W\theta}{K_{33}} = \sqrt{\frac{x_a}{K_{33}}} H \theta \tan\left(\frac{\pi H}{2 U}\right),$$

Eq. 2.69

which, when combined with the expression for the threshold field in the case of infinite anchoring $U = (\pi/d)\sqrt{K_{ii}/x_a}$, finally results in the generalized equation:

$$\frac{\pi}{d} \frac{K_{ii} H}{W U} = \cot\left(\frac{\pi H}{2 U}\right),$$

Eq. 2.70

where $K_{ii}$ is the appropriate elastic constant for the given Freedericksz geometry. This is the primary relationship between the Freedericksz threshold field $H$, in the case of finite surface anchoring, and the Freedericksz threshold field $U$, for the conditions of infinite anchoring. Notice that as the anchoring energy increases ($W \to \infty$), the finite anchoring threshold field $H$ (which is always less than or equal to $U$) approaches the infinite anchoring field $U$ ($H \to U$). This is the expected result. The detailed analysis of surface anchoring measurements and field determination will be presented in Chapter 4.
2.14 – Fluctuations in Nematic Alignment

To conclude the theoretical discussion on distortions in nematic liquid crystals, the orientational thermal average of the nematic director \( \langle n_{\alpha}(q) \rangle \), as well as the differential cross-section (per unit solid angle) for scattered light \( d\sigma/d\Omega \), are derived according to the development of P. G. de Gennes\(^{[5]} \). The final results are the basis of the light scattering experiments which comprise the bulk of the data presented in later sections.

The first detailed experiments on the scattering of light from well-aligned nematic liquid crystals began in 1948 by P. Chatelain\(^{[21]} \) (coincidentally in that same year, the Cleveland Indians would win their most recent Major League World Series)\(^{[22]} \). Since then, the use of light scattering techniques to probe the distortions occurring in nematic liquid crystals has become quite popular and well-documented\(^{[5,23,24]} \). The typical light scattering geometries are shown below:

![Figure 2 – 13: Typical Light Scattering Geometries](image)

Configuration A  Configuration B  Configuration C
These geometries will be discussed later in great detail but are presently shown to describe their generalities. Regardless of the scattering configuration, the relevant parameters are:

\[ \vec{k}_{\text{out}} = \text{out-going wavevector of the probing beam inside the sample}, \]
\[ \vec{k}_{\text{in}} = \text{in-coming wavevector of the probing beam inside the sample}, \]
\[ \hat{f} = \text{polarization of the out-going beam}, \]
\[ \hat{i} = \text{polarization of the in-coming beam}, \]
\[ \vec{q} = \text{defines the "internal scattering vector" as: } \vec{q} = \vec{k}_{\text{out}} - \vec{k}_{\text{in}}, \]
\[ \phi = \text{"internal scattering angle" is the angle between } \vec{k}_{\text{out}} \text{ and } \vec{k}_{\text{in}}. \]

The "scattering plane", of course, is defined by the plane \((\vec{k}_{\text{out}}, \vec{k}_{\text{in}})\).

Depending on the orientation of the polarizations relative to the optical axis of the nematic sample, the beams will propagate with the "ordinary" refractive index \(n_\perp\), the "extraordinary" refractive index \(n_{||}\), or some geometric combination of the two (see Appendix B). In order to determine the absolute differential cross-section of scattered light, the small fluctuations in the nematic director \(n(\vec{r})\) as well as the correlation between \(n(\vec{r}_1)\) and \(n(\vec{r}_2)\), must be rigorously derived.
2.15 – Orientation Fluctuations and Correlations in Nematic Liquid Crystals

Consider a nematic sample whose average director $\vec{n}_a$ is oriented along the $z$-axis. The fluctuations in the optical axis at any point $\vec{r}$ are described by small, non-vanishing components $n_x(\vec{r})$ and $n_y(\vec{r})$. To second order in these fluctuations, the distortion free-energy (neither per unit area nor per unit volume) is[5]:

$$F_d = \frac{1}{2} \left[ \left\{ K_{11} \left( \frac{\partial n_x}{\partial x} + \frac{\partial n_x}{\partial y} \right) \right\}^2 + \left\{ K_{22} \left( \frac{\partial n_x}{\partial y} - \frac{\partial n_y}{\partial x} \right) \right\}^2 + \left\{ K_{33} \left[ \left( \frac{\partial n_z}{\partial x} \right)^2 + \left( \frac{\partial n_z}{\partial z} \right)^2 \right] \right\} \right] d\vec{r}.$$  

Eq. 2. 71

External field contributions, from an applied magnetic field for example, will be ignored since the relevant experimental measurements were taken in the absence of such fields. However, keep in mind that the results presented below are significantly altered by external field effects; these may be mentioned at appropriate points. For notational convenience, $n_x(\vec{r})$ and $n_y(\vec{r})$ are analyzed in terms of Fourier components (again, this prescription is chosen so as not to change the dimensions of the transformed quantities):

$$n_s(\vec{r}) = V \int n_s(\vec{q}) e^{-i\vec{q}\cdot\vec{r}} d\vec{q},$$  

(Eq. 2.26 and Eq. 2.27)

where $V$ is the sample volume, such that the free-energy becomes:
\[ F_d = \frac{1}{2} V \sum_q \left\{ K_{11}|n_x(q)q_x + n_y(q)q_y|^2 + K_{22}|n_z(q)q_z|^2 \right. \\
\left. + K_{33}q_z^2 (|n_x(q)|^2 + |n_y(q)|^2) \right\} \]  

Eq. 2.72

The free-energy can now be diagonalized by a linear transformation from \((n_x, n_y)\) to \((n_1, n_2)\). For each \(q\) component, two unit vectors \(\hat{e}_i\) and \(\hat{e}_z\) are introduced such that \(\hat{e}_z\) is normal to \(\vec{q}\) and \(\hat{e}_i\) is normal to \(\vec{e}_z\). These conditions correspond to the following prescription:

\[ \hat{e}_z = \frac{\hat{n}_x \times \vec{q}}{||\hat{n}_x \times \vec{q}||} \quad \text{and} \quad \hat{e}_i = \frac{\hat{e}_z \times \hat{n}_x}{||\hat{e}_z \times \hat{n}_x||} \]  

Eq. 2.73

The component of \(\hat{n}(\vec{q})\) along \(\hat{e}_z\) (\(\alpha = 1, 2\)) is labeled \(n_\alpha(\vec{q})\). Notice that \(\hat{n}_1(\vec{q})\) corresponds to a periodic distortion which is a mixture of pure splay and bend, while \(\hat{n}_2(\vec{q})\) describes a periodic distortion which is a mixture of twist and bend (see Appendix D). Noting that \(n_x^2 + n_y^2 = n_z^2 + n_\perp^2\), and that in the present geometry, \(n_1 = (n_x, n_y, 0)\) and \(n_2 = (-n_x, n_y, 0)\), the free-energy (Eq. 2.71) takes on the very simple form:

\[ F_d = \frac{1}{2} V \sum_q \sum_{\alpha=1,2} |n_\alpha(q)|^2 \left( K_{33}q_z^2 + K_{\alpha\alpha}q_\perp^2 \right) \]  

Eq. 2.74

where \(\vec{q}_\parallel = \vec{q} \cdot \hat{z}\) is the component of the scattering vector parallel to the optical axis, while \(\vec{q}_\perp = \vec{q} \cdot \hat{e}_i\) is the normal component. By transforming the free-energy into the \(\hat{n}(\vec{q})\) and \(\hat{n}_z(\vec{q})\) notation, the various degrees of freedom are decoupled; hence, the thermal average of \(|n_\alpha(\vec{q})|^2\) can be calculated by invoking the _equipartition theorem_. The equipartition theorem states:
for a classical system with the energy quadratic in the amplitudes \( n_\alpha (\vec{q}) \), the average of the free-energy, per degree of freedom, at thermal equilibrium, is equal to \( K_B T/2 \).

The result of the application of the equipartition theorem is:

\[
\left\langle \frac{1}{2} V \left| n_\alpha (\vec{q}) \right|^2 \left( K_{\alpha\alpha} q^2 \right) \right\rangle = \frac{1}{2} K_B T, \text{ or}
\]

\[
\left\langle \left| n_\alpha (\vec{q}) \right|^2 \right\rangle = \frac{(K_B T/V)}{(K_{\alpha\alpha}^2 + K_{\beta\beta}^2)}.
\]

\text{(Eq. 2.75)}

where the notation \( \langle \rangle \) denotes a thermal average. The result for \( \left\langle \left| n_\alpha (\vec{q}) \right|^2 \right\rangle \) is the central formula for fluctuations in nematic liquid crystals.

From this point, the correlation between the director at two different points, \( n(\vec{r}_1) \) and \( n(\vec{r}_2) \), can be calculated. Again making the Fourier substitution:

\[
n_s (\vec{r}) = V \int n_\alpha (\vec{q}) e^{-i\vec{q} \cdot \vec{r}} \, d\vec{q}.
\]

\text{(Eq. 2.26 and Eq. 2.27)}

gives the result:

\[
\left\langle n_s (\vec{r}_1) n_s (\vec{r}_2) \right\rangle = V^2 \iint \langle n_\alpha (\vec{q}) n_\alpha (-\vec{q}') \rangle e^{i(\vec{q} \cdot \vec{r}_1 - \vec{q}' \cdot \vec{r}_2)} d\vec{q} d\vec{q}'.
\]

\text{Eq. 2.76}

which becomes:
\begin{equation}
\langle n_z(\vec{r}_1)n_z(\vec{r}_2) \rangle = \sum_{q,q'} \langle n_z(\vec{q})n_z(-\vec{q}') \rangle e^{i(q \cdot \vec{r}_1 - q' \cdot \vec{r}_2)}. \tag{Eq. 2.77}
\end{equation}

However, noting that $n_z(\vec{q})$ and $n_z(-\vec{q}')$ are uncorrelated, the correlation becomes:

\begin{equation}
\langle n_z(\vec{r}_1)n_z(\vec{r}_2) \rangle = \sum_q \langle |n_z(\vec{q})|^2 \rangle e^{-i(q \cdot \vec{R})}. \tag{Eq. 2.78}
\end{equation}

where $\vec{R} = \vec{r}_2 - \vec{r}_1$. Once again, the procedure is to transform from $(n_x, n_y)$ to $(n_1, n_2)$ according to the same linear transformation previously outlined. The algebra is rather tedious and is simplified only for the approximation $K = K_{11} = K_{22} = K_{33}$. The result for this one constant approximation is interesting only in the presence of an applied magnetic field\textsuperscript{[5]}. For the more general case, $K_{11} \neq K_{22} \neq K_{33}$, the exact result is:

\begin{equation}
\langle n_z(\vec{r}_1)n_z(\vec{r}_2) + n_z(\vec{r}_1)n_z(\vec{r}_2) \rangle = \frac{K_BT}{4\pi} \left\{ \frac{1}{R_1 \sqrt{K_{11}K_{33}}} + \frac{1}{R_2 \sqrt{K_{22}K_{33}}} \right\}, \tag{Eq. 2.79}
\end{equation}

where

\begin{equation*}
R_\alpha = \sqrt{x^2 + y^2 + z_\alpha^2}, \text{ and } z_\alpha = z_\sqrt{K_{dd}/K_{33}}. \tag{Eq. 2.79}
\end{equation*}

This type of correlation behavior is found in all physical systems (involving only short range interactions) which exhibit a preferred direction or privileged axis, provided the axis is arbitrary\textsuperscript{[5]}. 

2.16 – Scattering of Light by Orientation Fluctuations

Fluctuations in the dielectric tensor,

\[ \varepsilon_{\alpha\beta} = \varepsilon_\perp \delta_{\alpha\beta} + (\varepsilon_n - \varepsilon_\perp) n_\alpha n_\beta = \varepsilon_\perp \delta_{\alpha\beta} + \varepsilon_\| n_\alpha n_\beta, \quad \text{Eq. 2.80} \]

drastically affect the outcome of scattered light and are generally ascribed, specifically for the nematic phase, to fluctuations in the nematic director. The ultimate goal of the analysis presently under investigation is to derive a formula for the differential cross section per unit solid angle of scattered light, defined as:

\[ \frac{d\sigma}{d\Omega} = \frac{\text{(power out / solid angle)}}{\text{(power in / unit area of incident beam)}}, \quad \text{Eq. 2.81} \]

which has units of area \((\text{cm}^2)\)\(^{25}\). Note that \(d\sigma\) denotes a differential cross-sectional area of scattered light per unit differential solid angle, \(d\Omega\). The treatment, again as outlined by P. G. de Gennes\(^{[5]}\), begins with the expression for the electric field at an observation point \(\vec{r}'\), radiated by a dipole \(\vec{P}\), oscillating at an angular frequency \(\omega\), and located at the point \(\vec{r}\). The geometry is represented below:
Figure 2 – 14: Geometry for Dipole Radiation

The field \( \tilde{E}(\bar{r}') \), given by J. D. Jackson (equation 9.18)\(^{[25]}\), is:

\[
\tilde{E}(\bar{r}') = \frac{\omega^2}{c^2} \frac{1}{R} e^{iR} \tilde{p}_n(\bar{r}).
\]

Eq. 2. 82

where \( k = \bar{n} \omega/c \), \( \bar{R} = \bar{r}' - \bar{r} \) is the direction of observation, \( \bar{n} \) is the average refractive index, and \( \tilde{p} \) is the component of \( \tilde{P} \) normal to the observation direction. Assuming that the radiating dipoles \( \tilde{P} \) (within the sample), are induced by the incident radiation, written as \( \tilde{E}_\alpha(\bar{r}) = \left( E_\alpha e^{i\bar{\omega} \cdot \bar{r}} \right) \hat{\epsilon} \), then the dipoles will have the form\(^{[25]}\):

\[
\tilde{P}(\bar{r}) = \frac{1}{4\pi} (\tilde{D} - \tilde{E}) = \frac{1}{4\pi} (\tilde{E}(\bar{r}) - 1) \tilde{E}_\alpha(\bar{r}).
\]

Eq. 2. 83
The outgoing field, the field of ultimate interest, is obtained by summing all of the radiating fields \( \vec{E}(\vec{r}') \), over the entire sample volume. However, by moving the observation point \( \vec{r}' \) far enough from the scattering region (i.e. the "far zone": \( \vec{k} \cdot \vec{r}' \gg 1 \)), the required summation is greatly simplified. First, the factor \( 1/R \) does not vary much within the integral and may therefore be factored from the integrand. Secondly, the exponent \( kR \), may be taken to be \( kR = \vec{k}_{\text{out}} \cdot \vec{R} = k_{\text{out}} (r' - r) \), where \( \vec{k}_{\text{out}} \) is the direction of the outgoing, or final, beam. With these assumptions, and using the notation \( \vec{q} = \vec{k}_{\text{out}} - \vec{k}_{\text{in}} \), the component of \( \vec{E}_{\text{out}} \) along the direction of the final polarization \( \hat{f} \) (i.e. \( \hat{f} \) is normal to \( \vec{k}_{\text{out}} \)), is\(^{[5,25]}\):

\[
\hat{f} \cdot \vec{E}_{\text{out}}(\vec{r}') = E_{\text{out}} \left( \frac{\mathcal{R}}{R} \right) e^{i\vec{q} \cdot \vec{r}'}, \tag{Eq. 2.84}
\]

where

\[
\mathcal{R} = \frac{\omega^2}{4\pi c^2} \int \left\{ \hat{f} \cdot (\vec{E}(\vec{r}) - 1) \right\} e^{-i\vec{q} \cdot \vec{r}} d\vec{r}, \tag{Eq. 2.85}
\]

is called the *scattering amplitude*, and has units of length. Once again, transforming into Fourier components:

\[
\vec{E}(\vec{q}) = \frac{1}{V} \int_{V} \vec{E}(\vec{r}) e^{i\vec{q} \cdot \vec{r}} d\vec{r} . \tag{Eq. 2.26 and Eq. 2.27}
\]
the scattering amplitude reduces to:

\[ \mathcal{R} = \frac{\omega^2 V}{4 \pi c^2} \hat{i} \cdot \hat{e}(\hat{q}) \cdot \hat{f}. \]  

Eq. 2.86

Therefore, the power radiated in the direction of \( \hat{R} \) with polarization \( \hat{f} \), per unit solid angle \( d\Omega \); per unit incident flux (power per unit area) in the direction \( \hat{r} \) with polarization \( \hat{i} \), is a quantity with dimensions of area per unit solid angle. It is called the differential scattering cross section and is given by:

\[ \frac{d\sigma}{d\Omega} = \left\langle \frac{|\hat{f} \cdot \hat{E}_{\text{scattered}}|^2}{|\hat{i} \cdot \hat{E}_{\text{incident}}|^2 / R^2} \right\rangle = \left\langle \frac{\mathcal{R}^2}{|\mathcal{E}_0|^2} \right\rangle = \left\langle |\mathcal{R}|^2 \right\rangle. \]

Eq. 2.87

However, as stated at the outset, the relevant contribution to the differential cross section of scattered light comes from the fluctuations in the dielectric tensor. Thus, writing the director as the sum of the average and fluctuating terms, \( \hat{n} = \hat{n}_a + \delta\hat{n} \), and keeping terms linear in \( \delta\hat{n} \), the term \( \hat{f} \cdot \hat{e} \cdot \hat{i} \) (Eq. 2.86) reduces to:

\[ \hat{f} \cdot \hat{e} \cdot \hat{i} = \left( \hat{f} \cdot \langle \hat{e} \rangle \cdot \hat{i} \right) + \left( \epsilon_a \left( \hat{f} \cdot \delta\hat{n} \right) \left( \hat{n}_a \cdot \hat{i} \right) \right) + \left( \epsilon_a \left( \hat{i} \cdot \delta\hat{n} \right) \left( \hat{n}_a \cdot \hat{f} \right) \right). \]

Eq. 2.88

The first term, being independent of the fluctuations, is ignored while the second and third terms are simplified by transforming to the modes \( (n_1, n_2) \)
according to:
\[ \delta \hat{n}(\vec{q}) = \hat{e}_1 \hat{n}_1(\vec{q}) + \hat{e}_2 \hat{n}_2(\vec{q}). \]  
Eq. 2. 89

The final result for the differential cross section, assuming that the cross terms \( n_1 n_2^* \) vanish since the two modes are uncorrelated, gives:
\[ \frac{d\sigma}{d\Omega} = \left( \frac{e^2 \alpha^2 \nu}{4 \pi c^2} \right)^2 \sum_{\alpha=1,2} \langle |\hat{n}_\alpha(\vec{q})|^2 \rangle (i_{\alpha f_\alpha} + i_{f_\alpha})^2. \]  
Eq. 2. 90

or, upon substituting the expression for \( \langle |\hat{n}_\alpha(\vec{q})|^2 \rangle \) becomes:
\[ \frac{d\sigma}{d\Omega} = \frac{\pi^3 V (\Delta \epsilon)^2}{\lambda^4} K_b T \sum_{\omega, \alpha, \beta} \frac{(i_{\omega f_\alpha} + i_{f_\alpha})^2}{K_{\omega \alpha}^2 + K_{\omega \alpha}^2}. \]  
Eq. 2. 91

which can be rewritten, on a per unit volume basis, as:
\[ \frac{d\sigma}{d\Omega}_{\text{Volume}} = \frac{\pi^3 (\Delta \epsilon)^2}{\lambda^4} K_b T \sum_{\omega, \alpha, \beta} \frac{(i_{\omega f_\alpha} + i_{f_\alpha})^2}{K_{\omega \alpha}^2 + K_{\omega \alpha}^2}. \]  
Eq. 2. 92

This result represents the absolute differential cross section per unit volume per unit of solid angle for light scattered from the thermal fluctuations of the nematic director in the absence of externally applied fields\(^5\). It is the primary result of the discussions concerning the probing of distortions in nematic liquid crystals using light scattering techniques and forms the basis for the results presented herein. Experimentally, for a particular liquid crystal sample at a fixed temperature, the absolute differential cross section will be
measured as a function of internal scattering angle. At different angles, the cross sectional ratios will enable one to extract information on the elastic constant ratios. The entire process can then be performed as a function of temperature. The ultimate goal, therefore, is to combine Freedericksz threshold field measurements (which provide absolute elastic constant values) with light scattering techniques (which provide elastic constant ratios) in order to characterize the viscoelastic properties of the oligomeric system under investigation.
References


[9] Haller, I. and H. A. Huggins, U. S. Pat. 3 656 834 (Cl. 350/150; G02f) (1972)


3. EXPERIMENTAL:
LIGHT-SCATTERING

3.1 – Quasi-Elastic Light Scattering

Light scattered by the long wavelength angular fluctuations of the nematic director \( \hat{n} \) is comprised of two diffusive modes corresponding to the splay-bend distortion (\( \hat{\varepsilon}_t \)-mode) and the twist-bend distortion (\( \hat{\varepsilon}_z \)-mode). For the undisturbed case, where the director \( \hat{n} \) points along the z-axis, the differential scattering cross-section per unit volume per unit solid angle is given by\(^{1-3}\):

\[
\frac{d\sigma}{d\Omega}_{\text{Volume}} = \frac{\pi^2(\Delta\varepsilon)^2}{\lambda^4} K_B T \sum_{\nu=1,2} \frac{(i_{\nu\sigma} f_{\nu\sigma} + i_{\nu\nu} f_{\nu\nu})^2}{K_{33} q_{\parallel}^2 + K_{\nu\nu} q_{\perp}^2}
\]

Eq. 3.1

where \( K_B \) is the Boltzmann constant, \( T \) is the absolute temperature, \( \lambda \) is the wavelength of light, \( \Delta\varepsilon = \varepsilon_{\parallel} - \varepsilon_{\perp} \) is the optical dielectric anisotropy, and \( K_{11}, K_{22}, \) and \( K_{33} \) are the splay, twist, and bend elastic constants, respectively. The volume dependence of the differential cross section will be treated in the Angular Calibration section of this chapter. The scattering vector \( \vec{q} \), with parallel and perpendicular components appearing in the denominator of the

110
equation, corresponds to the momentum transfer between the incident and scattered wavevectors:

\[ \vec{q} = \vec{k}_{\text{final}} - \vec{k}_{\text{incident}}. \]  

Eq. 3. 2

The scattering vector has components \( q_i \) and \( q_\perp \) which are parallel to \( \hat{n}_o \) and in the plane perpendicular to \( \hat{n}_o \), respectively. The terms \( i_u \) and \( f_u \) describe the polarizations of the incident and final wavevectors along the direction given by \( u \ (u = 1, 2) \). The numerator contains the polarization factor, \((i_u f_a + i_a f_u)\) defined as:

\[ (i_u f_a + i_a f_u) = (\hat{\imath} \cdot \hat{e}_a)(\hat{\jmath} \cdot \hat{e}_b) + (\hat{\imath} \cdot \hat{e}_b)(\hat{\jmath} \cdot \hat{e}_a) \]  

Eq. 3. 3

where \( \hat{\imath} \) and \( \hat{\jmath} \) are unit vectors related to the nematic director and the scattering vector by the relations:

\[ \hat{e}_2 = \frac{\hat{n} \times \vec{q}}{|\hat{n} \times \vec{q}|} \text{ and } \hat{e}_1 = \frac{\hat{e}_2 \times \hat{n}}{|\hat{e}_2 \times \hat{n}|}. \]  

Eq. 3. 4

The mean relaxation frequencies (\( \Gamma \)) for the two director deformation modes are determined by means of photon correlation spectroscopy and are given by[41]:

\[ \Gamma_u(q) = \frac{(K_{33}q_\perp^2 + K_{11}q_\parallel^2)}{\eta_u(q)} \]  

Eq. 3. 5

where \( \eta_u(q) \) are the two viscosity functions:
\[ \eta_1(q) = \gamma_1 - \frac{(q_1^2 \alpha_3 - q_4^2 \alpha_2)^2}{q_1^2 \eta_a + q_4^2 q_s (\alpha_1 + \alpha_3 + \alpha_4 + \alpha_5) + q_4^2 \eta_c} \]

Eq. 3. 6

and

\[ \eta_2(q) = \gamma_1 - \frac{(q_4 \alpha_2)^2}{q_1^2 \eta_a + q_4^2 \eta_c} . \]

Eq. 3. 7

Each \( \alpha_i \) refers to one of the five Leslie viscosity coefficients, \( \gamma_1 \) is the twist viscosity, and \( \eta_a, \eta_b, \) and \( \eta_c \) are the Miesowicz viscosities which can be parametrized in terms of the Leslie coefficients.

For quantifying the viscoelastic properties of the desired oligomeric system, three light scattering configurations were established. Although only the first two of these geometries have produced relevant data, all three configurations are discussed.
3.2 – Configuration A - Homogeneous Alignment

Splay / Twist Geometry

In configuration A, the scattering vector is selectively chosen such that the resulting scattered intensity contains contributions arising from both the splay-bend and the twist-bend modes. In particular, $q_i$ is chosen to vanish such that the scattered intensity is actually due to the sum of splay and twist contributions. Notice that by choosing $q_i$ to equal zero, the bend distortion lends no contribution to the measured intensity.

First, the sample is oriented with $\hat{n}_o$ along the z-axis, perpendicular to the scattering plane. The liquid crystal is considered to be homogeneously aligned with respect to its glass container. The incident polarization is likewise positioned along the z-axis while the final polarization lies in the xy-plane. Such a configuration is commonly referred to as a depolarized VH experiment due to the vertical and horizontal nature of the initial and final polarizations, respectively. Obviously, with $\vec{q}$ lying in the xy-plane and $\hat{n}_o$ oriented along the z-axis, the component $q_i$ identically vanishes, as desired. With this configuration properly established, the intensity (Eq. 3.1) reduces to:

$$I_{\text{scanned}} = \frac{\pi^2 (\Delta \varepsilon)^2}{\lambda^4} K_T \left[ k_i^2 \left\{ \frac{n_x^2}{K_{11} q_{I}^2 + \left( \frac{n_o - n_c \cos \phi}{K_{22} q_{I}^2} \right)^2} \right\} \right]$$

Eq. 3.8

with
\[ q_\perp = k_0 \sqrt{(n_o \cos \phi - n_r)^2 + (-n_o \sin \phi)^2} \text{.} \quad \text{Eq. 3.9} \]

The angle \( \phi \) is the internal liquid crystal angle related to the lab angle by applying Snell's law at the air-to-glass and glass-to-liquid crystal interfaces, and \( k_0 \) is the wavevector of light in vacuum, \((2\pi / \lambda)\). Once the scattering \textit{plane} is properly chosen, there still remains the possibility of manipulating the polarization factors appearing in the numerator by appropriately choosing the scattering vector (i.e. by specifying a particular scattering angle, one of the polarization factors can be made to vanish). By examining the above equation (Eq. 3.8), one realizes that the factor \((n_o - n_r \cos \phi)\) can be made to vanish with proper selection of the internal angle, \( \phi \). Hence, there exists some angle, the “magic” angle \( \phi^* \), at which the scattered intensity arises solely from the splay director distortion. Calculations involving this magic angle appear frequently not only in this configuration, but in configuration B as well, so for notational convenience, the asterisk (*) will subsequently denote the magic angle. In this set-up, the magic angle can be solved as:

\[ \phi^* = \arccos \left( \frac{n_o}{n_r} \right) \text{.} \quad \text{Eq. 3.10} \]

However, to translate this into the lab scattering angle \( \theta^* \), Snell's law must be applied at the appropriate boundaries, resulting in:

\[ \theta^*_{lab} = \arcsin \left( n_o \sqrt{1 - \frac{n_o^2}{n_r^2}} \right) \text{.} \quad \text{Eq. 3.11} \]
This laboratory magic angle is a function of temperature because of its dependence on the refractive indices. For the oligomeric system under investigation, $\theta^*$ ranges from 25 to 35 degrees, varying over the 20 degree temperature sweep used in the collection of each data set. At the magic angle, the measured intensity (Eq. 3. 1) therefore simplifies to:

$$I_{\text{scattered}}(\theta^*) = \frac{\pi^2(\Delta \varepsilon)^2}{\lambda^2} \frac{K_{11}}{-K_{22}} \left[ k_s^2 \left\{ \frac{n_1^2 \sin^2 \phi^*}{K_{11} q_{11}^2 + K_{22} q_{22}^2} \right\} \right].$$  

Eq. 3. 12

Having outlined the principles involved in this particular configuration, the experimental measurements proceed as follows: first the temperature is fixed and recorded to within 10 mK. At the fixed temperature, the autocorrelation function and absolute intensity measurements are taken at $\theta_{\text{lab}} = 10^0$ and $\theta_{\text{lab}} = \theta^*$. The first angle was chosen to be ten degrees because at this angle, the polarization factors for the splay and twist contributions were of comparable magnitude. Finally, because of the singular-mode property of scattering at the magic angle, the $K_{11} / K_{22}$ ratio could easily be obtain by using the ratio of the measured intensities. Notice that since only the angle is changed between the two measurements, the temperature, wavelength, and dielectric anisotropy dependencies conveniently cancel. Also note that the measured intensity is considered to be the total number of counts, $I_{\text{measured}}(\theta)$; divided by the acquisition time, $t_{\text{collection}}$; multiplied by the angular calibration factor, $C(\theta)$; which is discussed later.
\[ I_{\text{normalized}}(\theta) = \frac{I_{\text{measured}}(\theta)}{I_{\text{collection}}} C(\theta). \]  

Eq. 3. 13

Thus, the intensity ratio has the form:

\[ \frac{I_{\text{norm}}(\theta = 10^\circ)}{I_{\text{norm}}(\theta = \theta^*)} = \frac{\frac{n_i^2 \sin^2 \phi + (n_o - n_i \cos \phi)^2}{K_{11}q_1^4}}{\frac{n_i^2 \sin^2 \phi^*}{K_{11}q_1^4}} \]  

Eq. 3. 14

which results in the elastic constant ratio:

\[ \frac{K_{11}}{K_{22}} = \frac{n_i^2 \sin^2 \phi}{(n_o - n_i \sin \phi)^2} \left[ \left( \frac{I_{\text{norm}}(\theta = 10^\circ)}{I_{\text{norm}}(\theta = \theta^*)} \right) \frac{\sin^2 \phi^* q_1^4}{\sin^2 \phi q_1^4} - 1 \right]. \]  

Eq. 3. 15

As for the decay rates and viscosities, they too simplify quite nicely due to the choice of \( q_1 = 0 \). They (Eq. 3. 5, Eq. 3. 6, and Eq. 3. 7) reduce to scattering modes of pure splay and pure twist:

\[ \Gamma_r = \frac{K_{11}q_1^2}{\eta_{\text{splay}}}, \]  

Eq. 3. 16

\[ \eta_{\text{splay}} = \gamma_1 - \frac{\alpha_s^2}{\eta_b}, \]  

Eq. 3. 17

and

\[ \Gamma_2 = \frac{K_{22}q_1^2}{\gamma_2}. \]  

Eq. 3. 18
The important results regarding configuration A are summarized on the following three pages:
CONFIGURATION A: HOMOGENEOUS ALIGNMENT
SPLAY / TWIST GEOMETRY

GEOMETRY

SCATTERING VECTORS:

\[ \hat{i} = \hat{z} = (0,0,1) \]
\[ \hat{n} = \hat{z} = (0,0,1) \]
\[ \hat{f} = (\sin \phi, \cos \phi, 0) \]
\[ \vec{k}_{e} = \hat{i}, \hat{n}, \hat{f} = k_{e} n_{e}(1,0,0) \]
\[ \vec{k}_{	ext{out}} = k_{e} n_{e}(\cos \phi, -\sin \phi, 0) \]
\[ \vec{q} = \vec{k}_{	ext{out}} - \vec{k}_{	ext{in}} = k_{s}(n_{c} \cos \phi - n_{c} \sin \phi, 0) \]
\[ q_{s} = q_{t} = 0 \]
\[ q_{z} = \sqrt{q_{s}^{2} + q_{t}^{2}} = k_{s} \sqrt{(n_{c} \cos \phi - n_{c} \sin \phi)^{2} + (-n_{c} \sin \phi)^{2}} \]
\[ \hat{e}_{z} = \frac{\hat{i} \times \hat{q}}{|\hat{i} \times \hat{q}|} \]
\[ \hat{e}_{s} = \frac{\hat{e}_{z} \times \hat{n}}{|\hat{e}_{z} \times \hat{n}|} = \frac{(q_{s}, q_{t}, 0)}{|q_{z}|} \]

Results 3 – 1: Configuration A Summary
POLARIZATION FACTORS:

Note: \( i.f_s = (i \cdot \hat{e}_z)(\hat{f} \cdot \hat{e}_z) \)

\( i.f_x = (i \cdot \hat{e}_z)(\hat{f} \cdot \hat{e}_z) = 0 \)

\( i.f_y = (i \cdot \hat{e}_z)(\hat{f} \cdot \hat{e}_z) = (1) \left( \frac{q_z \sin \phi}{q_z} + \frac{q_z \cos \phi}{q_z} \right) = k_z \left( \frac{-n_z \sin \phi}{q_z} \right) \)

\( i.f_z = (i \cdot \hat{e}_z)(\hat{f} \cdot \hat{e}_z) = 0 \)

\( i.f_x = (i \cdot \hat{e}_z)(\hat{f} \cdot \hat{e}_z) = (1) \left( \frac{-q_z \sin \phi}{q_z} + \frac{q_z \cos \phi}{q_z} \right) = k_z \left( \frac{n_z - n_z \cos \phi}{q_z} \right) \)

RESULT:

\[
I_{\text{scattered}} = \frac{(i.f_x + i.f_y)}{K_x q_z^2 + K_y q_z^2} \frac{(i.f_x + i.f_y)}{K_x q_z^2 + K_y q_z^2} \Rightarrow \]

\[
I_{\text{scattered}} = k_z \left( \frac{n_z \sin \phi}{K_z q_z^2} \frac{(n_z - n_z \cos \phi)^2}{K_z q_z^2} \right) \]

Results 3 – 1: Configuration A Summary Continued
INTERNAL ANGLE FOR CONFIGURATION A: HOMOGENEOUS ALIGNMENT SPLAY / TWIST GEOMETRY

\[ n_{\text{lab}} = 1 \quad \theta_{\text{lab}} \]
\[ n_{\text{glass}} = 1.526 \quad \phi \quad \theta_{\text{g}} \]
\[ n_{\text{lc}} = n_0 \]

FOR THE SPLAY / TWIST GEOMETRY, THE ANGLES ARE RELATED AS FOLLOWS:

**AIR-TO-GLASS:**
\[ n_{\text{air}} \sin \theta_{\text{lab}} = n_{\text{glass}} \sin \theta_{\text{glass}} \]
\[ \theta_{\text{glass}} = \arcsin \left( \frac{n_{\text{air}} \sin \theta_{\text{lab}}}{n_{\text{glass}}} \right) \]

**GLASS-TO-LIQUID CRYSTAL:**
\[ n_0 \sin \phi = n_{\text{glass}} \sin \theta_{\text{glass}} \]
\[ \phi = \arcsin \left( \frac{\sin \theta_{\text{lab}}}{n_0} \right) \]

Figure 3 – 1: Internal Angle for Configuration A Light Scattering Geometry
3.3 – Configuration B - Homogeneous Alignment

Bend / Twist Geometry

Configuration B, unlike configuration A, contains components of $\vec{q}$ both parallel to $\hat{n}_o$ and in the plane perpendicular to $\hat{n}_o$. In this configuration, the polarization factors determine which modes are sampled. Namely, both $\hat{n}_o$ and the distortion direction given by $\hat{e}_i$ lie in the scattering plane, hence the polarization factors for the $\hat{e}_i$-mode vanish. The resulting deformations arise solely from the $\hat{e}_z$-mode.

The sample is oriented with $\hat{n}_o$ along the (-y)-axis, in the scattering plane. Again, this corresponds to a homogeneously aligned liquid crystalline sample. The incident and final polarizations remain unchanged in the laboratory frame from configuration A. Obviously, with $\vec{q}$ defining the scattering plane and $\hat{n}_o$ oriented along the (-y)-axis, the component $q_\parallel$ will lie along the y-axis while $q_\perp$ will lie along the x-axis. Before calculating the measured intensities, one important consideration must be accounted for at the very outset. In configuration A, the sample director lies perpendicular to the scattering plane. Hence, the final index is always $n_o$ and incident index is always $n_e$. In the present and final configurations, the extraordinary index (which is now the final index) is slightly more complicated, having an angular dependence. For the case of the director lying in the scattering plane along the (-y)-axis, the extraordinary index is given by\textsuperscript{[6]}:

$$n_{\text{effective}} = n_{\text{eff}}(\phi) = \left(\frac{\cos^2 \phi}{n_e^2} + \frac{\sin^2 \phi}{n_o^2}\right)^{\frac{1}{2}}.$$  \hspace{1cm} \text{Eq. 3.19}
The full derivation of the functional form of \( n_{\text{eff}} \) is presented in Appendix B. Also, for notational convenience, \( n_{\text{eff}} \) is understood to be a function of the internal angle; its explicit dependence on \( \phi \) is emphasized in relevant situations. With this in mind, the scattered intensity (Eq. 3.1) becomes:

\[
I_{\text{scattered}} = \frac{\pi^2 (\Delta \varepsilon)^2}{\lambda^2} k_0 T \left[ \frac{\cos^2 \phi}{K_{33} q_{\parallel}^2 + K_{22} q_{\perp}^2} \right] \text{ with Eq. 3.20}
\]

\[
q_{\perp} = k_0 \left( n_{\text{eff}} \cos \phi - n_{\varepsilon} \right) \quad \text{and Eq. 3.21}
\]

\[
q_{\parallel} = k_0 \left( n_{\text{eff}} \sin \phi \right). \quad \text{Eq. 3.22}
\]

Noticing that the polarization states have defined the resulting deformations modes, the selection of the scattering vector \( \vec{q} \), specified by scattering at a particular angle, still allows one the freedom to single-out one individual director distortion. This “magic” angle can be obtained by letting \( q_{\perp} \) vanish:

\[
q_{\perp}(\phi^*) = k_0 \left( n_{\text{eff}}^* \cos \phi^* - n_{\varepsilon} \right) = 0 \quad \rightarrow \quad \phi^* = \arccos \left( \frac{n_{\varepsilon}}{n_{\text{eff}}(\phi^*)} \right). \quad \text{Eq. 3.23}
\]

Since the functional form of \( n_{\text{eff}} \) is known and by applying Snell’s law at the appropriate boundaries, the magic angle for configuration B reduces to:

\[
\theta^*_{\text{wh}} = \arcsin \left( n_{\varepsilon} \sqrt{1 - \frac{n_{\varepsilon}^2}{n_{\text{eff}}^2}} \right) \quad \text{Eq. 3.24}
\]

which is exactly the same as for the previous configuration (Eq. 3.11). This
result makes light scattering in these two geometries much more convenient. The experimentalist can start with his sample's director oriented along the z-axis to obtain the $K_{11}/K_{22}$ ratio. Next, he can rotate the sample $90^0$ and as easily obtain the $K_{22}/K_{33}$ ratio. The magic angle does not change between these two geometries. Hence, at the magic angle, the measured intensity (Eq. 3.1) for configuration B simplifies to:

$$I_{\text{scattered}}(\phi^*) = \frac{\pi^2(\Delta\varepsilon)^2}{\lambda^4} K_\theta T \left[ \frac{\cos^2 \phi^*}{K_{33} q_{\|}^2} \right].$$

Eq. 3. 25

Experimentally, the procedure is the same as in the previous set-up, including recording the correlation function and absolute intensity at $\theta_{\text{lab}} = 10^0$ and $\theta_{\text{lab}} = \theta^*$. Unlike before, the goal is to determine the $K_{22}/K_{33}$ ratio. Once again noting that all non-angular factors cancel and that the measured intensity must be normalized by time and the angular calibration factor, the intensity ratio becomes:

$$\frac{I_{\text{norm}}(\theta = 10^0)}{I_{\text{norm}}(\theta = \theta^*)} = \frac{\frac{\cos^2 \phi}{K_{33} q_{\|}^2 + K_{22} q_{\|}^2}}{\frac{\cos^2 \phi^*}{K_{33} q_{\|}^2}}.$$

Eq. 3. 26

which results in the desired elastic constant ratio:

$$\frac{K_{22}}{K_{33}} = \left[ \frac{I_{\text{norm}}(\theta = \theta^*) \cos^2 \phi \nu_{\text{eff}}(\phi^*) \sin^2 \phi^* - \nu_{\text{eff}}(\phi) \sin^2 \phi}{(\nu_{\text{eff}}(\phi) \cos \phi - \nu_{\text{o}})^2} \right].$$

Eq. 3. 27
Since the scattered intensity is determined only by the $\hat{e}_z$-mode, only one decay rate and viscosity (Eq. 3.5, Eq. 3.6, and Eq. 3.7) are present:

$$\Gamma_z = \frac{(K_{33}q_r^2 + K_{22}q_\perp^2)}{\eta_z}, \quad \text{Eq. 3.28}$$

$$\eta_z = \gamma_1 - \frac{(q_\perp \alpha_z)^2}{q_\perp^2 \eta_s + q_\parallel^2 \eta_c}. \quad \text{Eq. 3.29}$$

Notice that at the magic angle, $q_\perp=0$ and the viscosity takes on the simpler form:

$$\Gamma_z^* = \frac{K_{33}q(\phi^*)^2}{\eta_{\text{bend}}} \quad \text{with} \quad \text{Eq. 3.30}$$

$$\eta_{\text{bend}} = \gamma_1 - \frac{\alpha_z^2}{\eta_c}. \quad \text{Eq. 3.31}$$

A schematic representation of the configuration B geometry and a summary of its important results are presented on the following three pages:
CONFIGURATION B:
HOMOGENEOUS ALIGNMENT
TWIST / BEND GEOMETRY

SCATTERING VECTORS:
\[ \hat{i} = (0, 0, 1) \]
\[ \hat{n} = -\hat{z} = (0, -1, 0) \]
\[ \hat{r} = (\sin \phi, \cos \phi, 0) \]
\[ n'_s = \begin{pmatrix} \cos \phi & \sin \phi \\ n'_s & -n'_s \end{pmatrix} \]
\[ \hat{k}_s = k_s n'_s \]
\[ \hat{k}_\text{out} = k_s (\cos \phi, -\sin \phi, 0) \]
\[ \hat{q} = \hat{k}_\text{in} - \hat{k}_s = k_s (n'_s \cos \phi - n_s, -n'_s \sin \phi, 0) \]
\[ q_z = q_x = k_s (-n'_s \sin \phi) \]
\[ q_y = q_z = k_s (n'_s \cos \phi - n_s) \]
\[ \hat{\epsilon}_z = \frac{\hat{n} \times \hat{q}}{\lVert \hat{n} \times \hat{q} \rVert} = (0, 0, 1) \]
\[ \hat{\epsilon}_z = \frac{\hat{\epsilon}_z \times \hat{n}}{\lVert \hat{\epsilon}_z \times \hat{n} \rVert} = (1, 0, 0) \]

Results 3 – 2: Configuration B Summary
Polarization Factors:

Note: \( i \cdot f = (i \cdot \hat{e}_x) (\hat{f} \cdot \hat{e}_x) \)

\[ i \cdot f_x = (i \cdot \hat{e}_x) (\hat{f} \cdot \hat{e}_x) = 0 \]
\[ i \cdot f_y = (i \cdot \hat{e}_y) (\hat{f} \cdot \hat{e}_y) = 0 \]
\[ i \cdot f_z = (i \cdot \hat{e}_z) (\hat{f} \cdot \hat{e}_z) = 1 (-\cos \theta) \]
\[ i \cdot f_z = (i \cdot \hat{e}_z) (\hat{f} \cdot \hat{e}_z) = 0 \]

Result:

\[ I_{\text{scattered}} = \frac{(i \cdot f_x + i \cdot f_y)^2}{K_{\|} q_x^2 + K_{\perp} q_y^2} = \frac{(i \cdot f_x + i \cdot f_z)^2}{K_{\|} q_z^2 + K_{\perp} q_y^2} \]

\[ I_{\text{scattered}} = \frac{\cos^2 \phi}{K_{\|} q_x^2 + K_{\perp} q_y^2} = \frac{\cos^2 \phi}{K_{\|} (n_x \sin \theta)^2 + K_{\perp} (n_x \cos \theta - n)^2} \]

Results 3 – 2: Configuration B Summary Continued
INTERNAL ANGLE FOR CONFIGURATION B: HOMOGENEOUS ALIGNMENT TWIST / BEND GEOMETRY

FOR THE TWIST / BEND GEOMETRY, THE ANGLES ARE RELATED AS FOLLOWS:

**AIR-TO-GLASS:**
\[ n_{air} \sin \theta_{lab} = n_{glass} \sin \theta_{glass} \]
\[ \theta_{glass} = \arcsin \left( \frac{n_{air} \sin \theta_{lab}}{n_{glass}} \right) \]

**GLASS-TO-LIQUID CRYSTAL:**
\[ n_{eff}(\phi) \sin \phi = n_{glass} \sin \theta_{glass} \]
\[ n_{eff}(\phi) = \frac{\cos^2 \phi - 1}{n_e^2 - n_o^2} \left( \frac{n_e}{n_o} \right)^2 \]
\[ \phi = \arctan \left( \frac{1}{n_e \sin^2 \theta_{lab} - n_o^2} \right)^{\frac{1}{2}} \]

Figure 3 - 2: Internal Angle for Configuration B Light Scattering Geometry
3.4 – Configuration C - Homeotropic Alignment

Bend / Twist Geometry

The final configuration has many similarities to configuration B: it involves components of \( \vec{q} \) both parallel to \( \hat{n}_x \) and in the plane perpendicular to \( \hat{n}_z \); the polarization factors determine which modes are sampled; and the resulting deformations arise solely from the \( \hat{e}_z \)-mode. As in the previous case, both \( \hat{n}_o \) (now lying along the \((-x)\)-axis) and the distortion direction given by \( \hat{e}_i \) lie in the scattering plane, hence the polarization factors for the \( \hat{e}_z \)-mode vanish.

The sample is oriented with \( \hat{n}_x \) along the \((-x)\)-axis, in the scattering plane. This is different from the other two geometries in as much as the material must be aligned homeotropically with respect to the glass holder. The incident and final polarizations remain unchanged. The component \( q_{||} \) will lie along the \( x \)-axis while \( q_{\perp} \) will lie along the \( y \)-axis. Once again, the sample’s index cannot be taken as independent of scattering angle; the functional form for \( n_{eff} \) is only slightly different from the previous situation and is obtained merely by switching \( n_r \) and \( n_s \) (again, see Appendix B)\(^5\):

\[
n_{\text{effective}} = n_{\text{eff}}(\phi) = \left( \frac{\cos^2 \phi}{n_s^2} + \frac{\sin^2 \phi}{n_r^2} \right)^{-\frac{1}{2}}.
\]

Eq. 3.32

With this in mind, the scattered intensity (Eq. 3.1) becomes:

\[
I_{\text{scattered}} = \frac{\pi^2 (\Delta \varepsilon)^2}{\lambda^2} K g T \left[ \frac{\sin^2 \phi}{K_{33} q_{||}^2 + K_{23} q_{\perp}^2} \right] \quad \text{with}
\]

Eq. 3.33
\[ q_\perp = k_0 \left( n_{\text{eff}} \sin \phi \right) \quad \text{and} \quad Eq. 3.34 \]
\[ q_\parallel = k_0 \left( n_{\text{eff}} \cos \phi - n_0 \right). \quad \text{Eq. 3.35} \]

Examining the functional form of \( n_{\text{eff}} \) reveals that no magic angle exists for this particular geometry. Only at \( \phi = 0^\circ \) do both \( q_\parallel \) and \( q_\perp \) identically vanish. In other words, at no angle does the \( \hat{z}_3 \)-mode scattered light reduce to that from a single distortion. With this being the case, the elastic constant ratio is still obtainable from normalized intensity measurements taken at different angles, however, the book-keeping is a little more tedious.

Experimentally, the procedure is the same as in the other set-ups with the final goal being the determination of the \( K_{22} / K_{33} \) ratio. Let \( \theta_a \) and \( \theta_b \) denote two different scattering angles in the laboratory frame corresponding to angles \( \alpha \) and \( \beta \) internally. As usual, all non-angular factors cancel and the measured intensity must be normalized by time and the angular calibration factor, making the intensity ratio:

\[
\frac{I_{\text{norm}}(\theta_a)}{I_{\text{norm}}(\theta_b)} = \frac{\sin^2 \alpha}{K_{33} q(\alpha)_\parallel^2 + K_{22} q(\alpha)_\perp^2} \quad \frac{\sin^2 \beta}{K_{33} q(\beta)_\parallel^2 + K_{22} q(\beta)_\perp^2} \quad \text{Eq. 3.36}
\]

which results in the desired elastic constant ratio:
\[ \frac{K_{22}}{K_{33}} = \left[ \left( \frac{I_{\text{norm}}(\theta_s) \sin^2 \beta}{I_{\text{norm}}(\theta_s) \sin^2 \alpha} q(\alpha) \right) - q(\beta) \right]^2 \right] \]  

Eq. 3.37

Evidently, since the scattered intensity is determined only by the \( \hat{e}_z \)-mode, only one decay rate and viscosity (Eq. 3.5, Eq. 3.6, and Eq. 3.7) are again present:

\[ \Gamma_z = \frac{(K_{33}q_z^2 + K_{22}q_\perp^2)}{\eta_z} \]  

Eq. 3.38

\[ \eta_z = \gamma_1 - \frac{(q_a \alpha_z)^2}{q_\perp^2 \eta_a + q_z^2 \eta_c} \]  

Eq. 3.39

Of course, even though these expressions are the same as in the previous geometry, they differ by the changes in \( q_a \) and \( q_\perp \). As with the previous two configurations, the central results regarding configuration C are summarized on the following three pages:
**CONFIGURATION C:**
**HOMEOTROPIC ALIGNMENT BEND / TWIST GEOMETRY**

**GEOMETRY**

**SCATTERING VECTORS:**

\[ \hat{i} = \hat{z} = (0, 0, 1) \]
\[ \hat{n} = -\hat{z} = (-1, 0, 0) \]
\[ \hat{j} = \sin \phi \cdot \cos \phi \cdot \hat{\phi} \]
\[ n_{z} = \frac{\cos \phi}{n_{z}} \cdot \frac{\sin \phi}{n_{z}} \]
\[ \vec{k}_{\text{out}} = k \cdot n_{\phi} \cos \phi \cdot \sin \phi \cdot \hat{\theta} \]
\[ \vec{q} = \vec{k}_{\text{out}} - \vec{k}_{\phi} = k \cdot (n_{\phi} \cos \phi - n_{\phi} \sin \phi) \]
\[ q_{\phi} = \vec{q} \cdot (n_{\phi} \cos \phi - n_{\phi} \sin \phi) \]
\[ q_{\phi} = \vec{q} \cdot (n_{\phi} \sin \phi) \]
\[ \vec{e} = \frac{\vec{n} \times \vec{q}}{||\vec{n} \times \vec{q}||} = (0, 0, 1) \]
\[ \vec{e} = \frac{\vec{e} \times \hat{n}}{||\vec{e} \times \hat{n}||} = (0, -1, 0) \]

Results 3 - 3: Configuration C Summary
POLARIZATION FACTORS:

Note: \( i \cdot f = (i \cdot \hat{e}_i)(\hat{f} \cdot \hat{e}_i) \)

\[ i \cdot f_1 = (i \cdot \hat{e}_i)(\hat{f} \cdot \hat{e}_i) = 0 \]
\[ i \cdot f_2 = (i \cdot \hat{e}_i)(\hat{f} \cdot \hat{e}_i) = 0 \]
\[ i \cdot f_3 = (i \cdot \hat{e}_i)(\hat{f} \cdot \hat{e}_i) = (-1)(-\sin \phi) \]
\[ i \cdot f_4 = (i \cdot \hat{e}_i)(\hat{f} \cdot \hat{e}_i) = 0 \]

RESULT:

\[ I_{\text{trans}} = \frac{i \cdot f_1 + i \cdot f_2}{K_{\text{trans}} + K_{\text{trans}}'} \]
\[ \frac{(i \cdot f_3 + i \cdot f_4)}{K_{\text{trans}} + K_{\text{trans}}'} \]

\[ I_{\text{trans}} = \frac{\sin \phi}{K_{\text{trans}} + K_{\text{trans}}'} = \frac{\sin \phi}{K_{\text{trans}}(n_{\text{trans}} \cos \phi - n^2) + K_{\text{trans}}' n_{\text{trans}} \sin \phi} \]
INTERNAL ANGLE FOR CONFIGURATION C: HOMEOTROPIC ALIGNMENT TWIST / BEND GEOMETRY

FOR THE HOMEOTROPIC GEOMETRY, THE ANGLES ARE RELATED AS FOLLOWS:

**AIR-TO-GLASS:**
\[ n_{\text{air}} \sin \theta_{\text{lab}} = n_{\text{glass}} \sin \theta_{\text{glass}} \]
\[ \theta_{\text{glass}} = \arcsin \left( \frac{n_{\text{air}} \sin \theta_{\text{lab}}}{n_{\text{glass}}} \right) \]

**GLASS-TO-LIQUID CRYSTAL:**
\[ n_{\text{eff}}(\phi) \sin \phi = n_{\text{glass}} \sin \theta_{\text{glass}} \]
\[ n_{\text{eff}}(\phi) = \left[ \cos^2 \phi - \frac{\sin^2 \phi}{n_o^2 - \frac{1}{n_e^2}} \right]^{-\frac{1}{2}} \]
\[ \phi = \arctan \left( \frac{1}{\frac{1}{n_o} \sin^2 \theta_{\text{lab}} - \frac{1}{n_e} \sin^2 \phi} \right)^{-\frac{1}{2}} \]

Figure 3 – 3: Internal Angle for Configuration C Light Scattering Geometry
3.5 – Light Scattering Techniques

In a typical light scattering experiment, the detected field is often viewed as a superposition of scattered waves from the sample’s individual scattering centers. Thus, the scattered field fluctuates in response to the molecular motions of the scatterers. The particular method used for detecting the time-dependence of the molecular motion depends on the time scale of these fluctuations. Traditionally, filter methods are used to study the more rapid molecular motions, occurring on a time scale faster than one microsecond, while optical mixing or beating techniques are used for measuring those processes which respond on a time scale slower than one microsecond\[6\]. Although the results and discussions of this thesis are based on data obtained using an optical mixing technique (more specifically, a homodyne optical mixing method), a short review is presented for all three of the main light scattering experimental methods.
3.6 – Filter Methods

The filter method involves the frequency-decomposition of the scattered light by a device such as a diffraction grating or an interferometer. These devices are interposed between the scattering sample and the photomultiplier and act as filters, passing only a single frequency component $\omega_i$ of the scattered light into the photomultiplier. Actually, the filter's output is a function of the frequency shift ($\omega = \omega_i - \omega_f$) between the frequency of the $i^{th}$ scatterer and the filter frequency. Thus, the photomultiplier's dc output is proportional to the spectral density of the scattered electric field $E_s$ at the filter frequency. For processes faster than $10^{-10}$ seconds, a diffraction grating serves as the filter (i.e. "Raman scattering") while for processes with response times ranging between $10^{-6}$ and $10^{-10}$ seconds, an interferometer is used (i.e. "Brillouin scattering"). Filtering techniques do not have the resolution to study processes slower than one microsecond. The typical filtering set-up is illustrated below[^6]:

![Diagram](image)

**Figure 3 – 4: Typical Filter Method Light Scattering Experimental Set-up**
3.7 - Optical Mixing Techniques

In optical mixing methods, no "filter" is inserted between the scattering sample and the photomultiplier; thus scattered light directly impinges upon the PM cathode. In the homodyne method, the method used in this thesis, only the scattered light impinges on the photomultiplier, while in the heterodyne method a local oscillator, usually a small portion of the unscattered laser beam, is directly mixed with the scattered light at the photocathode. The differences between these two optical mixing techniques will be discussed shortly; presently, however, the generalities of conventional optical mixing methods are discussed\cite{6}.

Regardless of which optical mixing method is employed, scattered light emerges from the sample and strikes a photocathode surface. The photomultiplier is a square-law detector, making its instantaneous current output proportional to the square of the scattered electric field \(i(t) \propto |E(t)|^2\). Thus the photomultiplier's output directly measures the intensity of the scattered light or, in other words, represents a count of the number of photons scattering from the illuminated sample. The photomultiplier output is then fed into a digital autocorrelator. The digital autocorrelator is a device which counts, then autocorrelates, current pulses (photons) and therefore calculates the time-autocorrelation function, defined as:

\[
\langle I(0)I(t) \rangle = B \langle |E(0)|^2 |E(t)|^2 \rangle = \lim_{\tau' \to \tau} \frac{1}{\tau} \int_0^{\tau} I(t')I(t + t') dt'.
\]

Eq. 3.40

where \(B\) is a proportionality constant. The proportionality constant \(B\) contains
quantities which are related to the efficiency of the photomultiplier tube; usually, however, the autocorrelation function is normalized by a baseline \( \langle I(0)I(0) \rangle \), and the proportionality constant may be ignored. For subsequent calculations, \( B \) may be taken to be unity. The routine by which the autocorrelator calculates \( \langle I(0)I(t) \rangle \) is detailed in Appendix C. At this point, the differences between heterodyne and homodyne scattering must be distinguished. To facilitate the discussion, two separate scattered field autocorrelation functions are defined:

\[
I_1(t) = \langle E_{\text{scattered}}^*(0) E_{\text{scattered}}(t) \rangle 
\]  
Eq. 3.41
(i.e. “field–field autocorrelation function”)

\[
I_2(t) = \langle |E_{\text{scattered}}(0)|^2 |E_{\text{scattered}}(t)|^2 \rangle 
\]  
Eq. 3.42
(i.e. “intensity–intensity autocorrelation function”)

As will be demonstrated in the following two sections, \( I_2(t) \) will correspond to the “homodyne correlation function” while the expression \( \text{Re}(I_1(t)) \) will contain all the relevant information pertaining to heterodyne scattering. Thus, \( \text{Re}(I_1(t)) \) will come to be denoted as the “heterodyne correlation function”.

3.8 – Homodyne Scattering

The typical homodyne scattering geometry is shown below:

![Diagram of homodyne scattering setup]

**Figure 3 – 5: Typical Homodyne Light Scattering Experimental Set-up**

Obviously, in such a configuration, only scattered light impinges on the photocathode and thus the autocorrelation function \( \langle I(0)I(t) \rangle \) (Eq. 3.40) is comprised of a field term \( E(t) \) which is equal to the scattered field \( E_s(t) \).

Hence, \( \langle I(0)I(t) \rangle \) is proportional to \( I_s(t) \) (Eq. 3.42) which is defined as the "homodyne autocorrelation function". The amplitude of \( E_s(t) \) is proportional to the instantaneous dielectric constant fluctuations in the scattering volume and therefore fluctuates in the same manner. The analysis of the homodyne autocorrelation function is simplified in most circumstances by relating \( I_s(t) \) (Eq. 3.42) to the autocorrelation function \( I_i(t) \) (Eq. 3.41)\[6\]. In order to make this relation, certain assumptions must be made. The scattering volume \( V \) can be subdivided into subregions of volume small compared to the wavelength of light. Then the scattered field \( E_s \) can be regarded as a superposition of fields from each of the subregions:
\[ E_z = \sum_n E_z^{(n)}, \quad \text{Eq. 3.43} \]

where \( E_z^{(n)} \) is the scattered field from the \( n \)th subregion. The crucial assumption required to related \( I_z(t) \) to \( I_i(t) \) is that the scattering volume is assumed to be divided into a large number of statistically independent subregions. Hence, the particle motions in one subregion are independent of those in another. \( E_s \) can then be regarded as a sum of independent random variables \( (E_z^{(1)}, E_z^{(2)}, E_z^{(3)}, \ldots) \), which means that \( E_s \) is distributed according to the Gaussian distribution. From this consideration, one can show that the fourth moment of the Gaussian distribution \( I_z(t) \), is related to the second moment of the Gaussian distribution \( I_i(t) \), by the relation\(^6\):

\[ I_z(t) = |I_i(0)|^2 + |I_i(t)|^2. \quad \text{Eq. 3.44} \]

The term \( |I_i(0)|^2 \) represents a dc term that determines the baseline of the homodyne scattering autocorrelation function. For nematic liquid crystals, P.C. Martin et. al., have shown that the director fluctuations correspond to diffusive modes whose equations of motion correspond to, \textit{but are not physically the same as}, an over-damped oscillator that decays exponentially\(^7\). Hence, \( I_i(t) \) is written as the sum of exponentials:

\[ I_i(t) = \sum_i a_i \exp(-t/\tau_i), \quad \text{Eq. 3.45} \]

where the sum is over multiple relaxation processes. Therefore, the homodyne autocorrelation function (\textbf{Eq. 3.42}) becomes:
\[ I_i(t) = |I_i(0)|^2 + |I_i(t)|^2 = \sum_{i,j} a_i a_j \left[ 1 + \exp \left( \frac{-t}{\tau_i} + \frac{-t}{\tau_j} \right) \right] \]  

Eq. 3. 46

For processes with several relaxation times, the analysis of homodyne data can be quite difficult. However, for a one-relaxation time process (i.e. \( \tau_i = \tau_j \) for all \( j \)), the homodyne correlation function is a single exponential decay with a relaxation time of \( \tau/2 \) rather than \( \tau \). This single-relaxation time analysis, with a response time of \( \tau/2 \), will be used to treat the light scattering data corresponding to single-decay time processes. Such instances occur in the splay/twist (configuration A) and bend/twist (configuration B) geometries when accumulating data at the "magic" angle. Also, for processes where \( I_i(t) \) is composed of two exponentials,

\[ I_i(t) = a_i e^{-t/\tau_i} + a_j e^{-t/\tau_j}. \]  

Eq. 3. 47

the autocorrelation analysis is likewise relatively easy to handle with a bi-exponential fit. The bi-exponential fitting functions will be used when analyzing data acquired at a laboratory scattering angle of 10°. Recall that at 10°, the splay and twist (or twist and bend) contributions to the autocorrelation function are of comparable magnitude and thus the autocorrelation function is bi-exponential:

\[ \langle I(0)I(t) \rangle = \left( a_i \exp(-t / \tau_i) + a_j \exp(-t / \tau_j) \right)^2. \]
3.9 - Heterodyne Scattering

The typical heterodyne scattering geometry is shown below:

![Diagram of heterodyne scattering setup]

**Figure 3 - 6: Typical Heterodyne Light Scattering Experimental Set-up**

In a heterodyne configuration, a small portion of unscattered laser light, called the *local oscillator*, is mixed with the scattered light at the photomultiplier. Other types of heterodyne configurations are also possible. For example, in a homodyne experiment, an intentional (or unintentional) dust speck in the sample volume may be sufficiently large enough to serve as a local oscillator: thus "converting" the homodyne scattering into heterodyne scattering. For
this reason, careful treatment of the final autocorrelation function is required.
In either case, for heterodyne scattering, the local oscillator is assumed to vary at the same frequency as the incident laser beam. Denoting the local oscillator's electric field as \(E_{\text{LO}}(t)\), the electric field impinging upon the photomultiplier is a superposition of \(E_{\text{LO}}(t)\) and \(E_s(t)\). Hence, the autocorrelation function (Eq. 3.40) of the photocathode output is:

\[
\langle I(0)I(t) \rangle = \langle |E(0)|^2 |E(t)|^2 \rangle = \langle |E_{\text{LO}}(0) + E_s(0)|^2 |E_{\text{LO}}(t) + E_s(t)|^2 \rangle
\]

\[
= \left\{ \langle (E_{\text{LO}}(0) + E_s(0)) (E_{\text{LO}}^*(0) + E_s^*(0)) \rangle \right\} + \\
\left\{ \langle (E_{\text{LO}}(t) + E_s(t)) (E_{\text{LO}}^*(t) + E_s^*(t)) \rangle \right\}
\]

Eq. 3.48

which, when written in all of its excruciatingly painful glory, results in one rather large time-averaged expression containing sixteen terms. In order to simplify the ensuing analysis, several approximations are made:

(i.) The experimental conditions are arranged such that \(|E_{\text{LO}}| >> |E_s|\).
(ii.) Fluctuations of the local oscillator field are negligible.
(iii.) The local oscillator field and the scattered field are statistically independent so that, \(\langle I_s I_{\text{LO}} \rangle = \langle I_s \rangle \langle I_{\text{LO}} \rangle\).
Making these reasonable assumptions, the sixteen terms separate resulting in:

(i.) ten terms which vanish on average (i.e. terms which are proportional to $E_{\text{LO}}^3E_\text{x}$ or $E_{\text{LO}}^2E_\text{x}$);

(ii.) two terms which are dc in nature (i.e. terms like $\langle E_\text{x}(0)E_\text{x}^*(0)E_{\text{LO}}(t)E_{\text{LO}}^*(t)\rangle = \langle I_\text{x}(0)\rangle\langle I_{\text{LO}}(t)\rangle$);

(iii.) one term which is negligible (i.e. the term $\langle |E_\text{x}(0)|^2|E_\text{x}(t)|^2\rangle$);

(iv.) and two remaining terms of interest.

The remaining two terms give:

$$\langle I(0)I(t)\rangle = \left[I_{\text{LO}}^2 + 2I_{\text{LO}} \text{Re}(I_\text{x}(t))\right],$$  \hspace{1cm} \text{Eq. 3.49}

where $I_{\text{LO}} = \langle |E_{\text{LO}}|^2 \rangle$ is the intensity of the local oscillator signal and $\text{Re}(I_\text{x}(t))$ is the real part of $I_\text{x}(t)$. The term $I_{\text{LO}}$ represents the dc or background term in a typical heterodyne experiment while the contribution from $\text{Re}(I_\text{x}(t))$ contains all the information concerning the heterodyne correlation function. For this reason, $\text{Re}(I_\text{x}(t))$ is commonly referred to as the "heterodyne correlation function". Comparing the homodyne and heterodyne autocorrelation functions for light scattered from fluctuations whose response time is characterized as a sum of decaying exponentials:
Homodyne Autocorrelation Function:
\[
\langle I(0)I(t) \rangle = |I_1(t)|^2 = |I_1(0)|^2 + |I_i(t)|^2 = \sum_{i,j} a_i a_j \left[ 1 + \exp \left( \frac{-t}{\tau_i} + \frac{-t}{\tau_j} \right) \right]
\]  
Eq. 3.46

Heterodyne Autocorrelation Function:
\[
\langle I(0)I(t) \rangle = [I_{lo}^2 + 2I_{lo} \Re(I_1(t))] = \left[ I_{lo}^2 + 2I_{lo} \Re \left( \sum_i a_i \exp \left( \frac{-t}{\tau_i} \right) \right) \right]
\]
Eq. 3.49

It is clear that the heterodyne technique introduces no extra terms into the scattered field time-correlation function as is the case for the homodyne result. Thus, homodyne and heterodyne optical mixing techniques clearly measure different autocorrelation functions of the dielectric constant fluctuations.
3.10 - Experimental Homodyne Autocorrelation Function

Experimentally, photon correlation analysis of the scattered light was performed by a Brookhaven Instruments model BI-2030AT 136-channel autocorrelator, equipped with six delay (infinite-time) channels and multi-decay time (multi-tau) options. In homodyne photon correlation spectroscopy, the autocorrelator measures the intensity-intensity autocorrelation function, minus the measured, or calculated, baseline:

$$f_{\text{measured}}(t) = \langle I(0)I(t) \rangle - \langle I(0) \rangle^2 = \langle |E_x(0)|^2|E_x(t)|^2 \rangle - \langle |E_x(0)|^2 \rangle^2. \quad \text{Eq. 3.50}$$

where $I(t)$ refers to the detected photon intensity (i.e. the number of photon counts) occurring at time $t$ and the notation $\langle \cdot \rangle$ refers to a time average. As mentioned before, light scattering from liquid crystalline nematic director fluctuations corresponds to processes whose relaxation times are written as a sum of decaying exponentials:

$$I_x(t) = \langle E_x^*(0)E_x(t) \rangle = \sum_i a_i \exp(-t/\tau_i). \quad \text{Eq. 3.45}$$

To measure the relaxation times of the three director distortions occurring in the nematic samples, the Brookhaven autocorrelator measures the autocorrelation function for a particular light scattering process and extracts the response times according to the following formulation\(^{[6]}\): First, the autocorrelation function was normalized:
\[ y(t) = \frac{I_i(t)}{I_i(0)} = \frac{\sum a_i \exp(-t/\tau_i)}{\sum a_i} = \frac{\sum a_i \exp(-tD_i q_i^2)}{\sum a_i}. \]

Eq. 3.51

where \( \tau_i = (D_i q_i^2)^{-1} \) is the decay time of the director fluctuations and \( D_i \) is the effective diffusion coefficient of the \( i \)th mode occurring for a particular \( q \) component. Next, by denoting the operation \( \langle x \rangle = \sum_i a_i x / \sum_i a_i \), and expanding the exponential in a power series for small \( t \), the normalized autocorrelation function becomes:

\[
y(t) = \left\langle e^{-Dq^2t} \right\rangle = \left[ 1 - \left( Dq^2 \right) + \frac{\left( Dq^2 \right)^2}{2} - \frac{\left( Dq^2 \right)^3}{6} + \frac{\left( Dq^2 \right)^4}{24} - \ldots \right]
\]

\[
= 1 - \left\langle Dq^2 \right\rangle t + \frac{\left\langle (Dq^2)^2 \right\rangle}{2} t^2 - \frac{\left\langle (Dq^2)^3 \right\rangle}{6} t^3 + \frac{\left\langle (Dq^2)^4 \right\rangle}{24} t^4 - \ldots \quad \text{Eq. 3.52}
\]

Finally, taking the log of both sides and using the power series

\[
\log(1 + x) = x - \frac{x^2}{2} + \frac{x^3}{3} - \frac{x^4}{4} + \ldots
\]

the log of the autocorrelation function reduces to:

\[
\ln(y(t)) = 1 - K_1 t + \frac{1}{2} K_2 t^2 - \frac{1}{3!} K_3 t^3 + \frac{1}{4!} K_4 t^4 - \ldots \quad \text{Eq. 3.53}
\]

where

\[
K_1 = \left\langle Dq^2 \right\rangle,
\]

\[
K_2 = \left\langle (Dq^2 - \left\langle Dq^2 \right\rangle)^2 \right\rangle.
\]
\[ K_3 = \left( (Dq^2 - \langle Dq^2 \rangle)^3 \right) \]
\[ K_4 = \left( (Dq^2 - \langle Dq^2 \rangle)^4 \right) - 3K_2^2. \]

Eq. 3.54

Note that these K's, called the *cumulants*, are not to be confused with the elastic constant moduli; they merely represent the first four coefficients in an expansion of the logarithm of the normalized autocorrelation function. \( K_1 \) simply represents the reciprocal of the central decay time; \( K_2 \) is the *variance* of the distribution of decay times; \( K_3 \), called the *skewness*, represents the asymmetry of the decay time distribution; and \( K_4 \), labeled the *kurtosis*, represents the peakedness, or flatness, of the decay time distribution. The Brookhaven Instruments BI-2030AT correlator comes equipped with software options which can determine the various cumulants according to:

\[ K_n = \left[ (-1)^n \left. \frac{d^n}{dt^n} \ln(y(t)) \right|_{t=0} \right]. \]

Eq. 3.55

For most experimentally measured autocorrelation functions, it is a relatively simple matter to determine the first few cumulants. For processes where mono-exponential behavior is expected (i.e. light scattering data taken at the appropriate "magic" angles), the variance of the decay time distribution was indeed sufficiently negligible; thus reassuring that a single-decay time process was indeed being sampled. Likewise for double-exponential processes (i.e. light scattering data taken at \( \theta_{\text{lab}} = 10^0 \)), the single-exponential decay variance was quite high, suggesting a bi-exponential fit was more appropriate. Fortunately, the Brookhaven Instruments software package likewise executes
a bi-exponential fitting procedure which was used only to verify the existence of two exponential decay peaks. The actual data fitting to bi-exponential functions was performed by a fitting routine already perfected for general laboratory use. Note that several fake data files were generated to test the fitting code. Data files consisting of pure bi-exponential decays, with decay times both near and far from each other, as well as bi-exponential decays superimposed upon a small amplitude periodic ripple were tested. The fitting procedure returned excellent results, in complete agreement with the decay times used to generate the data.
3.11 – Sample Preparation and Experimental Apparatus

The monomer and dimers were synthesized according to procedures described elsewhere[^8-10]. Microscope slides, of nominal thickness 1 mm, were cut to approximately 1 cm by 3 cm in area and sonicated successively in baths of detergent (alconox), distilled water, acetone, and ethanol. The slides were subsequently vapor de-greased over a boiling bath of isopropyl alcohol. Next, the slides were treated with a nylon coating to achieve homogeneous alignment of the liquid crystals. The nylon coating was prepared as follows: a mixture of 0.04 grams of nylon 6/6, dissolved in 80 ml of formic acid, was placed on the glass slides and allowed to fully cure at room temperature. Once the wet film was dried, the coating was rubbed unidirectionally using a Kimwipe. The slides were separated by mylar spacers of nominal thickness 25 μm and optically adjusted for optimum parallelism. The holder was glued together with a high-temperature epoxy whose distortion temperature was well above 250°C; thus all oligomeric samples could be heated into their isotropic phase without altering or disrupting the sample holder. The liquid crystals were loaded into the holder while in their isotropic phase, then cooled to the appropriate reduced temperature; the sample alignment was checked using optical microscopy. The holder was next seated in an aluminum plug which was in turn inserted into an insulated aluminum oven. The entire aluminum oven was anodized, making it flat black in color, to prevent unwanted scattering and reflections near the sample. The oven was temperature controlled to approximately 20 mK using a Yellow Springs Instrument proportional controller. The sample was illuminated with vertically
polarized light from a 1 Watt (all-wavelengths) Argon-ion laser operating at a wavelength of 5145 Å; the power at this particular wavelength was approximately 300 mW. The light entered the oven normally through a flat window while the scattered light emerged undisturbed through a small movable hole, approximately 3 mm in diameter. The transmitted portion of the incident beam passed through a slot in the oven which remained covered by a segment of curved glass. Using this set-up, the scattered light could leave the oven undistorted by possible flaws in glass windows, while the sample remained well insulated from temperature gradients caused by air convection.

The scattering optics were based upon the model of Taratuta, et al\textsuperscript{11}. The oven was placed atop a three axis translator at the center of a micro-rotation stage having an angular resolution of approximately $5 \times 10^{-5}$ radians. A Newport micro-optical rail, approximately 30 cm in length, was mounted radially on a separate, concentric rotation stage having the same angular resolution, thus allowing for independent rotation of the sample and collection optics. Light emerging from the sample passed consecutively through an iris diaphragm, an analyzer, and a 2.5 cm focal length lens mounted in such a way as to allow for translation along three axes and rotation about two axes. The scattered light then entered a small aluminum box which contained a polished brass foil plate whose normal was tilted $15^\circ$ with respect to the optic axis. The 2.5 cm focal length lens was positioned in such a way as to produce a real image of the sample volume on the brass disk. This image could be viewed using an adjustable mirror-lens combination also housed in the aluminum box. A 250 μm diameter pinhole
was bored through the center of the brass foil, thus defining the actual sample volume which passed undisturbed to a second, similar aluminum box and into the detector. The scattered light passed through the pinhole, through a light-proof bellows, and into a second aluminum box of similar design and having its own pinhole of diameter 300 μm. The distance between the pinholes varied between 10 to 15 cm. The purpose of the collection optics is twofold: first, this arrangement allows the experimentalist to view the sample volume and, if dust or disclinations are present, to translate the sample so that only scattered light from a well-aligned portion of the sample was detected. Also, the aluminum boxes allow the experimentalist to easily align the scattering optics and to adjust the position of the second aluminum box such that the scattered light could actually be seen, ensuring that only one coherence area was sampled. Finally, the scattered light entered a single mode fiber optic and was focused onto a Thorn-EMI 9863B photomultiplier tube. After passing through a pulse amplifier / discriminator, the signal was input to a Brookhaven Instruments model BI-2030AT 136-channel digital autocorrelator for processing. The following two pages diagrammatically illustrate the experimental light scattering apparatus:
Figure 3–7: Experimental Light Scattering Apparatus
Figure 3–8: Experimental Data Acquisition and Processing Set-up
3.12 – Experimental Caveats

Despite the two major advantages of this scattering apparatus, two important drawbacks exist, both arising from the presence of the 2.5 cm focal length lens\textsuperscript{[12]}. First, since the lens produces an inverted image of the sample at the first pinhole, the light entering the detector has an inherent spread in the scattered wavevector, $\Delta q$ in addition to that which ordinarily arises from the solid angle of the finite-sized pinholes. For the apparatus described above, this corresponds to a spread of approximately one-quarter of a degree. This spread in $\bar{q}$ will be accounted for in subsequent error analyses. Secondly, although the lens maps each point of the sample volume into a single point in the image at the first pinhole, the lens does not reconstruct a perfect three dimensional duplicate image of the sample volume at the first pinhole. This complicates the data processing routine which relies heavily on normalizing the measured intensity by angular correction factors $C(\beta)$, arising from the angular dependence of the sample volume, transmission coefficients, and the in-plane and out-of-plane internal solid angles. Thus describing the sample volume and internal solid angle of the sample as functions of scattering angle becomes an extremely complicated function of pinhole diameter, focal length, image-to-lens distance, and object-to-lens distance. Although this distortion by the lens makes an analytical form to the angular corrections very difficult to obtain, the apparatus can be calibrated against a known standard to achieve the same goal. In effect, the measured intensity ratios are subsequently scaled by an angular dependent factor inherent to the apparatus’ optics and geometry, previously determined from
two known liquid crystal standards having refractive indices similar to those of the samples under investigation. This will be described later.
3.13 – Refractive Indices

The light scattering geometries previously outlined depend entirely upon proper selection of the scattering vector $\vec{q}$. Thus, for each material, the extraordinary ($n_e$) and ordinary ($n_o$) refractive indices had to be obtained in the nematic phase as functions of reduced temperature. For this purpose, three experiments were designed: the first to determine the average refractive index ($\bar{n}$) of a material in the isotropic phase, by measuring the displacement of a laser beam. For most materials, ($\bar{n}$) is a single value independent of temperature, while for others, this quantity has a very slight temperature dependence which is easily measured and fit to a linear relationship. The second experiment is used to measure the birefringence ($\Delta n$) of a material in the nematic phase as a function of reduced temperature. Finally, using a wedge-shaped sample, the last experiment is used to measure both the isotropic ($\bar{n}$) and ordinary ($n_o$) refractive indices, directly, in the nematic phase as a function of reduced temperature. Armed with these quantities, the desired refractive indices are produced according to the equations:

$$n_e = \frac{2}{3} \Delta n + \sqrt{\bar{n}^2 - \frac{2}{9} \Delta n^2}, \quad \text{and}$$  \hspace{1cm} Eq. 3. 56

$$n_o = n_e - \Delta n.$$  \hspace{1cm} Eq. 3. 57

The recent purchase of an Abbe' refractometer makes some of these methods seem a bit archaic, not to mention painfully tedious, especially when considering the amount of time needed for setting-up and aligning the different optical devices. However, in sentimental defense of the more
“home-made” techniques, note that all indices measured on the Abbe' refractometer have completely agreed with those obtained using the various "poor man's refractometers".
3.14 – Measuring the Average (Isotropic) Refractive Index

To determine $\bar{n}$, a one-centimeter pathlength cuvette, with one-millimeter width glass sides, was filled with the material under study. The cuvette was seated in a specially-designed oven enabling refracted light to leave the oven at angles ranging from 0 to 45 degrees. Laser light entering the oven passed normally through a window and exited the oven, undisturbed, through the slot. The material was heated into its isotropic phase while the cuvette portion of the assembly was placed on a precision rotation stage. Laser light of wavelength $\lambda=5145\text{Å}$ passed through the oven window, the front cuvette glass, the sample, the back cuvette glass, and was displaced as the sample was rotated. The displacement of the refracted light was measured using a diode detector, with a 25$\mu$m pinhole aperture, mounted on a translation stage. Four interfaces are involved at which Snell’s law must be applied: the incident air-glass interface, the incident glass-liquid crystal interface, and the two similar exiting interfaces. By using Snell’s law, one can obtain an equation for $\bar{n}$ involving known quantities and the measured value of the beam displacement. Values for $\bar{n}$ were determined to within two per cent and are presented in the materials summary portion of this chapter.
Figure 3–9: Experimental Apparatus Used to Determine the Isotropic Refractive Index
EXPERIMENTAL SET-UP TO MEASURE THE ISOTROPIC (AVERAGE) REFRACTIVE INDEX

\[ \lambda = 5145 \text{ Å} \]

APPLE SNELL'S LAW AT THE FOUR INTERFACES:

**INCIDENT**

\[ n_{\text{air}} \sin \theta_{\text{in}} = n_{\text{glass}} \sin \theta_{\text{glass}} \]

\[ n_{\text{lc.}} \sin \theta_{\text{lc.}} = n_{\text{glass}} \sin \theta_{\text{glass}} \]

**EXITING**

\[ n_{\text{lc.}} \sin \theta_{\text{lc.}} = n_{\text{glass}} \sin \theta_{\text{glass}} \]

\[ n_{\text{air}} \sin \theta_{\text{out}} = n_{\text{glass}} \sin \theta_{\text{glass}} \]

Figure 3–10: Application of Snell's Law at Four Interfaces – Used to determine the isotropic refractive index of a liquid crystalline sample.
Figure 3 – 11: Typical Trace of Unrefracted Beam and Refracted Beam Displacement – Note that the refracted beam is both smaller in intensity and broader in spread about its central location.
3.15 – Measuring the Birefringence

To determine the sample’s birefringence ($\Delta n$) in the nematic phase, a common procedure involving a calibrated Pockels cell was utilized. Thin sample cells, with liquid crystals aligned in the homeotropic orientation, were constructed. The samples’ thickness ranged from 5 to 10 $\mu$m and were measured to better than 0.5 per cent. The thickness measurement was determined using an interferometric scheme (see Appendix A)[13]. For a birefringent sample, the phase difference between the two components is given by:

\[ \delta_{\text{sample}} = k(\Delta n)d , \quad \text{Eq. 3.58} \]

where $k$ is the wavevector of the light used to illuminate the sample, and $d$ is the measured sample thickness. The Pockels cell produces a voltage-dependent optical phase shift given by $\delta_{\text{pockels}} = \pi \left( \frac{V_{\text{applied}}}{V_{\text{maximum}}} \right)$, between two polarizers. Hence, the total phase seen by the detector is:

\[ \delta_{\text{total}} = \delta_{\text{sample}} - \delta_{\text{pockels}} . \quad \text{Eq. 3.59} \]

Thus, by adjusting the voltage applied to the Pockels cell, one can cancel the total phase shift at the detector. Once the total phase shift is nulled, one can measure the applied voltage to the Pockels cell and thereby convert this into the sample’s birefringence ($\Delta n$) according to the formulas:
$$\Delta n = \left( \frac{V_{\text{applied}}}{V_{\text{max}}} + m \right) \frac{\pi}{kd}, \text{ or}$$

$$\Delta n = \left( \frac{V_{\text{max}} - V_{\text{applied}}}{V_{\text{max}}} + (m + 1) \right) \frac{\pi}{kd}. \quad \text{Eq. 3.60}$$

The value of $m$ is an integer that depends on the number of cycles of $2\pi$ through which the sample’s phase has passed while $2V_{\text{max}}$ represents the Pockels cell voltage corresponding to a full cycle of $2\pi$. The Pockels cell used in this study was calibrated and found to have a value of $V_{\text{max}}$ (in Volts) given by: $V_{\text{max}} = (\lambda / 6328\text{Å}) \times 3800$, where $\lambda$ is the wavelength of light used in the study, $\lambda = 5145\text{Å}$. Thus a phase shift of $\pi$ corresponds to an applied voltage of approximately 3090 Volts ($\delta_{\text{pockels}} = \pi \times V_{\text{applied}} / 3090$). Usually, one determines $m$ such that the birefringence ranges from 0.05 to 0.15 which are typical values for liquid crystals.
Figure 3 – 12: Block Diagram of the Experimental Set-up Used to Measure a Sample's Birefringence
3.16 – Measuring the Ordinary Refractive Index

In the final experiment, using a variation of the first technique, the ordinary refractive index is determined by again measuring the displacement of a refracted laser beam. The technique is based on the design of R. G. Horn[14]. A sample is constructed by placing a spacer at only one side of the holder. In this way, the sample volume is actually wedged-shape, where the wedge opens at some measurable angle $\alpha$. Note that $\alpha$ can easily be determined by measuring the displacement of a reflected laser beam in an empty cell. The sample is aligned homeotropically with respect to the glass holder. Laser light polarized perpendicular to the plane of the molecules strikes the sample normally and is refracted out of the sample at some angle. In this configuration, the light beam sees a sample index corresponding to the ordinary index (or the average index if the sample is heated into its isotropic phase). Once again, by applying Snell’s law at the interfaces, the value of $n_s$ can be computed by measuring the wedge angle $\alpha$ and the beam displacement. As a caveat, one must realize that this technique requires the sample to be oriented homeotropically with respect to the glass holder, otherwise a much more complicated expression is required to describe the liquid crystal index. A typical plot of the unrefracted and refracted beams is similar to that depicted in (Figure 3 – 11).
EXPERIMENTAL SET-UP TO MEASURE
THE ISOTROPIC (AVERAGE)
REFRACTIVE INDEX AND THE
ORDINARY REFRACTIVE INDEX

\[ \text{REFRACTED BEAM} \quad \rightarrow \quad \text{TRANSMITTED BEAM} \]

\[ d = \text{BEAM DISPLACEMENT} \]

\[ \theta \quad \alpha \]

FOR A
HOMEOTROPICALLY-ALIGNED
SAMPLE, A BEAM POLARIZED
PERPENDICULAR TO THE PLANE
OF THE PAPER WILL SEE AN
INDEX \( n_0 \)

\[ \text{INCIDENT BEAM} \]

APPLY SNELL'S LAW:

\[ n_{\text{air}} \sin(\alpha + \theta) = n_0 \sin \alpha \]

\[ n_0 = \frac{\sin(\alpha + \theta)}{\sin \alpha} \]

Typical Values:

\[ \alpha: \quad 1^\circ \leq \alpha \leq 2^\circ \]

\[ n_0: \quad 1.63 \leq n_0 \leq 1.67 \]

Figure 3 – 13: Schematic Representation of the Scheme Used to
Determine the Ordinary Refractive Index
3.17 – Materials Summary

Listed below is a summary of the refractive indices measurements:

- Wavelength used in measurements: \( \lambda = 5145 \text{ Å} \).
- In the fits below, the parameter \( T \) represents the quantity \( (T_{NI} - T) \) which is a positive quantity.
- Calibration Factor \( \equiv C(\beta) = 0.95736 + (\beta \times 1.0231 \text{e}^{-3}) \); where \( \beta \equiv \) Laboratory Angle.

<table>
<thead>
<tr>
<th>NAME</th>
<th>( T_{NI} )</th>
<th>( n_{\text{avg}} )</th>
<th>( n_e - \text{fit} )</th>
<th>( n_o - \text{fit} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monomer</td>
<td>80.97</td>
<td>1.53914</td>
<td>1.58802 + 4.34107 \text{e}^{-3} T - 2.39462 \text{e}^{-4} T^2 + 5.3325 \text{e}^{-6} T^3</td>
<td>1.51412 - 2.29305 \text{e}^{-3} T + 1.26556 \text{e}^{-4} T^2 - 2.84752 \text{e}^{-6} T^3</td>
</tr>
<tr>
<td>Even-Dimer</td>
<td>149.70</td>
<td>1.53351</td>
<td>1.59663 + 2.45535 \text{e}^{-3} T - 1.11185 \text{e}^{-4} T^2 + 2.21981 \text{e}^{-6} T^3</td>
<td>1.50096 - 1.31023 \text{e}^{-3} T + 5.98654 \text{e}^{-5} T^2 - 1.22965 \text{e}^{-6} T^3</td>
</tr>
<tr>
<td>Odd-Dimer</td>
<td>133.80</td>
<td>1.536474</td>
<td>1.5855 + 2.9974 \text{e}^{-3} T - 1.299 \text{e}^{-4} T^2 + 2.8533 \text{e}^{-6} T^3</td>
<td>1.5114 - 1.58 \text{e}^{-3} T + 6.7798 \text{e}^{-5} T^2 - 1.4919 \text{e}^{-6} T^3</td>
</tr>
</tbody>
</table>

Results 3 – 4: Refractive Index Results for Monomer, Even-Dimer, and Odd-Dimer
Figure 3 – 14: Birefringence versus Reduced Temperature for the Monomer, Even-Dimer, and Odd-Dimer
Figure 3–15: Monomer Refractive Indices
Figure 3 – 16: Even-Dimer Refractive Indices
Figure 3 – 17: Odd-Dimer Refractive Indices
3.18 – Normalized Intensity Measurements

When the scattered intensity is measured (Eq. 3.1), it must first be normalized by several factors, most of them involving an angular dependence:

(i) **Time Correction:**
The correlator provides the total number of counts occurring at a particular scattering angle. Instead, the relevant quantity is the total number of counts per unit time (or count rate) occurring at this angle: thus the actual intensity must be taken as the total number of counts divided by the corresponding time of data collection.

(ii) **Volume Correction:**
As the finite-sized detector is moved to different scattering angles, the actual sampled volume is changing as a function of angle. At larger angles, a larger volume is being sampled; hence the intensity would have to be reduced by a volume correction term.

(iii) **Solid Angle Correction:**
Recall that the differential scattering cross-section is actually an intensity per internal solid angle, so the measured intensity must be normalized by an in-plane and out-of-plane internal solid angle.

(iv) **Transmission Correction:**
Obviously, some intensity is lost due to index mismatches at the glass-to-air and glass-to-liquid crystal interfaces. At each interface, the scattered light will undergo some degree of back reflection while only a certain percentage (albeit a large percentage) will transmit out of the sample. Of course, the fraction of scattered light transmitted through the system is a function of the scattering angle\(^{[15]}\).
Eventually, the measured intensity would have to be normalized by all of these factors according to the form:

\[ I_{\text{normalized}} = I_{\text{measured}} \left( \frac{\Omega(\beta)_{\text{sample}} \Omega(\beta)_{\text{air-of-plane}}}{\text{time}_{\text{collection}} \text{Volume}(\beta) \text{Transmission}(\beta)} \right) \]  \hspace{1cm} \text{Eq. 3.61}

However as noted earlier, the presence of the 2.5 cm focal length lens distorts the sample image at the first pinhole; the lens does not reconstruct a perfect three dimensional image of the sampled volume at the first pinhole.

In other words, the presence of the lens sufficiently alters the image that no analytical expression describing the sampled volume at the pinhole is in practice, derivable. Thus, these angular-dependent terms are incorporated into the normalized intensity by experimentally calibrating the apparatus using two known liquid crystal samples. Once the calibration is done, the measured intensities are normalized according to the expression:

\[ I(\beta)_{\text{normalized}} = \frac{I(\beta)_{\text{measured}}}{\text{time}_{\text{collection}}} C(\beta), \]  \hspace{1cm} \text{Eq. 3.62}

where \( C(\beta) \) is the experimentally determined angular calibration factor.
3.19 – Experimental Angular Calibration

To establish this angular-dependent factor, light scattering measurements were performed on the two liquid crystals: pentylycyanobiphenyl (5CB) and octylycyanobiphenyl (8CB). Both materials were obtained from BDH Ltd. and used without further purification. The following literature values were used in the comparison (A. M. Jamieson\textsuperscript{[4]} and N. V. Madhusudana\textsuperscript{[16]}):

### 5CB (Jamieson)

<table>
<thead>
<tr>
<th></th>
<th>$T_{NI} - T = 2.1^\circ C$</th>
<th>$T_{NI} - T = 5.1^\circ C$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_{11}$ (x$10^{-8}$ dynes)</td>
<td>30</td>
<td>45</td>
</tr>
<tr>
<td>$K_{22}$ (x$10^{-8}$ dynes)</td>
<td>20.5</td>
<td>30.5</td>
</tr>
<tr>
<td>$K_{33}$ (x$10^{-8}$ dynes)</td>
<td>41</td>
<td>54</td>
</tr>
<tr>
<td>$K_{11} / K_{22}$</td>
<td>1.4634</td>
<td>1.4754</td>
</tr>
<tr>
<td>$K_{22} / K_{33}$</td>
<td>0.5</td>
<td>0.5648</td>
</tr>
</tbody>
</table>

### 8CB (Madhusudana)

<table>
<thead>
<tr>
<th></th>
<th>$T_{NI} - T = 2.7^\circ C$</th>
<th>$T_{NI} - T = 4.2^\circ C$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_{11}$ (x$10^{-8}$ dynes)</td>
<td>49</td>
<td>58</td>
</tr>
<tr>
<td>$K_{22}$ (x$10^{-8}$ dynes)</td>
<td>22.5</td>
<td>25</td>
</tr>
<tr>
<td>$K_{33}$ (x$10^{-8}$ dynes)</td>
<td>44.4</td>
<td>58</td>
</tr>
<tr>
<td>$K_{11} / K_{22}$</td>
<td>2.177</td>
<td>2.32</td>
</tr>
<tr>
<td>$K_{22} / K_{33}$</td>
<td>0.5067</td>
<td>0.431</td>
</tr>
</tbody>
</table>

For 5CB, an intensity measurement was taken at the magic angle, as well as six intensity measurements at laboratory angles of 10, 15, 20, 25, 30,
and 35 degrees. This procedure was done in the splay / twist configuration (configuration A) and performed at two reduced temperatures of $T_{NI} - T = 2.1^\circ C$ and $T_{NI} - T = 5.1^\circ C$. Likewise for 8CB in the splay / twist configuration, intensity measurements were taken at the same six angles and magic angle, but only for $T_{NI} - T = 2.7^\circ C$. At each of these six angles, the measured intensity ratio $I(\beta) / I(\beta^*)$, was plotted as well as a calculated (correct or published) value of the intensity ratio. At each temperature, knowing all the relevant quantities such as $n_r$ and $n_s$, one can calculate the correct intensity ratio needed to produce the elastic constant ratio given in the above references. Thus at each angle, a scaling factor between measured and known values of intensity ratios is obtained. The angular-dependent intensity scaling factor was fit to a linear relationship and used in all subsequent calculations involving normalized intensities. The calibration factor was found to be essentially unity, with a somewhat weak linear dependence on the laboratory-frame angle:

$$C(\beta) = 0.95736 + 0.0010231 \times \beta.$$  \hspace{1cm} \text{Eq. 3.63}

In other words, given all the possible corrections to the measured intensity due to angular considerations, one finds that the measured intensity rate is essentially the desired absolute intensity rate. Also, note that the scaling factor between measured and known intensities is plotted for two different materials at three different temperatures, all of which very consistently reproduce the same angular dependence. As expected, the angular scaling factor is inherent to the scattering geometry and should not be dependent on
temperature. Note that the calibration factor is valid for the entire system of oligomers under study, as well as for many of the more common liquid crystals, since the system was calibrated for a material whose indices range between 1.5 and 1.7. If the indices were very different, then the scattering angles, and hence \( \frac{d\sigma}{d\Omega} \), would be different. Since \( C(\beta) \) is almost constant for these approximate indices, the calibration can be retained for all materials and also used with confidence in the bend / twist geometries (configurations B and C).
Figure 3 – 18: Measured and Calculated Intensity Ratios versus Laboratory Scattering Angle for 5CB at a Reduced Temperature of 2.1 °C
Figure 3-19: Measured and Calculated Intensity Ratios versus Laboratory Scattering Angle for 5CB at a Reduced Temperature of 5.1 °C
Figure 3 – 20: Measured and Calculated Intensity Ratios versus Laboratory Scattering Angle for 8CB at a Reduced Temperature of 2.7 °C
Figure 3-21: Scaling Factor versus Laboratory Scattering Angle – At each angle, the three points represent two trial calibrations for 5CB and one trial calibration for 8CB.
3.20 – Freedericksz and Angular Calibration Verification

As a verification of the initial Freedericksz measurements used to
cetermine $K_{11}$ for the monomer and even-dimer, as well as a verification of
the experimental calibration technique, the light scattering results are
compared to values obtained in separate Freedericksz measurements of the
splay and bend elastic constants. The initial splay elastic constant values for
the monomer and even-dimer were obtained from Freedericksz
measurements performed in the Summer of 1990. The verification
measurements were conducted in the Spring of 1991. Likewise, the bend
elastic constant values, obtained only for the monomer, were determined in
the Fall of 1989. Subsequent light scattering measurements, made in late
1991, verified this determination as well as verified the effectiveness of the
calibration technique. Given the reproducibility of the results, the light
scattering measurements proceeded with confidence.

Freedericksz Verification:

The splay elastic constant, for both the monomer and even-dimer, was
rechecked using the Freedericksz technique when measuring the anchoring
strength coefficient at a polymer-coated interface\(^{17,18}\). Although this
Freedericksz method involved treating the substrate interface with a buffed
polyimide, compared to the initial Freedericksz technique which utilized a
sample treatment consisting of rubbed nylon 6 / 6, the monomer splay elastic
constant was essentially identical using the different surface treatments; the
values were the same to within experimental resolution. For the even-dimer,
the Freedericksz results for $K_{11}$ were only approximately ten per cent higher
than those obtained using the initial technique.
Figure 3 – 22: Splay Elastic Modulus Comparison between Independent Freedericksz Measurements
Calibration Verifications:

The bend elastic constant of the monomer was also obtained separately using the Freedericksz method in determining the anchoring strength coefficient at a structural phase transition occurring in the monomer's nematic phase\textsuperscript{[19]}. The value of $K_{33}$ using the Freedericksz technique was found to be roughly nine per cent higher than the values obtained using the technique of quasi-elastic light scattering. Once again, however, note that a difference in surface treatment did exist between these two techniques. The light scattering results were for samples prepared with rubbed \textit{nylon 6 / 6}, while the Freedericksz bend geometry required treating the sample with the diacetylenic phospholipid surfactant $\text{DC}_{8,9}\text{PC}$ ($1, 2$ - bis ($10, 12$, tricosadiynoyl) -$sn$- glycerol -3- phosphocholine). However, recall that the surface treatments, while playing the major role in surface interactions such as anchoring strength measurements, play only a weak role when considering bulk properties like the elastic moduli. The consistency of values, for both oligomers, is convincing that the scaling procedure was accurate.

As a final note, in a more recent experiment\textsuperscript{[20]}, the angular calibration technique was again verified by examining the $K_{22} / K_{33}$ ratio for 5CB using the homeotropic (configuration \textit{C}) geometry. The results were within 5% of the published values: a somewhat reassuring confirmation of the validity of the calibration technique.
Figure 3 – 23: Bend Elastic Modulus Comparison between the Freedericksz Method and that Extracted from Light Scattering Measurements
3.21 – Data Analysis

The determination and analyses of the light scattering results were fairly straightforward. Values of $K_{11}$ for the monomer and even-dimer are known absolutely as a function of reduced temperature from previous Freedericksz measurements\(^{[17,18]}\). In the case of the odd-dimer, the values of the magnetic susceptibility $\Delta \chi$, versus reduced temperature have as yet not been measured. Although the Freedericksz threshold fields have been measured for the odd-dimer, the splay elastic constant remains undetermined until the magnetic susceptibilities are obtained. Absolute intensity measurements are recorded in configurations A and B at $\theta_{\text{lab}} = 10^\circ$ and $\theta_{\text{lab}} = \theta^*$. The elastic constant ratios $K_{11} / K_{22}$ and $K_{22} / K_{33}$ are calculated from the quantity $[I(10^\circ)/I(\theta^*)]$ occurring in the appropriate geometry, based upon the previous equations (Eq. 3. 14 and Eq. 3. 26). The ratios $K_{11} / K_{22}$ and $K_{22} / K_{33}$ are then plotted, with errors, versus reduced temperature and fit to a straight line using algorithms commonly employed for such fitting procedures\(^{[21]}\). In conjunction with the absolute values of $K_{11}$ from Freedericksz measurements, the absolute values of $K_{22}$ and $K_{33}$ versus reduced temperature are thus extracted from these fits.

In order to obtain viscosity values, the first step is to perform single exponential fits to correlation functions measured at the magic angles. Consider configuration A involving the splay / twist geometry. To calculate $\eta_{\text{splay}}$, recall that at the magic angle, only a single distortion mode is present, and therefore only a single exponential decay exists in the recorded correlation function. For a homodyne scattering experiment, the data is fit to
the decay time,

\[ \tau_{1}^{*} = \frac{1}{2\Gamma_{1}^{*}} \]  

Eq. 3.64

which permits the determination of the splay viscosity according to:

\[ \eta_{\text{splay}} = \frac{K_{11} q(\phi^{*})^{2}}{\Gamma_{1}^{*}} = K_{11} q(\phi^{*})^{2} (2\tau^{*}) \]

Eq. 3.65

where \( \tau^{*} \) is the single exponential decay time for the autocorrelation function recorded at the magic angle. Notice that the splay viscosity is calculated from the correlation function taken at the magic angle, hence the scattering vector \( \vec{q} \), when appearing in this equation, must likewise be calculated at the magic angle. Based upon the smallness of the second and higher order coefficients in a follow-up cumulant fit, the single exponential behavior of the data at the magic angle is verified.

The viscosity analysis for the bend distortion is entirely analogous to that for the splay distortion; the only difference being that the data is recorded while in configuration B. To calculate the bend viscosity, the decay time obtained by fitting the autocorrelation function to a single exponential at the magic angle must be used. At the magic angle, \( q_{\perp} \) vanishes and the relaxation frequency reduces to:

\[ \Gamma_{2}^{*} = \frac{K_{33} q(\phi^{*})^{2}}{\eta_{\text{bend}}} \]

Eq. 3.66
making the viscosity a simple function of the fitted single exponential decay time,

\[ \eta_{\text{bend}} = K_{33} q(\phi^*) \bar{v}_Q(2 \tau^*), \]  

Eq. 3.67

To obtain the twist viscosity \( \gamma_1 \), a slightly more complicated procedure was used. A fit must be performed at an angle which involves either splay-to-twist or twist-to-bend components of comparable magnitude. As mentioned earlier, in both configurations A and B, at \( \theta_{\text{lab}} = 10^\circ \), the contributions from the twist distortion were of comparable magnitude to both the splay and bend distortions. The splay / twist configuration was chosen, somewhat arbitrarily, as the geometry from which to extract the twist viscosity. At scattering angles involving mixed modes, the intensity-intensity autocorrelation function is the square of the sum of two exponentials involving five parameters: a baseline, a splay and twist decay time at the appropriate scattering angle, and two coefficients:

\[ \langle I(0)I(\tau) \rangle = I_{\text{baseline}}^2 + \left( C_{\text{splay}} \exp \left( \frac{\tau}{\tau_{\text{splay}}(10^\circ)} \right) + C_{\text{twist}} \exp \left( \frac{\tau}{\tau_{\text{twist}}(10^\circ)} \right) \right)^2. \]  

Eq. 3.68

This five parameter fit could easily be reduced to one involving only two fitted parameters. First, the baseline could be measured using the correlator's six delay channels. Second, since \( \tau_{\text{splay}} \) and \( \tau_{*\text{splay}} \) have already been obtained at the magic angle, \( \tau_{\text{splay}}(10^\circ) \) can be obtained by scaling \( \tau_{*\text{splay}} \) by the appropriate values of \( q_\perp \):
\[ \tau_{\text{splay}}(10^\circ) = \tau_{\text{splay}}(\phi^*) \frac{q(10^\circ)^2}{q(\phi^*)^2}. \]  

Eq. 3. 69

Finally, since \( K_{11} / K_{22} \) is fit as a function of reduced temperature, the ratio of the two coefficients \( C_{\text{splay}} / C_{\text{twist}} \) is also known based upon the intensity ratio equation occurring in configuration A. Hence, a two parameter fit is performed on the intensity-intensity autocorrelation function at 10\(^\circ\). The fitted decay time \( \tau_{\text{twist}}(10^\circ) \), is therefore extracted and used to calculate the twist viscosity according to:

\[ \Gamma_2 = \frac{1}{2 \tau_{\text{twist}}(10^\circ)} \text{ and} \]  

Eq. 3. 70

\[ \eta_{\text{twist}} = \gamma_1 = K_{\text{twist}} q(10^\circ)^2 (2 \tau_{\text{twist}}(10^\circ))^2. \]  

Eq. 3. 71
3.22 – Error Contributions and Analysis

Several sources contributed to the overall error associated with the final results, most caused by the use of the 2.5 cm focal length lens\textsuperscript{12}; these sources were treated as follows:

(i.) Spread in the Scattering Vector, $\Delta q$ by 2.5 cm Focal Length Lens:
Due to the presence of the 2.5 cm focal length lens in the system of collection optics, scattered light from the sample crisscrosses across the optic axis before finally entering the detector:

![Diagram of light scattering through a lens.]

Figure 3–24: Crisscrossing of the Scattered Light Across the 2.5 cm Focal Length Lens Before Entering Detector

Hence, scattered light entering the second pinhole may have a spread in scattered wavevector, $\Delta q$ of approximately (1 / 4)$^0$. Although the sampled wavevector, scattering from the sample at an internal angle of $\phi$, is centered about the desired internal
angle, unwanted wavevectors may be entering the detector. The spread in $\vec{q}$ contribution to the overall error is treated by calculating the elastic constant ratios at $\phi$ and comparing this value to that obtained by averaging the ratios calculated at $\phi + (1/4)^\circ$ and $\phi - (1/4)^\circ$. Consider, for example, the determination of the $K_{11} / K_{22}$ ratio. The error due to the spread in wavevector is calculated by comparing the values:

$$\frac{K_{11}(\phi)}{K_{22}} \quad \text{and} \quad \frac{K_{11}\left(\phi + \frac{1}{4}^\circ\right) + K_{11}\left(\phi - \frac{1}{4}^\circ\right)}{2}.$$ 

The difference in these values varied between 1 and 2.5% for all of the data presented. The small magnitude of this error contribution is understood by examining the behavior of the scattering vectors and polarization factors versus scattering angle; specifically near the magic angles and near $10^\circ$, where the data were taken. Near these angles, the behavior of the polarization factors and scattering wavevectors versus scattering angle is sufficiently flat (or linear) such that deviations by as little as $(1 / 4)^\circ$ to either side do not significantly alter the determination of the elastic constant ratio. For example, the graph below shows the almost negligible variation of the scattering vectors over a spread in $q$ of approximately $1^\circ$ to either side of the center angle, taken in this case to be $10^\circ$ (the relevant scattering factors versus the entire range of laboratory scattering angles are plotted in Figure 3 – 29 and Figure 3 – 30):
Figure 3 – 25: Scattering Vector Components for a Typical Oligomer near $\beta = 10^\circ$ – Note that the scattering vectors depend on the refractive indices of the different oligomers; hence, the scattering vectors depend entirely on which oligomer is being treated. However, for a graph with the resolution above, the difference (between the various oligomers) in scattering vectors is essentially negligible. Therefore, (Figure 3 – 25) represents either of the three oligomers presently studied.
(ii.) **Spread in the Scattering Vector, $\Delta q$ by Finite Size of Pinholes:**

The treatment of this source of error is entirely analogous to that outlined above for the spread in $q$ due to the presence of the 2.5 cm focal length lens. In this case, the finite acceptance angle of the pinholes produces a spread in $q$ of approximately $1^\circ$. The pinhole configuration, although designed to minimize acceptance of unwanted scattering vectors and centered in fact about the desired scattering angle, does inherently pick-up wavevectors washed-out as much as $1^\circ$ from the central angle. Once again, this source contributes to the overall error only by 1 to 3% for all the oligomers; the smallness of the error likewise being due to the behavior of the scattering vectors and polarization factors as functions of scattering angle.

![Diagram](image)

**Figure 3-26: Acceptance Angle of the Pinholes**
(iii.) **Distortion of the Sample by the 2.5 cm Focal Length Lens:**

As mentioned several times before, the lens does not perfectly duplicate the object at the first pinhole; a rectangular sampling area, tilted at some angle $\beta$, with respect to the optic axis, is distorted into a parallelogram when finally imaged. As a result, the sample volume and most especially, the in-plane and out-of-plane solid angles of the sample no longer involve simple angular expressions. Instead, to accomplish this same type of angular description, it is better (and easier) to merely calibrate the angular terms using known liquid crystals. Using the experimentally determined angular calibrations, the two liquid crystal standards that were used in the calibration, were reproducible to within error bars of the published values$^{[4,16]}$. In this light, no further treatment of the sample's distorted volume is needed in the error analysis.

![Diagram](diagram.png)

**Figure 3 – 27: Distortion of Sample at the Detector**
(iv.) Scattering at Erroneous Angles, $\beta \pm \Delta \beta$:
Aligning the collection optics at some erroneous angle is a potentially major, possibly fatal, source of error. For example, consider taking intensity measurements at a lab angle of 10°. Consider the possibility that due to alignment problems, or unknown glitches in the rotation stage, or maybe even an accidental bumping of the collection optics by wandering colleagues, the scattering light is now being collected at 9°. This problem is drastically different, and much more significant in its effect, than the previous cases of having a spread in the scattering wavevector of a quarter of a degree or a full degree. In the previous cases, the scattering vector is centered about the appropriate angle, yet due to practical considerations, some unwanted wavevectors make it into the detector. In this case, the same spread in $\vec{q}$ still exists but this spread is now centered about an erroneous angle. The magnitude of such an error can be enormous. For the monomer alone, increasing the angle from 10° to 10.25° changes the calculated elastic constant ratios anywhere from 15 to 25% for configuration A. The effects in configuration B are even more devastating; increasing the angle from 10° to 10.25° changes the calculated elastic constant ratios by 45 to 80% depending on the value of the reduced temperature. Similar changes occur for all the oligomers. Fortunately, the effects of this source of error were anticipated then minimized to the point where they became almost negligible. The alignment of
the collection optics with respect to the sample relies on two factors, the angular resolution of the rotation stage and the "zeroing" of the incident beam with respect to the sample. The laser light struck the sample normally while the back reflection of the beam was made to coincide with the incident beam to within 0.25 mm at a distance of over 50 cm from the sample, this corresponds to a zeroing of the incident beam to better than 0.02°:

![Diagram showing the zeroing of the incident beam](image)

**Figure 3 – 28: Zeroing of the Incident Beam**

Recalling that the angular resolution of the scattering arm's rotation stage was better than 0.003°, the error in absolute scattering angle is therefore taken to be roughly 0.02°, due mainly to the limitations in establishing the zero-point of the rotation stage. The resulting error in the calculated elastic constant ratios never exceeds 1.5% and is less than 1% over most of the temperature sweep. The accuracy of the angular settings was tested in the calibration procedure and verified in the comparison
of the absolute elastic constants using the Freedericksz technique. Recall that the experimental angular calibration was determined using the liquid crystal 5CB\textsuperscript{[4]}, and as an additional check the material 8CB was examined; the elastic constant ratios for the latter material found by N. V. Madhusudana\textsuperscript{[16]} were quite accurately reproduced using the intensity scaling factors obtained from 5CB. Also, the reproducibility of $K_{33}$ for the monomer, determined using the separate technique of Freedericksz magnetic threshold field measurements, is considered final proof of the efficacy of the angular settings\textsuperscript{[17,18,19]}. 
(v.) **Deviations in Measured Intensity, \( I \pm \Delta I \):**

Errors in absolute intensity measurements were the easiest to treat and were handled in a statistical fashion. At all scattering angles, and at most temperatures, the absolute intensity was taken three to four times in order to statistically measure the variation of the recorded value. Several possible processes could alter the intensity count between consecutive runs: the background count can fluctuate due to changing lighting conditions in the laboratory; the laser intensity [see item (vi)] can vary due to noise in the laser's power unit; dust particles can float through the beam's path causing the detector to see sudden bursts of light; or dust / bubbles can move within the sample itself, across the illuminated region, causing similar fluctuations in the count rate. The percent error due to the intensity fluctuations varied between the two configurations; in configuration A, the intensity variations resulted in an approximate 1% error in the elastic constant ratio while the fluctuations in configuration B were slightly more substantial, resulting in elastic constant ratio errors ranging from 6 to 9%, depending on the oligomer and reduced temperature.
(vi.) **Deviations in Relaxation Times, \( \tau \pm \Delta \tau \):**

Statistical variations in the relaxation times were essentially negligible. Again, at each temperature, three to four auto-correlation measurements were taken to provide some statistical understanding of the variations in absolute intensity and response time. The relaxation times showed variations of less than 0.25% and thus were not treated in the subsequent error analysis.
(vii.) **Variations in Laser Intensity or Photomultiplier Performance:**

Long term variations in the laser intensity ("laser noise") and/or photomultiplier efficiency likewise contribute to fluctuations in the measured scattered intensity and more importantly, can cause discrepancies in the relaxation times which are determined by computer fits of mono-exponential and bi-exponential functions to the autocorrelator's raw data. For the results presented here, a combination of line-noise in the laser's power unit and noise pick-up in the photomultiplier tube, caused a periodic ripple in the incident intensity. Recent investigations, however, suggest that 60 Hz magnetic pick-up by the photomultiplier was the major culprit and has since been rectified. Nevertheless, data was gathered before this problem was corrected, hence the 60 Hz variations must be treated in the error analysis. This periodic ripple was approximately 0.25% (peak-to-peak) of the baseline intensity and occurred with a frequency of $v_{\text{noise}} = 60$ Hz.

Fortunately, the effect of this noise was minimized by several factors. Due to the small amplitude of the noise relative to the baseline and the frequency of the noise, the ripple's contribution to the measured signal was made significant only for times well past the desired relaxation time. This was done by judiciously choosing the number of microseconds per channel used by the correlator while taking data. Also, the periodic nature of the noise [approximated by: $\langle f(0)f(\tau) \rangle_{\text{noise}} = A_0 \sin(\nu_{\text{noise}} \tau)$, where $A_0$ is approximately 0.25% of the baseline intensity] makes it quite easy
to divide-out the noise from the measured auto-correlation function. The relaxation times calculated with this periodic function subtracted from the data, do not differ from those obtained using the raw data. Thus, error contributions involving the laser noise were deemed negligible and were not necessary to perform.
3.23 – Error Summary

Considering all of the error sources outlined above, the absolute error in the elastic constant ratio was calculated for all oligomers, in all geometries, at all reduced temperatures. The error bars turn out to be approximately the following values for the different oligomers:

<table>
<thead>
<tr>
<th>Oligomer</th>
<th>Ratio Value</th>
<th>Typical Value</th>
<th>Absolute Error</th>
<th>Relative Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monomer</td>
<td>$K_{11}/K_{22}$</td>
<td>2.51</td>
<td>0.08</td>
<td>3.2 %</td>
</tr>
<tr>
<td></td>
<td>$K_{22}/K_{33}$</td>
<td>0.451</td>
<td>0.045</td>
<td>9.9 %</td>
</tr>
<tr>
<td>Even-Dimer</td>
<td>$K_{11}/K_{22}$</td>
<td>2.53</td>
<td>0.085</td>
<td>3.4 %</td>
</tr>
<tr>
<td></td>
<td>$K_{22}/K_{33}$</td>
<td>0.374</td>
<td>0.05</td>
<td>13.4 %</td>
</tr>
<tr>
<td>Odd-Dimer</td>
<td>$K_{11}/K_{22}$</td>
<td>2.84</td>
<td>0.07</td>
<td>2.5 %</td>
</tr>
<tr>
<td></td>
<td>$K_{22}/K_{33}$</td>
<td>0.562</td>
<td>0.05</td>
<td>8.8 %</td>
</tr>
</tbody>
</table>

Results 3 – 5: Summary of Typical Errors

The scattering data were then treated statistically to determine the errors in linear fits to the elastic constant ratios. The procedure was to fit N data points $(x_i, y_i)$ to a straight-line model, $y(x) = y(x; m, b) = mx + b$, where the $y$ variable represents the elastic constant ratios in the different geometries and the $x$ variable represents the reduced temperature. The uncertainty $\sigma_i$ associated with each measurement $y_i$ is known from above, and the $x_i$'s are assumed to be known exactly. Using the Least Squares Method as a
maximum likelihood estimator, the value of chi-squared is minimized:

$$\chi^2 = \sum_{i=1}^{N} \left( \frac{y_i - (mx_i + b)}{\sigma_i} \right)^2$$  \hspace{1cm} \text{Eq. 3.72}

The derivations for the Least Squares Method's results are well known and well documented\cite{21}. The results for each oligomer are presented, along with the following relevant fitting parameters:
3.24 - Analysis Parameters

**Quantity** | **Interpretation**
--- | ---
\( \chi^2 = \sum_{i=1}^{N} \left( \frac{y_i - (mx_i + b)}{\sigma_i} \right) \) | chi-squared is considered to be a measure of the goodness of the fit.

N | number of points that were used in the fit.

\( \sigma_m \) | the probable uncertainty in the slope coefficient that results from a straight-line fit, \( y(x) = mx + b \).

\( \sigma_h \) | the probable uncertainty in the intercept coefficient that results from a straight-line fit, \( y(x) = mx + b \).

\[ q = \Gamma_r \left( \frac{N - 2}{2}, \frac{\chi^2}{2} \right) \] | where \( \Gamma_r \) is the incomplete gamma function. \( q \) is a measure of the believability of the chi-squared fit. A \( q \) of 0.1 or higher indicates that the goodness of the fit is believable. A \( q \) of 0.001 indicates that the goodness of the fit may be believable. A \( q \) of less than 0.001 indicates systematic errors in the data or that the data is being fit to the wrong function.

\( \sigma_{mb} \) | the coefficient of correlation between the uncertainty in the slope and the uncertainty in the intercept.

Pr | Pearson's \( r \) is the linear correlation coefficient \( r \). Values of +1 or -1 indicate complete correlation while values near zero indicate no correlation.
Figure 3 – 29: Scattering Vector Components for Configurations A, B, and C – The internal scattering angle ranges from $\beta = 0^\circ$ to $90^\circ$
Figure 3–30: Polarization Factors for Configurations A, B, and C – The internal scattering angle ranges from $\beta = 0^\circ$ to $90^\circ$
### MONOMER

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_{NI}$</td>
<td>80.97 °C</td>
</tr>
<tr>
<td>$\eta_0$</td>
<td>1.58802 $- 4.34107 e^{-3} T^{2}$ $+ 2.39462 e^{-4} T^{3}$ $- 5.3325 e^{-6} T^{4}$</td>
</tr>
<tr>
<td>$n_0$</td>
<td>1.51412 $+ 2.29305 e^{-3} T^{2}$ $+ 1.26556 e^{-4} T^{3}$ $+ 2.84752 e^{-6} T^{4}$</td>
</tr>
<tr>
<td>$n_{average}$</td>
<td>1.53914</td>
</tr>
<tr>
<td>$K_{11}/K_{22}$</td>
<td>2.51332 $- 2.30494 e^{-3} T$</td>
</tr>
<tr>
<td>$K_{22}/K_{33}$</td>
<td>0.45105 $+ 1.96487 e^{-3} T$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\chi$</td>
<td>$7.065410$</td>
</tr>
<tr>
<td>$\sigma_{aa}$</td>
<td>$0.043023$</td>
</tr>
<tr>
<td>$\sigma_{cc}$</td>
<td>$0.003992$</td>
</tr>
<tr>
<td>$\sigma_{ab}$</td>
<td>$0.052592$</td>
</tr>
<tr>
<td>$Pr$</td>
<td>$0.010690$</td>
</tr>
<tr>
<td>$\eta$</td>
<td>$0.212272$</td>
</tr>
<tr>
<td>Error</td>
<td>$0.08$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\tau(\star)$ - Splay</td>
<td>$1.91022 e^{-5}$ $- 2.67059 e^{-7} T$ seconds</td>
</tr>
<tr>
<td>$\sigma_{aa}$</td>
<td>$4.5249 e^{-5}$</td>
</tr>
<tr>
<td>$\sigma_{cc}$</td>
<td>$3.6658 e^{-7}$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\tau(10^6)$ - Splay</td>
<td>$5.9729 e^{-4}$ $- 5.29162 e^{-5} T$ seconds</td>
</tr>
<tr>
<td>$\sigma_{aa}$</td>
<td>$3.0226 e^{-5}$</td>
</tr>
<tr>
<td>$\sigma_{cc}$</td>
<td>$2.4516 e^{-7}$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\tau(10^6)$ - Twist</td>
<td>$1.7951 e^{-3}$ $- 6.34616 e^{-5} T$ seconds</td>
</tr>
<tr>
<td>$\sigma_{aa}$</td>
<td>$2.7134 e^{-4}$</td>
</tr>
<tr>
<td>$\sigma_{cc}$</td>
<td>$2.1981 e^{-5}$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\tau(\star)$ - Bend</td>
<td>$2.9123 e^{-5}$ $- 9.57575 e^{-7} T$ seconds</td>
</tr>
<tr>
<td>$\sigma_{aa}$</td>
<td>$1.8574 e^{-5}$</td>
</tr>
<tr>
<td>$\sigma_{cc}$</td>
<td>$1.8199 e^{-7}$</td>
</tr>
</tbody>
</table>

### Results 3 – 6: Monomer Fitting Results
Figure 3 – 31: Monomer Elastic Constant Ratios versus Reduced Temperature
Figure 3-32: Monomer Splay and Twist Relaxation Times
Figure 3 – 33: Monomer Bend Relaxation Time
### EVEN-DIMER

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_{NI}$</td>
<td>149.70 $^\circ$C</td>
</tr>
<tr>
<td>$n_e$</td>
<td>1.59663 - 2.45535e$^{-3}T$ + 1.11185e$^{-4}T^2$ + 2.21981e$^{-5}T^3$</td>
</tr>
<tr>
<td>$n_0$</td>
<td>1.50096 + 1.31023e$^{-3}T$ + 5.98654e$^{-5}T^2$ + 1.22665e$^{-6}T^3$</td>
</tr>
<tr>
<td>$n_{average}$</td>
<td>1.53351</td>
</tr>
</tbody>
</table>

\[
\frac{K_{11}}{K_{22}} = 2.53436 - 3.84242e^{-3}T
\]

\[
\chi^* = 11.607700
\]

\[
N = 11.0
\]

\[
\sigma_r = 0.049833
\]

\[
\sigma_\tau = 0.004262
\]

\[
q = 0.023636
\]

\[
\sigma_{\theta} = 0.012499
\]

\[
Pr = 0.255787
\]

\[
error = 0.085
\]

\[
\frac{K_{22}}{K_{33}} = 0.374465 + 1.2302e^{-2}T
\]

\[
\chi^* = 13.5029
\]

\[
N = 10.0
\]

\[
\sigma_r = 0.029924
\]

\[
\sigma_\tau = 0.002538
\]

\[
q = 0.095678
\]

\[
\sigma_{\theta} = 0.007398
\]

\[
Pr = 0.769359
\]

\[
error = 0.05
\]

\[
\tau (\ast)* - Splay: 0.9196e^{-4} = 2.1152e^{-5}T \text{ seconds}
\]

\[
\sigma_r = 1.6207e^{-5}
\]

\[
\sigma_\tau = 1.3853e^{-6}
\]

\[
\tau (10^6)* - Splay: 6.9054e^{-4} = 7.3474e^{-5}T \text{ seconds}
\]

\[
\sigma_r = 1.4006e^{-5}
\]

\[
\sigma_\tau = 1.40318e^{-6}
\]

\[
\tau (10^9)* - Twist: 6.8928e^{-3} = 1.3398e^{-5}T \text{ seconds}
\]

\[
\sigma_r = 8.26814e^{-4}
\]

\[
\sigma_\tau = 7.0717e^{-5}
\]

\[
\tau (\ast)* - Bend: 9.4448e^{-5} = 5.12298e^{-6}T \text{ seconds}
\]

\[
\sigma_r = 4.6625e^{-6}
\]

\[
\sigma_\tau = 3.8794e^{-7}
\]

---

**Results 3 – 7: Even-Dimer Fitting Results**
Figure 3-34: Even-Dimer Elastic Constant Ratios versus Reduced Temperature
Figure 3 - 35: Even-Dimer Splay and Twist Relaxation Times
Figure 3 – 36: Even-Dimer Bend Relaxation Time
**ODD-DIMER**

\[ T_{NI} = 133.80 \, ^\circ C \]
\[ n_e = 1.5855 - 2.9974e^{-3}T + 1.2990e^{-4}T^2 - 2.8533e^{-5}T^3 \]
\[ n_o = 1.5114 + 1.5800e^{-3}T + 6.7798e^{-5}T^2 + 1.4919e^{-6}T^3 \]
\[ n_{\text{average}} = 1.536474 \]
\[ K_{11} / K_{22} = 2.84459 - 7.61981e^{-3}T \]
\[ \chi^2 = 14.968400 \]
\[ N = 11.0 \]
\[ \sigma_n = 0.044499 \]
\[ \sigma_r = 0.003956 \]
\[ q = 0.091807 \]
\[ \sigma_{\alpha \beta} = 0.011680 \]
\[ Pr = 0.445680 \]
\[ \text{error} = 0.07 \]

\[ K_{22} \cdot K_{33} = 0.562109 + 90612e^{-2}T \]
\[ \chi^2 = 12.925000 \]
\[ N = 11.0 \]
\[ \sigma_n = 0.029938 \]
\[ \sigma_r = 0.002768 \]
\[ q = 0.166031 \]
\[ \sigma_{\alpha \beta} = 0.007864 \]
\[ Pr = 0.886485 \]
\[ \text{error} = 0.05 \]

\[ \tau (\ast) - \text{Splay} \quad 2.2027e^{-5} - 1.6015e^{-3}T \text{ seconds} \]
\[ \sigma_n = 8.887e^{-6} \]
\[ \sigma_r = 7.9000e^{-7} \]

\[ \tau (10^6) - \text{Splay} \quad 1.4610e^{-3} - 4.4109e^{-5}T \text{ seconds} \]
\[ \sigma_n = 5.5692e^{-5} \]
\[ \sigma_r = 4.9509e^{-5} \]

\[ \tau (10^3) - \text{Twist} \quad 9.5428e^{-3} - 6.7017e^{-4}T \text{ seconds} \]
\[ \sigma_n = 3.4699e^{-3} \]
\[ \sigma_r = 3.0847e^{-4} \]

\[ \tau (\ast) - \text{Bend} \quad 6.1376e^{-3} - 3.5251e^{-4}T \text{ seconds} \]
\[ \sigma_n = 8.5567e^{-4} \]
\[ \sigma_r = 7.5303e^{-5} \]

Results 3 – 8: Odd-Dimer Fitting Results
Figure 3 – 37: Odd-Dimer Elastic Constant Ratios versus Reduced Temperature
Figure 3 – 38: Odd-Dimer Splay and Twist Relaxation Times
Figure 3 – 39: Odd-Dimer Bend Relaxation Time
Absolute Elastic Constants for Monomer and Even-Dimer

Figure 3 - 40: Monomer and Even-Dimer Elastic Constants versus Reduced Temperature
Figure 3-41: Monomer and Even-Dimer Viscosity Coefficients versus Reduced Temperature
Figure 3-42: Monomer and Even-Dimer Splay Elastic Constant versus Reduced Temperature
Figure 3 – 43: Monomer and Even-Dimer Twist Elastic Constant versus Reduced Temperature
Figure 3 - 44: Monomer and Even-Dimer Bend Elastic Constant versus Reduced Temperature
Figure 3-45: Monomer and Even-Dimer Splay Viscosity Coefficient versus Reduced Temperature
Figure 3 – 46: Monomer and Even-Dimer Twist Viscosity Coefficient versus Reduced Temperature
Figure 3 – 47: Monomer and Even-Dimer Bend Viscosity Coefficient versus Reduced Temperature
References


4. EXPERIMENTAL:
FREEDERICKSZ

4.1 – Anchoring Strength Coefficient:
Infinite and Finite Anchoring

Given the importance of anchoring effects to the fundamental understanding of surface science as well as its applications to such technologies as the display industry, it is important to assemble a systematic set of data from which a microscopic model of anchoring effects might emerge. Thus, to further illuminate the nature of liquid crystal anchoring, the oligomeric system, comprised of the “5-00-5” monomer and its even-dimer “5-10-5”, was studied.

The anchoring strength coefficients, for homeotropic and homogeneous alignment of the nematic director, are essentially extracted from experimental measurements in exactly the same fashion. Because of various practical considerations, however, the sample preparation and actual method of data acquisition are different for the two types of geometries. These will be discussed shortly.

In order to obtain the anchoring energy $W$, magnetic Freedericksz
measurements in the splay (homogeneous alignment) or bend (homeotropic alignment) geometry, for both a very narrow (thickness $\ell_{\text{narrow}} = $ several microns) and wide samples (thickness $\ell_{\text{wide}} = $ many tens of microns), are performed. For the case of rigid anchoring ($W \to \infty$), the magnetic Freedericksz threshold field $U(\ell)$ is given by\[^1\]:

$$U(\ell) = \frac{\pi}{\ell} \sqrt{\frac{K_{1,3}}{\Delta \chi}}$$

$$U(\ell_{\text{wide}}) = \frac{\pi}{\ell_{\text{wide}}} \sqrt{\frac{K_{1,3}}{\Delta \chi}}$$

and

$$U(\ell_{\text{narrow}}) = \frac{\pi}{\ell_{\text{narrow}}} \sqrt{\frac{K_{1,3}}{\Delta \chi}}$$

Eq. 4. 1

where $\ell$ is the sample thickness, $K_{1,3}$ the splay or bend elastic constant depending on the alignment under study, and $\Delta \chi$ the magnetic susceptibility anisotropy. On the other hand, for the case of finite anchoring, A. Rapini and M. Papular have shown (see Chapter 2) that the Freedericksz magnetic threshold field $H_{\text{th}}(\ell,W)$ is less than $U(\ell)$ and is given by the transcendental equation\[^2\]:

$$\cot\left(\frac{\pi H_{\text{th}}}{2U}\right) = \frac{\pi K_{1,3} H_{\text{th}}}{\ell W U}$$

$$\cot\left(\frac{\pi H_{\text{th}}(\ell_{\text{wide}})}{2U(\ell_{\text{wide}})}\right) = \frac{\pi K_{1,3} H_{\text{th}}(\ell_{\text{wide}})}{\ell_{\text{wide}} W U(\ell_{\text{wide}})}$$

and

$$\cot\left(\frac{\pi H_{\text{th}}(\ell_{\text{narrow}})}{2U(\ell_{\text{narrow}})}\right) = \frac{\pi K_{1,3} H_{\text{th}}(\ell_{\text{narrow}})}{\ell_{\text{narrow}} W U(\ell_{\text{narrow}})}.$$  

Eq. 4. 2

The cotangent equation can be expanded in the variable $H_{\text{th}}/U$ around
\( H_{th}/U = 1 \). The resulting equation, upon inversion, demonstrates explicitly that \( H_{th}(\ell,W) \leq U(\ell) \)⁻:

\[
\frac{H_{th}}{U} = 1 - 2 \frac{K_{1,3}}{\ell W} + \varphi \left( \frac{K_{1,3}}{\ell W} \right)^2 + \ldots
\]

Eq. 4. 3

As shown above, both (Eq. 4. 1) and (Eq. 4. 2) individually represents a pair of equations, one for the narrow sample and one for the wide sample, each involving the appropriate threshold fields \( H_{th}(\ell,W) \) and \( U(\ell) \). Thus these two equations combine to form a system of four equations in four unknowns. By measuring the threshold fields for two different samples of different thicknesses [i.e. measuring \( \ell_{narrow}, \ell_{wide}, H_{th}(\ell_{narrow},W), \) and \( H_{th}(\ell_{wide},W) \)], these equations can be solved simultaneously to obtain \( W, U(\ell_{narrow}), U(\ell_{wide}) \), and \( K_{1,3} \) as functions of reduced temperature. Notice that the first set of equations can be combined to give the scaling relation, which will be used later:

\[
U(\ell_{narrow}) = \frac{\ell_{wide}}{\ell_{narrow}} U(\ell_{wide})
\]

Eq. 4. 4
4.2 - Experimental Procedure

$H_{th}$ versus reduced temperature on two samples of very different thicknesses is measured: the narrow cell in which $H_{th}$ deviates significantly from $U(\ell)$ (due to weak or finite anchoring) and the wide cell in which $H_{th}$ nearly coincides with $U(\ell)$ (since the bulk properties dominate surface effects). Since $K_{1,3}$ versus reduced temperature can be approximated quite well (see following paragraph), at a given temperature the threshold field $H_{th}(\ell)$ and thickness were separately inserted for each sample into the cotangent equation.

The actual determination of the anchoring strength coefficient involves an iterative Newton-Raphson procedure using the above system of equations; a simple computer program can solve the system quite easily. The four measured quantities, in addition to the measured reduced temperature and values of the appropriate magnetic susceptibility anisotropy, are entered into the program. To start, $\ell_{\text{wide}}$ and $H_{th}(\ell_{\text{wide}}, W)$ are used to determine an initial guess for the elastic constant according to (Eq. 4.1). This initial guess assumes that in the wide sample, surface effects are negligible compared to bulk properties thereby allowing $U(\ell_{\text{wide}})$ to be reasonably well-approximated by $H_{th}(\ell_{\text{wide}}, W)$. The approximation is quite good since the initial guess values for $K_{1,3}$ differ from the final results by less than ten per cent. Next, using this initial guess for $K_{1,3}$, the remaining three equations [i.e. the two equations from (Eq. 4.2) and the one equation from (Eq. 4.4)] are solved simultaneously to obtain initial guesses for $U(\ell_{\text{narrow}})$ and $U(\ell_{\text{wide}})$. The value of $U(\ell_{\text{wide}})$ is then substituted into the equation for $K_{1,3}$ and the whole
procedure is iterated again until a self-consistent value is returned. Finally, then, the anchoring strength coefficient is calculated.

The sample preparation and subsequent experimental measurements depend drastically upon the desired orientation of the nematic director; hence, the two types of configurations are discussed separately.
4.3 - Homogeneous Alignment:

Sample Preparation

The monomer and even-dimer were aligned parallel to a buffed polyimide-coated glass substrate. A magnetically-induced Freedericksz transition in both thick and thin cells was used in conjunction with a capacitance technique to determine the anchoring strength coefficient \( W \), as a function of reduced temperature in the nematic phase\(^4\).

The monomer and even-dimer were synthesized according to procedures described elsewhere\(^{5-7}\). Four samples were prepared: a narrow and wide sample for both the monomer and even-dimer. A square glass slide, approximately 10 cm per side, and coated with stripes of indium tin oxide ("ITO" resistance = 20 \( \Omega \) / \( \Box \)), was first treated with a polyimide coating to achieve homogeneous alignment of the liquid crystals. The ITO stripes were approximately four mm in width and were spaced apart evenly every four to five mm. The polyimide coating was prepared as follows: a mixture of one part polyimide (DuPont PI-2555) and one part thinner (DuPont T-9039) was placed on the ITO-coated glass wafer and spun at 3000 rpms. The wet film was then fully cured for one hour at 200\( ^\circ \)C. Finally, the dry coating was buffed unidirectionally using a nylon cloth (Yoshikawa Kako Ltd., Grade \( Y_0 \)-10-N) and a rubbing density of 200. The resulting polyimide coating was nominally of thickness 0.5 \( \mu \)m. Upon completion of the surface treatment, the ITO-coated glass was scored and broken into smaller slides from which the sample cells were made. Note that this coating procedure represents a consistently reproducible surface treatment, especially since all surfaces were
treated simultaneously and uniformly from the same initial glass wafer. This is, of course, essential if data from different sample cells are to be compared. Note that except for the tetramer version of this mesogen, each member of the oligomeric series could also be aligned in the homogeneous orientation using a surface treatment of unidirectionally rubbed nylon 6 / 6. No surface treatment was found which could homogeneously (or homeotropically) align the tetramer mesogen. For this experiment, however, the polyimide-coating surface treatment was used in place of the nylon 6 / 6 approach because the polyimide-coating produced fewer defects in the sample alignment. This could easily be seen by viewing the nematic sample under crossed polarizers. For each sample, a pair of the smaller, treated glass slides were placed together, separated by mylar spacers, and adjusted for optimum parallelism. The overlap area of the ITO was measured by optical microscopy to within one per cent. Using an interferometric scheme (see Appendix A)[8], the thickness spacings (distance between polyimide coatings) of the four holders were measured at the center of the ITO overlap area; these thickness measurements were later verified by measuring the empty-cell capacitance of the holders and were found to be in complete agreement with the interferometric results. The results are summarized below:

<table>
<thead>
<tr>
<th>Sample</th>
<th>Area of ITO Overlap (cm²)</th>
<th>Thickness (Interferometric) (µm)</th>
<th>Empty Cell Capacitance (pF)</th>
<th>Effective Dielectric Constant (Isotropic)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monomer - narrow</td>
<td>0.293 ± 0.002</td>
<td>5.55 ± 0.15</td>
<td>46.18</td>
<td>4.53</td>
</tr>
<tr>
<td>Monomer - wide</td>
<td>0.390 ± 0.002</td>
<td>81.34 ± 0.8</td>
<td>4.50</td>
<td>4.57</td>
</tr>
<tr>
<td>Even-Dimer - narrow</td>
<td>0.368 ± 0.002</td>
<td>5.08 ± 0.15</td>
<td>64.48</td>
<td>4.35</td>
</tr>
<tr>
<td>Even-Dimer - wide</td>
<td>0.392 ± 0.002</td>
<td>54.9 ± 0.5</td>
<td>6.49</td>
<td>4.43</td>
</tr>
</tbody>
</table>
Experimentally, the appropriate liquid crystals, while heated into their isotropic phase, were loaded into their sample holders and placed in a brass oven temperature controlled to approximately 10 mK for the monomer and 50 mK for the even-dimer. The entire assembly was placed into the bore of an 8.2 T superconducting magnet such that the orientation of the magnetic field $\mathbf{B}$ was perpendicular to the plane of the glass holder and thus normal to the liquid crystal nematic director, which was aligned homogeneously by the polymer coating. This corresponds to the splay geometry of Freedericksz field measurements. The samples were connected, via high-temperature coaxial cable, to an Andeen Hagerling Model 2500A capacitance bridge operating at 0.0025 V (rms) and 1 kHz. This voltage was sufficiently small to prevent a measurable contribution to the Freedericksz torque from the electric field (which likewise scales as $E_0^2 = (K_{\perp} \pi^2)/(\ell^2 \Delta \chi)$, where $\Delta \chi$ is the electric susceptibility anisotropy$^{[1]}$). The samples were brought deep into the nematic phase ($T \leq T_N \approx -16^\circ \text{C}$) and at a fixed temperature, the samples’ capacitance was recorded as the field was slowly swept upward. Typically, the wide cells required a sweep rate of 1 G/s while the narrow samples [with a response time which scales as $\ell^2$ (see section 2.2)] required a sweep rate of 10 G/s. Note that the ramp rate for all the samples was chosen to be sufficiently slow to maintain quasi-equilibrium.
SPLAY GEOMETRY FOR A HOMOGENEously-ALIGNED LIQUID CRYSTAL

Undisturbed Sample

Magnetically-induced Splay Geometry

Figure 4 - 1: Magnetically-Induced Nematic Splay Distortion for a Sample Homogeneously-Aligned to an External Surface
OVEN AND SAMPLE HOLDER FOR HOMOGENEOUSLY-ALIGNED ANCHORING STRENGTH MEASUREMENT

![Diagram of oven and sample holder]

Figure 4 – 2: Schematic Diagram of Oven and Sample Holder Used to Determine the Anchoring Strength Coefficient
Figure 4 - 3: Block Diagram of Capacitance Technique Used to Determine the Anchoring Strength Coefficient
4.4 – Homogeneous Alignment:

Results

I. Dielectric Constant versus Field

Figure 4 – 4 shows a typical trace of the effective dielectric constant \( \varepsilon_{\text{effective}} \) (calculated as \( \varepsilon_{\text{effective}} = \frac{C(pF)d(m)}{A(m^2)\varepsilon_0} \)); where \( \varepsilon_0 = 8.85 \text{ pF/m} \) is the permittivity constant of free space) versus magnetic field, used to determine the Freedericksz threshold field. \( H_{th} \) is somewhat ambiguous because of the rounding of the data; this problem will be addressed and treated later.

II. Threshold Fields and Infinite Anchoring Fields

For each cell, the threshold field \( H_{th} \) was determined as a function of reduced temperature. For each oligomer, the data obtained for narrow and wide samples were fit using the system of four equations in four unknowns. The magnetic susceptibility anisotropy (\( \Delta\chi \) versus \( T_{NI-T} \)) was obtained from literature[8].

Figure 4 – 5 and Figure 4 – 6 show the measured threshold fields \( H_{th} \) and the calculated fields \( U \), in the limiting case of \( W \to \infty \), plotted versus reduced temperature for narrow and wide samples. Error bars, approximately 1 to 5% for the wide samples and approximately 1 to 10% for the narrow samples, are due to the uncertainty in determining \( H_{th} \). In order to compute the anchoring energy, the threshold fields had to be determined at
identical reduced temperatures, thus the data for the narrow samples represent interpolated values based upon measurements of $H_{th}(\ell_{\text{narrow}})$ in both the monomer and even-dimer cases. Notice that $H_{th}(\ell_{\text{narrow}})$ is considerably smaller than $U(\ell_{\text{narrow}})$ at each temperature while $U(\ell_{\text{wide}})$ is only slightly larger than $H_{th}(\ell_{\text{wide}})$ at each temperature; a result to be expected for wide samples.

III. **Splay Elastic Constant**

Results for the splay elastic constants, shown in Figure 4–7, are in excellent agreement with previous independent Freedericksz measurements$^{[10]}$. Overall, an uncertainty of approximately ± 5% is associated with the elastic constants due largely to systematic errors in the values for $\Delta \chi$ as well as the field rounding discussed earlier. Essentially, the splay elastic constants for the monomer and even-dimer are identical, especially when scaled by the square of the scalar nematic order parameter $S$.

IV. **Anchoring Strength Coefficient**

Finally, the calculated values for $W$ versus reduced temperature are plotted in Figure 4–8. Although both the monomer and even-dimer show $W$ increasing as temperature is dropped deeper into the nematic phase, $W$ for the dimer is clearly of the order ten times the monomer value. As will be shown later, the relative error in $W$ is much higher in the monomer case, due mainly to the
magnitude of $W$ in this system. The error bars associated with $W$ are dominated by the uncertainty in determining $H_{th}$, whereas contributions from uncertainties in absolute sample thickness and elastic constants were found to be negligible.
Figure 4 - 4: Typical Trace of the Effective Dielectric Constant versus Applied Magnetic Field
Figure 4 – 5: Threshold Fields for Monomer Liquid Crystal – Both Wide and Narrow samples are plotted.
Figure 4–6: Threshold Fields for Even-Dimer Liquid Crystal – Both Wide and Narrow samples are plotted.
Figure 4 – 7: Splay Elastic Constant for the Monomer and Even-Dimer versus Reduced Temperature
Figure 4 – 8: Anchoring Strength Coefficient for Homogeneous Alignment of the Monomer and Even-Dimer versus Reduced Temperature
4.5 – Homeotropic Alignment:

Sample Preparation

The monomer version of this oligomeric series was found to exhibit a transition from perpendicular to tilted alignment at a lecithin-treated glass substrate interface several degrees below the nematic-isotropic phase transition. By means of an optical Freedericksz transition measurement, the coefficient $W$ of the anchoring energy was obtained$^{[1]}$.

The monomer$^{[12]}$ was sandwiched between two glass slides coated with the diacetylenic phospholipid surfactant $\text{DC}_{8,9}\text{PC}$ (1,2 - bis (10,12, tricosadiynoyl) - sn - glycerol -3- phosphocholine ) and found to exhibit a structural transition several degrees below the nematic-isotropic transition temperature $T_{NI}$. Using polarized optical microscopy, the sample was uniformly aligned in the homeotropic orientation above $T_s$, where $T_s = T_{NI} - 6^\circ\text{C}$. Just below $T_s$ a Schlieren type texture (a typical texture for tilted or unaligned nematics) becomes visible, increasing in brightness as the temperature is further reduced. By exerting a slight pressure on the sample and optically observing the texture, the liquid crystal is verified to indeed be in the nematic phase (and not some other phase) below $T_s$; further conformation was obtained by differential scanning calorimetry. It should be noted that using the same surfactant, homeotropic alignment of the even and odd version of this mesogen is not possible. Likewise, for the tetramer version of this mesogen, homeotropic alignment could not be obtained. Moreover, neither the ionic surfactant hexadecyltrimethylammonium bromide (HTAB) nor the silane compound 3-(trimethoxysilyl) propyldimethyloctadecyl
ammonium chloride results in homeotropic orientation of any of the oligomers in the "5-00-5" series at any temperature. The alignment capabilities of DC$_{8,9}$PC may arise from the polymerizable nature of the end-chain, which would form a rigid comb-like network when the monolayer is irradiated with ambient ultraviolet light. This surfactant has also been found to form unusual morphologies (tubules) in water, which can be rigidified by exposure to either an ultraviolet or beta source$^{[13]}$.

The monomer liquid crystal (as were all of the "5-00-5" oligomers) were synthesized according to procedures described elsewhere$^{[5,6,7,12,14]}$. Two optical-flat windows were sonicated successively in baths of detergent (alconox), distilled water, acetone, and ethanol; then vapor de-greased over a boiling bath of isopropyl alcohol. The lipid DC$_{8,9}$PC was obtained from Avanti Polar Lipids (Birmingham, Alabama) and used as received. A small quantity of DC$_{8,9}$PC was dissolved in absolute ethanol, a drop of which was placed on each of two 12.7 mm diameter glass optical-flat windows. After drying, the residue was gently removed with a Kimwipe; a procedure resulting in almost defect-free alignment, given the good reproducibility of the results. The two windows were separated by narrow mylar spacers and optically adjusted for optimum parallelism. Using the interferometric scheme (see Appendix A)$^{[8]}$, the spacings of the samples were found to be:

$$l_{narrow} = 3.55 \pm 0.03 \, \mu m \quad \text{and} \quad l_{wide} = 85.33 \pm 0.04 \, \mu m.$$ 

The sample holders were then filled with the liquid crystalline material, inserted into a brass oven which was temperature controlled to 10 mK and
placed into the bore of an 8.2 T superconducting magnet with transverse and longitudinal optical ports. The orientation of the magnetic field $\vec{H}$ was parallel to the plane of the glass holders and thus perpendicular to the nematic director. Using the normal Freedericksz bend geometry, light from a He-Ne laser passed consecutively through a light chopper at frequency $\nu=319$ Hz, a lens of focal length 483 mm, a polarizer oriented at 45° with respect to the field, the sample, an analyzer, and into the detector. The diameter of the beam at the sample was measured to be less than 50 μm. The purpose of focusing the beam to such a narrow cross-section will be explained in the Error Contributions and Analysis section [see item (b)] of this chapter. The output from the detector was fed into a lock-in amplifier referenced by the light chopper, and the lock-in output, proportional to the intensity at the detector, was fed into a computer based data acquisition system. For the narrow sample, the field was ramped upward at 10.8 G / s, and the detector intensity was recorded versus magnetic field. The ramp rate was sufficiently slow to maintain quasi-equilibrium. For the wide sample, on the other hand, the ramp rate had to be much slower. In this case, the field was increased step-wise in 5 G intervals every 10 seconds. This rate was likewise found to produce reasonable equilibrium conditions, and is consistent with ramp rates reported in the literature for samples of comparable thickness[15].
BEND GEOMETRY FOR A HOMEOTROPICALLY-ALIGNED LIQUID CRYSTAL

Undisturbed Sample

Magnetically-Induced Bend Geometry

Figure 4 – 9: Magnetically-Induced Nematic Bend Distortion for a Sample Homeotropically-Aligned to an External Surface
Figure 4 – 10: Schematic Diagram of Oven and Sample Holder Used to Determine the Anchoring Strength Coefficient
Figure 4 - 11: Block Diagram of Laser Technique Used to Determine the Anchoring Strength Coefficient
4.6 – Homeotropic Alignment

Results

I. Detector Intensity versus Field

Intensity versus field traces were obtained at approximately twenty different temperatures; a typical trace is shown in Figure 4 – 12. Determination of $H_{th}$ was complicated by the rounding of the data. The treatment of this rounding is discussed shortly.

II. Threshold Fields and Infinite Anchoring Fields

Threshold fields $H_{th}$ versus reduced temperature for the narrow sample are plotted in Figure 4 – 13, where $T_{NI} = 80.97^\circ C$ and $T_s$ is shown. Error bars represent uncertainty in $H_{th}$ due to rounding of the intensity versus field data. $U$ represents the calculated infinite anchoring fields. Again notice that $H_{th}$ is considerably smaller than $U$ at each temperature, as is expected for very narrow samples. Likewise in Figure 4 – 13, $H_{th}$ and $U$ versus temperature for the wide sample are plotted. Once again, in order to compare the anchoring energy, $H_{th}$ was needed at identical reduced temperatures; thus the values of $H_{th}(\ell_{\text{wide}})$ represent interpolated values based upon the measured values of $H_{th}(\ell_{\text{wide}})$.

Note that the fractional error in $H_{th}(\ell_{\text{wide}})$ is smaller than in $H_{th}(\ell_{\text{narrow}})$. Also note that $U(\ell_{\text{wide}})$ is only slightly larger than $H_{th}(\ell_{\text{wide}})$ at each temperature.
III. **Bend Elastic Constant**

As in the case of homogeneous alignment where $K_{11}$ was determined, results for the monomer bend elastic constant, shown in Figure 4 - 14, are in excellent agreement with independent quasi-elastic light scattering measurements\[^{16}\]. Overall, an uncertainty of approximately $\pm$ 5% is associated with the elastic constant due largely to systematic errors in the values for $\Delta \gamma$ as well as the field rounding discussed earlier.

IV. **Anchoring Strength Coefficient**

Finally, the calculated values for $W$ versus reduced temperature are plotted in Figure 4 - 15. The error bars associated with $W$ are dominated by the uncertainty in determining $H_{th}$, whereas contributions from uncertainties in absolute sample thickness and elastic constants were again found to be negligible.
Figure 4-12: Typical Trace of the Detector Intensity versus Applied Magnetic Field
Figure 4 - 13: Threshold Fields for Monomer Liquid Crystal – Both Wide and Narrow samples are plotted.
Figure 4-14: Bend Elastic Constant for the Monomer versus Reduced Temperature
Figure 4–15: Anchoring Strength Coefficient for Homeotropic Alignment of the Monomer versus Reduced Temperature
4.7 - Error Contributions and Analysis

Magnetic Freedericksz measurements can be used to extract values for both the splay or bend elastic moduli, or the surface anchoring energy coefficient. Of course, the thickness of the sample determines which quantity is measured; as shown before, wide samples give excellent results for the elastic moduli while both narrow and wide samples are required to determine the anchoring strength coefficient. Thus the error analysis likewise is divided into procedures for the elastic moduli and the anchoring coefficient.

(i) **Elastic Moduli:**

The elastic moduli, for the different geometries, are given by the equation:

$$K_{1,3} = \frac{U(\ell_{\text{wide}})^2 \ell_{\text{wide}}^2 (\Delta \chi)}{\pi^2}.$$  \hspace{1cm} \text{Eq. 4.1}

[Recall that the equation becomes a very good approximation upon substitution of $H_{\text{th}}(\ell_{\text{wide}})$ for $U(\ell_{\text{wide}})$.] The usual error analysis treatment was performed to determine the error bars on the elastic constants. For a quantity $f(x, y, z, \ldots)$ which depends explicitly upon the measured quantities $x, y, z, \text{etc.}$, the error in quantity $f$ is determined by:

$$\sigma_f = \left( \frac{\partial f}{\partial x} \sigma_x \right)^2 + \left( \frac{\partial f}{\partial y} \sigma_y \right)^2 + \left( \frac{\partial f}{\partial z} \sigma_z \right)^2 + \ldots$$  \hspace{1cm} \text{Eq. 4.5}
where the $\sigma_i$'s are the absolute uncertainties in the measured quantities and the contributions from each measured quantity are added in quadrature. Thus, the errors in the elastic constants are determined by:

$$\sigma_{k_{13}}^2 = \left( \frac{\partial K_{13}}{\partial U} \sigma_U \right)^2 + \left( \frac{\partial K_{13}}{\partial (\Delta \chi)} \sigma_{(\Delta \chi)} \right)^2 + \left( \frac{\partial K_{13}}{\partial l} \sigma_l \right)^2 \quad \text{Eq. 4.6}$$

The uncertainties in the measured quantities have roughly the values summarized below:

<table>
<thead>
<tr>
<th>Quantity</th>
<th>Relative Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>Threshold Field</td>
<td>± 2 to 3%</td>
</tr>
<tr>
<td>Thickness</td>
<td>± 0.5%</td>
</tr>
<tr>
<td>$\Lambda \chi$</td>
<td>± 5%</td>
</tr>
</tbody>
</table>

The contribution from the published values of the magnetic susceptibility anisotropy dominates the overall error which for the monomer is between 1 to 2% for both $K_{11}$ and $K_{32}$, while for the even-dimer is slightly higher ranging from 1 to 4% for $K_{11}$. 
(ii) **Anchoring Strength Coefficient:**

Solving the cotangent equation for the anchoring energy gives:

$$ W = \frac{\pi K_{1,1} H_{th}}{\ell U} \tan \left( \frac{\pi H_{th}}{2U} \right), \quad \text{Eq. 4.2} $$

where the error in $W$ can be calculated according to the same procedure used to determine the error in the elastic constant. Namely, the partial derivatives are taken with respect to measured quantities and are added in quadrature:

$$ \sigma^2_W = \left( \frac{\partial W}{\partial U} \sigma_U \right)^2 + \left( \frac{\partial W}{\partial K_{1,1}} \sigma_{K_{1,1}} \right)^2 + \left( \frac{\partial W}{\partial \ell} \sigma_\ell \right)^2 + \left( \frac{\partial W}{\partial H_{th}} \sigma_{H_{th}} \right)^2, \quad \text{Eq. 4.7} $$

The resulting overall error in $W$ is completely dominated by the error in the measured threshold field, $H_{th}$. Determination of the threshold field at each temperature was complicated by the rounding of the data; thus the uncertainty in the threshold field $\sigma_{H_{th}}$, was estimated to range from $\pm 20$ to $60$ G ($= 2\%$ to $5\%$) for the wide samples and from $\pm 200$ to $2000$ G ($= 1\%$ to $10\%$) for the narrow samples, and ultimately dominated the errors in subsequent calculations. Overall, the anchoring energy had the following error bars (the relatively large error for the case of the monomer is due to the vanishingly small values of $W$ for homogeneously-aligned samples):
<table>
<thead>
<tr>
<th>Sample</th>
<th>Geometry</th>
<th>Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monomer</td>
<td>Homeotropic</td>
<td>± 5 to 15%</td>
</tr>
<tr>
<td>Monomer</td>
<td>Homogeneous</td>
<td>± 10 to 50%</td>
</tr>
<tr>
<td>Even-Dimer</td>
<td>Homogeneous</td>
<td>± 5 to 15%</td>
</tr>
</tbody>
</table>

The field rounding, which is relatively small at higher temperatures but much more severe at temperatures well into the nematic phase, is a common difficulty, and arises from a number of sources:\(^{11}\):

(a.) **Too rapid ramping of the field:**
This item was deemed unimportant for the ramping rates used. This assertion was confirmed by the reproducibility of the threshold fields upon reversal of the field sweep direction (i.e. no noticeable hysteresis was present).

(b.) **Thickness gradients across the face of the laser beam or across the overlap area of capacitance plates:**
Thickness variations of approximately ± 0.75 μm were found over the sample holders’ area. In optical Freedericksz experiments such gradients are of minor importance since the laser spot could easily be reduced to under 100 μm. However, in a capacitance experiment, required by the geometry of the splay distortion and the magnet hardware, cell thickness variations tend to round the Freedericksz transition, as has been discussed previously. This rounding gives rise to some uncertainty in \( H_{th} \), which is fractionally larger in the narrow sample. This uncertainty in \( H_{th} \), moreover, propagates to \( K_{11} \) and \( W \), and constitutes the largest component in their error bars.
(c.) **Tilt of the sample with respect to the magnetic field:**
For the optical measurements, the sample tilt was perhaps the most common source of rounding, becoming more severe near $T_s$, as the surface anchoring became weaker. Nevertheless, the rounding observed herein is considerably larger than found in previous measurements using the same apparatus\(^\text{[17]}\), thus suggesting that the sample tilt was not the dominant effect in the field rounding [see item (e.)].

(d.) **The presence of microscopic particulate matter:**
Microscopic particulate matter could have played a role in the data round-off, given the larger number of defects occurring in wide samples. At higher temperatures, moreover, the rounding was more severe in the wide sample than in the narrow sample, an observation consistent with the presence of small defects.

(e.) **Gradients in the anchoring coefficient W across one plate, differences in W between plates, or surface imperfections:**
Much of the rounding, especially at lower temperatures, arises from an inhomogeneous anchoring coefficient. This is the dominant effect in the optical Freedericksz field rounding. Inhomogeneities would be expected to play a more significant role in the narrow sample, which they apparently do. This effect is minimized by using a small beam diameter at the sample; however, unlike a free surface, it is quite difficult to apply an absolutely uniform and identical surface coating to both substrates. Other surface treatments, like Langmuir-Blodgett deposition may provide some improvement to this problem, although inhomogeneities in the substrates themselves are probably responsible for much of the rounding in the region of weak anchoring. Thus, it is important to remember that at lower
temperatures, the calculated value for W is likely to represent some average over the two surfaces.
References


5. RESULTS

5.1 – Homeotropically-Aligned Anchoring Results

The plot of $W$ (homeotropic-alignment) versus reduced temperature for the monomer shows that the magnitude of $W$, a few degrees below $T_{NP}$, is consistent with values previously obtained for other similar materials

Figure 5 – 1: Monomer Homeotropically-Aligned Anchoring Coefficient
At approximately, \( T - T_{NI} = -3.5^\circ C \), however, \( W \) no longer increases as the temperature is reduced, but rather begins to decrease. The rate of decrease becomes more rapid at lower temperatures. It appears that the transition to a tilted state is weakly discontinuous, although the resolution of the data is insufficient to be certain.

In order to understand the behavior of \( W \) versus \( T - T_{NI} \), the theory of Parsons is employed\(^2\). Parsons treats the tilt angle as a competition between dipolar and quadrupolar interactions. For sufficiently strong quadrupolar interactions, the director will be at some non-zero angle \( \theta \) relative to the interface normal. As the temperature changes, the relative strengths of the two interactions will vary, thereby causing \( \theta \) to have a temperature dependence. One of the interesting consequences of the Parsons theory is the prediction of a structural phase transition, similar to that observed for the monomeric sample, at a nematic-non-liquid crystal interface. At an interface boundary, polar molecules are expected to orient in a perpendicular fashion so as to bury their dipoles inside or close to the higher dielectric medium (i.e. the glass substrate). For molecules which, to lowest order, possess a quadrupole moment, Parsons has shown that the molecules prefer to lie parallel to the interface\(^2,3\). Parsons then writes the phenomenological surface energy as:

\[
\gamma = \gamma_o + \frac{1}{2} \chi_Q (\hat{n} \cdot \hat{k})^2 - \gamma_d (\hat{n} \cdot \hat{k}), \tag{Eq. 5.1}
\]

where \( \hat{n} \) is the nematic director, \( \hat{k} \) is the unit vector normal to the surface, and \( \chi_Q \) and \( \gamma_d \) are the temperature dependent coefficients of the quadrupolar and
dipolar surface free energies, respectively. Minimizing the expression for $\gamma$ (Eq. 5. 1) with respect to $\hat{n} \cdot \hat{k} = \cos \theta$, Parsons found a critical point when $\gamma_0 = \gamma_D$. For $\gamma_D > \gamma_0$, the director is normal to the interface, but for $\gamma_D < \gamma_0$ a tilt $\theta$ is obtained. The equilibrium tilt can be obtained by expanding the expression for $\gamma$ for small $\theta$ near $T_s$, resulting in:

$$\gamma(\theta) = \gamma_0 + \frac{1}{2} (\gamma_D - \gamma_0) \theta^2 + \frac{5}{48} \gamma_0 \theta^4 + ...$$  \hspace{1cm} \text{Eq. 5. 2}$$

Inasmuch as there is no reason to expect $\gamma_0$ and $\gamma_D$ to exhibit the same temperature dependence, one might expect a tilt transition to occur at the interface. This tilt transition was previously observed at the free surfaces of MBBA and EBBA by Chiarelli, Faetti, and Fronzoni\cite{4,5}; and is now seen at a surfactant-treated substrate\cite{6}. Presumably the small anisotropy arising from the ester group is sufficient to cause the molecules to remain normal to the interface just below $T_{NI}$. As the temperature is lowered however, the dipole interactions may weaken and a tilt transition ensues at $T_s$. The even- and odd--dimer versions of the oligomers could not be aligned perpendicularly to the surface at any temperature in the nematic phase; hence the homeotropic anchoring strength coefficient for these systems could not be determined.

Although the even-dimer version is a completely symmetric molecule and it possesses local dipoles, these are apparently insufficient to overcome the van der Waals interactions favoring parallel alignment. Since only DC$_{8,9}$PC produced perpendicular alignment of the monomer, the nature of the surfactant clearly plays an essential role in this transition. It is beyond the scope of this thesis to examine this role, which may be investigated in future
experiments.

It should be noted that the Parsons equation for $\gamma$ (Eq. 5.1) predicts a second-order structural transition. This may be the case for the observed behavior, although it appears that the transition may be weakly first order. If this is the case, the Parsons equation must be modified with additional terms.

To summarize, the coefficient $W$ of the anchoring energy for a homeotropically-aligned molecular monomer has been measured as a function of reduced temperature above a tilt transition of the director at a nematic-substrate interface. $W$ seems to decrease rapidly on approaching the transition temperature $T_s$ from above, corresponding to an increasing tilt susceptibility at this temperature$^{[6]}$.
5.2 – Homogeneously-Aligned Anchoring Results

The results of \( W \) and \( K_{11} \) versus reduced temperature are shown on the following two graphs:

![Anchoring Strength Coefficients: Homogeneous Alignment](image)

**Figure 5–2:** Monomer and Even-Dimer Homogeneously-Aligned Anchoring Coefficients
Figure 5–3: Monomer and Even-Dimer Splay Elastic Constants

The results immediately suggest an interesting dichotomy between the monomer and even-dimer systems. When considering the bulk sample, one finds that the splay constants for both species are quite similar (i.e. the values differ by approximately 10-to-20% over the entire nematic temperature range)\[7,8\]. These results, in conjunction with measurements of the viscosity coefficients, suggest that the small amount of flexibility associated with the even-dimer's spacer is sufficient to nullify the theoretical results for rigid rods which predict a strong dependence of $K_{11}$ on the molecular aspect ratio\[9-14\]. On the other hand, when comparing the surface interaction properties, a
substantial difference in $W$ between the monomer and even-dimer exists.
One possible explanation may lie with the orientational order parameter in the
vicinity of the surface, as discussed by Yokoyama, et. al.[15] and by Pikin and
Terentjev[16]. Based upon a van der Waals model of the liquid crystal
interface, Poniewierski and Sluckin[17,18] predict a degradation in $S$ at a
grooved interface[19] which is used to induced parallel alignment. This
behavior is consistent with the anchoring results near $T_{NI}$ obtained by Faetti,
et. al.[20] and by Yokoyama, et. al.[15] for an obliquely evaporated SiO
substrate, and may even explain the homeotropic results seen by
Rosenblatt[1] as well. The surface reduction of the order parameter is also
supported by
birefringence[21-23] and contact angle measurements[24,25]. Based on the
grooved surface model of Berreman[19], $W$ scales as the elastic moduli at the
surface; a reduction in $S$ would therefore result in a concomitant decrease in
both the elasticity and the surface anchoring strength.

Despite the superficial appeal of this mechanism, however, there are a
number of problems: First, in order to explain the experimental results, it
would be necessary that the nematic order parameter for the monomer at the
interface be substantially less than that of the even-dimer over the entire
nematic range, even though the bulk values of $S$ differ by no more than 20%
at comparable reduced temperatures[26]. This point is still open to question.
More critical, however, is the very nature of the alignment process. Geary, et.
al.[27], suggested that liquid crystal alignment can grow epitaxially on a buffed,
linear-polymer-coated substrate. Although their birefringence measurements
overlooked the possibility of shape birefringence[28] at a grooved surface, their
conjecture has nevertheless been verified by Chen, et. al. using second harmonic generation$^{[29]}$. In their experiment, they showed that the highly polar liquid crystal octylcyanobiphenyl (8CB) aligns at a rubbed polyimide surface by means of short range molecular interactions, as opposed to grooves. Moreover, the order at the surface was found to be enhanced relative to the bulk, with alignment observed near the surface even well into the isotropic phase. Although it is not clear whether the same mechanism would apply for the relatively nonpolar liquid crystal molecules reported herein, it must be considered as a reasonable alternative to the groove theory, which tends to apply to thermosetting (i.e. cross-linked, grooved), as opposed to thermoplastic (oriented-chains) polymers. Thus, if the epitaxial alignment mechanism proposed by Geary, et. al.$^{[27]}$ is indeed operative here, S would be expected to increase at the surface for both species, and for the even-dimer in particular. In this light, the even-dimer would be expected to exhibit a larger anchoring strength coefficient W, which was indeed observed.

In addition to the previously mentioned considerations, Yokoyama, et. al.$^{[15]}$ pointed out that the anchoring strength may also be affected by higher order orientational order parameters such as $\langle P_2(\cos \theta) \rangle$, biaxiality, incipient smectic order, adsorption, and the microstructure of the polyimide surface. Moreover, if S is indeed a function of position, then the finite anchoring equation may not be entirely correct, inasmuch as it involves an elastic modulus which is position-dependent near the interface. In a sense the, entire concept of anchoring strength may go beyond the microscopic nature of the interface, and include a host of macroscopic phenomena$^{[15]}$. Despite these considerations, however, it is important not to lose sight of the central
result of this work: the apparent anchoring strength of the even-dimer is much greater than that of the monomer, a result which likely arises from the even-dimer's spacer group behaving as a nearly rigid unit. This result is qualitatively quite different from the elastic moduli data\textsuperscript{[7,9]}.

To summarize the results, the splay elastic constants as a function of reduced temperature for a monomeric liquid crystal and its even-version dimer have been compared and found to be similar. These results agree with previous, independent measurements. Likewise, the homogeneous anchoring strength coefficients $W$, for these two systems were also determined as a function of reduced temperature. Although both the monomer and even-dimer anchoring energies behave qualitatively the same, it was found that the even-dimer values were approximately ten times the values measured for the monomer. It is beyond the intention of this thesis to offer a unified model for this phenomenon, although factors such as the nematic order parameter at the surface may be important\textsuperscript{[8]}.
5.3 - Light Scattering Results:

Characterizing the Viscoelastic Properties as a Function of the Molecular Length-to-Diameter Ratio by Comparing the Monomer and Even-Dimer Light Scattering Results

The light scattering results for the elastic moduli of the monomer and even-dimer are shown below:

![Graph showing Absolute Elastic Constants for Monomer and Even-Dimer vs Reduced Temperature]

**Figure 5 – 4: Comparison of Monomer and Even-Dimer Elastic Constants**
The splay elastic constants for the monomer and even-dimer are similar for corresponding reduced temperatures\[7,9\]. These results, of course, were determined from a Freedericksz threshold field experiment and were confirmed by a separate, independent set of Freedericksz measurements which were performed in order to determine the anchoring strength coefficient of a homogeneously-aligned oligomeric system\[8\]. Moreover, the ratios $K_{11}/S^2$ were found to be nearly identical for both species, and exhibit only a weak dependence on temperature. As is the case with the splay elastic constants, the twist elastic constants ($K_{22}$) versus reduced temperature for both the monomer and even-dimer are quite similar, again being nearly equal when scaled by the square of the nematic order parameter\[26\]. Only the bend elastic constants show marked differences between species, increasing significantly, relative to $K_{11}$, for the even-dimer, especially at lower temperatures. In fact, not only does $K_{33}$ cross-over from being smaller than $K_{11}$ in the monomer to being larger than $K_{11}$ in the even-dimer, but $|dK_{33}/dT|$ for the even-dimer also seems to increase with reduced temperature well into the nematic phase. Such behavior is often associated with a nearby smectic A phase, although corresponding behavior was not observed for the twist elastic constant. Moreover, a nematic-to-crystalline transition occurs at approximately $T_{NI} - 25^\circ$C, well below the temperature range over which data was obtained. Although one cannot discount the possibility that this behavior is an artifact arising from the relatively large uncertainty in determining $K_{33}$, such a possibility is unlikely given that the uncertainty in $K_{33}$ tends to represent point-by-point scatter rather than systematic error.

Monomers and semi-flexible dimers have been treated theoretically by
Terentjev and Petschek\textsuperscript{[30].} Since approximations such as nonflexibility, which are associated with some of the other models, tend to be physically unrepresentative of the system under investigation, those models will not be considered here. Instead, the viscoelastic results will be primarily examined using the Terentjev/Petschek model\textsuperscript{[30].}

Terentjev and Petschek considered anisotropic mesogens which interact via both an attractive potential (including isotropic and anisotropic contributions), as well as via a hard core repulsive potential. This repulsive term contributes to both the attraction cut-off on the molecular surface as well as to the translational packing entropy of the system. In addition, Terentjev and Petschek included both a stiffness parameter $\Omega$ for the spacer, which is determined by its effective bending energy $\Omega = E_b / k_BT$, and a “bare” (or characteristic) angle $\theta_0$ between the mesogens which, for the case of the even-dimer is approximately equal to zero. The case of $\theta_0 \neq 0$ corresponds to the version of the bent-dimer for which the Terentjev/Petschek model predicts very different behavior. The model’s predictions are consistent with the experimental results obtained for the “5-9-5” dimer and will be discussed in the next section\textsuperscript{[31].} Note that by incorporating spacer flexibility into the molecular architecture, the dimer is viewed as consisting of two mesogens separated by a semi-flexible string.

For both the monomer and the rigid dimer (i.e. in the limit $\Omega \to \infty$) Terentjev and Petschek obtained elastic moduli with the correct magnitudes. Moreover, they found that the splay and twist elastic constants remain almost unchanged with molecular length; this surprising result turns out to be completely consistent with the data obtained in this study. Also consistent
with the experimental data and, in fact, with the results of most rigid rod models as well, they found that $K_{22}/K_{11} = \frac{1}{3}$ for both the monomer and the even-dimer. In addition, they found that $K_{33}/K_{11}$ exhibits a temperature dependence similar to that observed experimentally. This behavior, which becomes more pronounced with increasing number of mesogens in the molecule, arises from the order parameter dependence of $K_{33}$, such that $K_{33}$ diverges as $(1-S)^{-1}$. Not limiting themselves to rigid spacers, Terentjev and Petschek also numerically examined finite values of $\Omega$, which would correspond to some degree of spacer flexibility. For physically reasonable values of $\Omega$ (i.e. $1 < \Omega < 25$), they found results qualitatively similar to those of the rigid dimer. Note that $\Omega=6$ corresponds approximately to the data obtained for the $[\text{CH}_2]_{10}$ spacer$^{[32]}$. More specifically, they found that the temperature dependence of $K_{33}/K_{11}$ remains, although the divergence at lower temperatures tends to be weaker. This result is in excellent agreement with the data presented herein. The picture which emerges has several discernible features:

(i.) First, the even-dimer cannot be considered entirely rigid and is too short to be analyzed in terms of semi-flexible polymer models.

(ii.) As the orientational order increases deep into the nematic phase, the bend elasticity tends to grow rapidly as the order parameter approaches unity.

(iii.) Finally, an interesting dichotomy results: from the standpoint of spacer conformation populations and such quantities as the latent heat near the nematic-isotropic phase transition$^{[36]}$, the even-dimer is, for all practical purposes, rigid. On the other hand, in terms of elastic moduli, the even-dimer must be
considered partially flexible. As a side note, the idea of a highly ordered yet partially flexible spacer is reinforced by the observation that dimers having shorter spacers (two methylene units, for example) exhibit a smectic A phase as well as a nematic phase\(^{[33]}\). For longer spacer dimers, the small degree of flexibility is likely responsible for inhibiting the formation of a smectic A phase. Note that with terminal alkyl chains, longer molecules normally imply a stronger smectic tendency.

The viscosity data are even more difficult to interpret:

**Figure 5–5: Comparison of Monomer and Even-Dimer Viscosity Coefficients**
For the monomer, both $\eta_{\text{splay}}$ and $\gamma_1$ are comparable to each other, and over
the entire temperature range are approximately four to six times $\eta_{\text{bend}}$. These results are completely consistent with those for other low molecular
weight materials, both in relative terms (i.e. $\gamma_1/\eta_{\text{bend}}$) as well as absolute
values$^{[34,35]}$. The only troubling result is that $\gamma_1$ appears to be smaller than
$\eta_{\text{splay}}$, a physical impossibility. The difference is likely an artifact of the
multi-exponential fit, and is characteristic of the sort of error bars expected in
the experimental analysis. On the other hand, the results for the even-dimer are considerably different. First, the magnitude of the splay viscosity is
comparable to the monomer counterpart, and that of the twist viscosity is up
to twice that of the monomer at comparable reduced temperatures. Clearly
the tendency of the even-dimer to be more viscous than the monomer is
largely offset by the higher even-dimer transition temperature and
concomitant Arrhenius behavior of the viscosities. Secondly, $\gamma_1 > \eta_{\text{splay}}$ by an
amount more substantial than that found in shorter mesogens. Finally, $\eta_{\text{bend}}$
for the even-dimer is much larger than for the monomer, and is of the same
order as, and even larger than, $\eta_{\text{splay}}$. $\eta_{\text{bend}}$ also appears to be larger than $\gamma_1$
well below $T_{\text{NI}}$, although this also may be an artifact of the fitting procedure.

The Brandeis group has extensively studied the issue of the viscosities
in elongated polypeptides$^{[13,36-40]}$. However, the oligomeric liquid crystalline
system differs from theirs in several important respects: the aspect ratios of
the monomer and even-dimer are relatively small and they tend to be far
more flexible, due to thermal considerations, than the polypeptides. These
differences give rise to very different types of viscous behavior for the
oligomeric materials. For example, the ratio $\gamma_1/\eta_{\text{bend}}$ for the even-dimer is not
only much smaller than that of PBG (polybenzylglutamate), but also trends in the opposite direction as a function of L/d. It is clear then, that the oligomeric system is considerably more complex than the lyotropic nematics, and cannot be adequately described by viscous theories of long rigid, or even semi-flexible, molecules. Thus, despite the fact that one can stretch the limits of applicability of models such as Osipov and Terentjev's\cite{41} to achieve results qualitatively consistent with the experimental results, utilization of such models is inappropriate due to the even-dimer's inherent flexibility.

Throughout the discussion of viscoelastic properties, the experimental results have been interpreted in terms of appropriate models for rigid and semi-flexible molecules. None of these models, however, properly accounts for effects such as permanent dipolar interactions, packing, and short range order important to dense systems of small molecules. In this light, the experimental results must be interpreted with a caveat: disagreement of experimental results with theoretical models may be due to the inherent incompleteness of any theoretical model\cite{69}.
5.4 – Light Scattering Results:

Characterizing the Viscoelastic Properties as a Function of Molecular Shape by Comparing the Even-Dimer and Odd-Dimer Light Scattering Results

The relevant ratios of elastic constants comparing the even- and odd-dimers are plotted below:

**Figure 5 – 6: Comparison of the Twist-to-Splay Elastic Constant Ratio between the Even- and Odd-Dimers**
Figure 5 – 7: Comparison of the Bend-to-Splay Elastic Constant Ratio between the Even- and Odd-Dimers

A comparison of these figures reveals the central result of the work comparing viscoelastic properties of straight and bent oligomers: a banana-shaped molecule significantly reduces the bend elasticity relative to the splay and twist. Over the entire temperature range, in fact, $K_{33}/K_{11}$ for the odd-dimer is only about 60 to 65% of the value of the even-dimer, whereas the $K_{22}/K_{11}$ ratios are nearly the same. Gruler$^{[42]}$ and Helfrich$^{[43]}$ independently suggested that a kinked molecule might exhibit a reduced bend elastic modulus, since the elastic strain can be partially relieved by a change in the distribution of molecular orientations; in a sense, the banana-shaped
molecules can partially align in "bunches". Gruler calculated the change in the elasticity as a function of empirical material parameters which describe the inherent bend of the molecule. Using reasonable values for these parameters, he pointed out that the bend modulus for a banana-shaped molecule might be reduced so much that it can even become negative\cite{42}; Helfrich's corrections, on the other hand, were somewhat smaller\cite{43}. In this light, the experimental results presented in this study indicate that the effective material parameters for the odd-dimer lie within a reasonable range. More recently, the Terentjev/Petschek model was developed specifically for dimers with a flexible spacer group\cite{30}. Recall that they found for the even-dimer, in the limit $\Omega \rightarrow \infty$, that $K_{22}/K_{11} = \frac{1}{3}$; similar results were found for the odd-dimer. Likewise assuming a completely rigid spacer, they found that $K_{33}/K_{11}$ exhibits a temperature dependence similar to that shown in Figure 5 - 7. Assuming more physically reasonable (i.e. finite) values of $\Omega$ (i.e. $1 < \Omega < 25$), they then found that the qualitative temperature dependence of $K_{33}/K_{11}$ remains, although the divergence at lower temperatures tends to be weaker. Finally, Terentjev and Petschek examined the behavior of $K_{33}/K_{11}$ as a function of the mesogenic angle $\theta_o$ for a fixed stiffness of $\Omega=10$. For $\theta_o=10^0$, the model closely mimics the behavior of the even-dimer experimental results. For $\theta_o=20^0$, they found a significant reduction in $K_{33}/K_{11}$ relative to the straight-dimer ($\theta_o=0^0$). Finally, for $\theta_o=40^0$, they found an even greater reduction, corresponding approximately to the odd-dimer experimental behavior. This is not to say that $\theta_o=40^0$ for the odd-dimer, but rather that when a significant angle exists between the mesogens (i.e. several tens of degrees), one can expect a significant reduction in $K_{33}$. Moreover,
note that the qualitative aspects of these results are consistent with the
predictions of Gruler and Helfrich, and are precisely what would be expected
on intuitive grounds.

The light scattering results show clearly that the bend elasticity is
reduced for banana-shaped molecules\cite{9}. Although comparisons with a
homologous series (i.e. a molecular series where only the terminal group
lengths are varied) are useful, they must be treated cautiously. As long as
the system is athermal and long range interactions are important, one cannot
base elasticity ratios solely on hard core aspect ratios. Rather, one
experimentally requires a system of virtually identical molecules to test these
theories; this would tend to suppress differences in the non-steric (i.e. long
range) contribution to the potential associated with various parts of the
molecule. Thus, only systems similar to those used in this investigation might
represent a fair test of the theories formulated by Gruler\cite{42}, Helfrich\cite{43}, and
Terentjev and Petschek\cite{30,32}. The predictions of the Terentjev/Petschek
model are compared to the experimental results on the following pages:
Figure 5 – 8: Experimental and Theoretical Comparison of $K_{33}/K_{11}$ for the Monomer and Even–Dimer
Even- and Odd-Dimer Comparison

Figure 5–9: Experimental and Theoretical Comparison of $K_{22}/K_{11}$ for the Even–Dimer and Odd–Dimers – Note that the theoretical prediction for the twist-to-splay elastic constant ratio is (1/3) for both oligomers.
Even- and Odd-Dimer Comparison

Figure 5–10: Experimental and Theoretical Comparison of $K_{33}/K_{11}$ for the Even-Dimer and Odd-Dimers
5.5 – Future Work

The theories, data, and experimental results discussed in this thesis, by no means exhaust the possible investigations into the viscoelastic properties and surface interactions of oligomeric liquid crystals. In fact, several interesting, and relatively straight-forward, follow-up experiments are suggested by the results. To conclude this thesis, a general outline of these ideas is presented:

(i.) Determination of the Absolute Elastic Constants and Viscosities for the Odd-Dimer:
The light scattering results for the odd-dimer proved to be very useful in formulating the Terentjev/Petschek\textsuperscript{[30,32]} model for dimer specimens whose spacer group can be characterized by two quantities: an inherent kink-angle $\theta_0$, and a "stiffness" parameter $\Omega$. However, recall that light scattering techniques are somewhat limited in their effectiveness inasmuch as they are only capable of determining the elastic constant ratios: $K_{11}/K_{22}$ and $K_{22}/K_{33}$. In order to determine absolute elastic moduli, and therefore absolute viscosity coefficients, other techniques, such as the Freedericksz threshold method, must be employed. Presently, such an absolute determination has not been performed for the odd-dimer; thus forcing its characterization to be limited to expressions involving elastic moduli ratios. A very easy, and satisfying experiment, would be to complete the viscoelastic characterization of the odd-dimer (i.e. "close the book"). Recall that the Freedericksz threshold technique provides a measurement of the elastic moduli based upon measurements of the critical threshold field $H_c$, sample thickness $d$, and magnetic susceptibility anisotropy $\chi_a$ (or $\Delta \chi$). For sufficiently thick samples, the elastic moduli are written as:
\[ K_{ii} = \left( \frac{H_i d}{\pi} \right)^2 \chi_a \], where \( K_{ii} \) depends on the particular Freedericksz geometry. Already, the threshold field measurements (for a known thickness) have been acquired versus reduced temperature for the odd-dimer oriented in the Freedericksz splay geometry. The only crucial missing information is a measurement of the magnetic susceptibility anisotropy as a function of reduced temperature. Hence, the absolute viscoelastic properties of the odd-dimer patiently await the arrival of a susceptometer and the subsequent determination of \( \chi_a \) versus reduced temperature.

(ii.) **Experimentation on Trimers and Tetramers:**

The effects of the molecular length-to-diameter ratio on viscoelastic properties and surface interactions can still be readily explored. Obviously, any experimental data concerning the trimer or tetramer version of this system would greatly augment the information-base from which theoretical models might emerge. The trimer species has yet to be synthesized. The tetramer species, on the other hand, has not only been processed, but experimented upon as well. Unfortunately, the tetramer has not been successfully aligned, neither homogeneously nor homeotropically, at a substrate interface. A variety of alignment techniques have been attempted: unidirectionally rubbed nylon 6/6, unidirectionally rubbed polyimide coatings, the lecithin surfactant \( \text{DC}_{8,9}\text{PC} \), the ionic surfactant \( \text{HTAB} \), and even a seldom-used silane compound. At this time, the tetramer simply has not been aligned well enough to allow either light scattering or magnetic field threshold measurements to proceed. If a successful alignment treatment were discovered, the tetramer characterization would represent an entirely new data-set from which the Terentjev/Petschek model may be tested.
(iii.)  **Further Experimentation on Chain-Flexibility and Chain-Length:**
As a final experimental consideration, future work may need to be done on oligomeric systems with different chain-lengths and/or chain-flexibilities. For instance, a shorter monomeric liquid crystalline system, a "2-00-2" monomeric system versus the "5-00-5" monomeric system, may provide further insight into the role of the molecular length-to-diameter ratio in predicting viscoelastic properties. Also, a different dimeric system, consisting of a different number of methylene groups in the spacer, could better pinpoint the role of spacer flexibility in predicting liquid crystalline viscoelastic properties. Likewise, the role of spacer flexibility can be further explored with a liquid crystalline system already synthesized and purified for laboratory work: the monomer $C_5H_{10}OC_6H_4COOC_6H_4NO_2$ and its dimer $[C_5H_{10}OC_6H_4COOC_6H_4NO_2]_2$ is currently waiting for appropriate Freedericksz and light scattering characterization.
References


[33] Griffin, A. C., unpublished


APPENDIX A:
INTERFEROMETRIC SCHEME FOR DETERMINING THE SAMPLE THICKNESS

As the name suggests, the interferometric scheme for determining sample thickness involves interference effects from the four interfaces of an empty sample holder: two air-to-glass boundaries and two cavity-to-glass boundaries\(^1\).

A typical sample cell is prepared by cutting microscope slides, usually 1 mm thick, and by coating the slides with relevant surface treatments. Mylar spacers, of appropriate thickness, are placed between the slides which are then epoxied together. If an accurate thickness measurement is required, the interferometric technique is used on the empty cell. Eventually, the material to be studied is heated into the isotropic phase and drawn into the sample holder by capillary-action:
Figure A – 1: Typical Empty Sample Holder and Filling of Sample via Capillary Action

To determine the thickness, the empty cell is placed atop a precision rotation stage and is centered such that an incident laser beam (whose wavelength is known) strikes the sample holder parallel to the normal of the glass slide. Once the incident angle has been zeroed, the sample is rotated while the reflection pattern is observed. In the reflection pattern, one will see three interference maxima; the first arising from reflections from the front glass interfaces; the second (middle pattern) arising from interference between reflections from the two cavity-to-glass interfaces; and the third arising from reflections from the back glass interfaces. As the holder is rotated, the middle pattern will pass through consecutive interference maxima and minima, which of course depend on the total phase difference of the two beams.
Figure A – 2: Reflections from Empty Cavity

In this geometry, the beam striking the back surface travels an extra path difference of \( \frac{2l}{\cos \theta} \) as well as experiences a phase shift of \( \pi \) upon reflection at the air-to-glass back surface. Meanwhile, the beam striking the front surface travels an extra path difference of \( \frac{2l \sin^2 \theta}{\cos \theta} \) but experiences no phase shift at the glass-to-air front surface. Thus, the total path difference is:

\[
\text{total path difference} = \frac{2l}{\cos \theta} - \frac{2l \sin^2 \theta}{\cos \theta} + \frac{\lambda}{2}.
\]

Eq. A. 1

which must equal \( (m + 1/2) \lambda \) as the condition for an interference minima.

(Note that \( m \) is an integer representing the order of the minima.)
resulting condition for minima in the middle interference pattern is therefore:

\[ 2\ell \cos \theta = m\lambda. \]  

**Eq. A. 2**

To experimentally determine the sample thickness, a simple iterative procedure is used. Several successive angles (say \( n \) measurements corresponding to: \( \theta_1, \theta_2, \ldots, \theta_n \)) are recorded at which the middle interference pattern vanishes. For each **successive** pair of measurements, a set \((n - 1)\) of approximations to the sample thickness is calculated according to:

**First minima:**  
\[ 2\ell \cos \theta_1 = m\lambda \]

\[ \rightarrow \ell = \frac{\lambda}{2(\cos \theta_2 - \cos \theta_1)} \]

**Second minima:**  
\[ 2\ell \cos \theta_2 = (m + 1)\lambda \]

**Eq. A. 3**

The \((n - 1)\) approximations are then averaged to determine an initial guess to the sample thickness, \( \bar{\ell} \). This guess is re-substituted into the minima equation and used to generate the order \( m \), of the minima at each angle; resulting in \( n \) values of the minima order. Recalling that \( m \) must be an integer, the calculated values of \( m \) are rounded to the nearest integers which are then used to calculate the next iteration of the sample thickness. Finally, these \( n \) thicknesses are averaged to determine the final sample thickness.

The interferometric scheme can measure sample thicknesses to approximately 1%; the error computed from the standard deviations of
thicknesses used to calculate the final average value. On a final note, for samples used in capacitance measurements (i.e. whose internal surfaces were coated with a conducting material, thus allowing for thickness determination via capacitive measurements), the thickness values determined using the interferometric scheme and the capacitance technique usually agreed to better than 4 per cent. In cases of more significant discrepancy, the interferometric value was used in subsequent calculations, since capacitive measurements are possibly more adversely affected by surface treatments.
APPENDIX B:
EIGEN-EQUATION FOR DETERMINING THE EFFECTIVE REFRACTIVE INDEX OF A UNIAXIAL OR BIAXIAL CRYSTAL

When dealing with crystal optics, a central concern is the determination of the dielectric eigenvalues and eigenvectors for a given direction of propagation. To accomplish this, an eigenequation describing the propagation of light in an anisotropic medium must be rigorously derived. The specific propagation configurations which were used in this research can then be formulated from this central eigenequation. The derivation starts with Maxwell's equations:

\[ \nabla \times \mathbf{H} = \frac{\partial \mathbf{D}}{\partial t}, \quad \text{and} \quad \nabla \times \mathbf{E} = -\frac{\partial \mathbf{B}}{\partial t}, \quad \text{Eq. B.1} \]

where, in nonmagnetic materials, \( \mathbf{B} = \mu_s \mathbf{H} \). Assuming that \( \mathbf{E} \), \( \mathbf{H} \), and \( \mathbf{D} \) are plane waves of the form:

\[ \mathbf{E} = \mathbf{E}_0 e^{i(\mathbf{k} \cdot \mathbf{r} - \omega t)}, \quad \text{Eq. B.2} \]

then the Maxwell equations become (i.e. \( \frac{\partial}{\partial t} \rightarrow -i \omega \) and \( \nabla \times \rightarrow i \mathbf{k} \times \)):

302
\[ \vec{k} \times \vec{H} = \omega \vec{D}, \text{ and } \vec{k} \times \vec{E} = -\omega \vec{B}. \]  
\text{Eq. B. 3}

However, these two equations can be combined by performing the operation \( \vec{k} \times (\vec{k} \times \vec{E}) \) which results in:

\[ \frac{1}{\mu_e \omega^2} \vec{k} \times (\vec{k} \times \vec{E}) = -\vec{D}. \]  
\text{Eq. B. 4}

By defining the wavevector \( \vec{k} \) as:

\[ \vec{k} = \frac{c}{\omega} \hat{n} \vec{k} = n \hat{k}. \]  
\text{Eq. B. 5}

where \( \hat{k} \) is a unit vector in the direction of \( \vec{k} \), the combined Maxwell equations become:

\[ \frac{1}{\mu_e c^2} \vec{k} \times (\vec{k} \times \vec{E}) = -\vec{D}. \]  
\text{Eq. B. 6}

At this point, the vector identity \( \vec{A} \times (\vec{B} \times \vec{C}) = (\vec{A} \cdot \vec{C})\vec{B} - (\vec{A} \cdot \vec{B})\vec{C} \), can be employed to rewrite the equation as:

\[ -(\vec{k} \cdot \vec{k}) \vec{E} + (\vec{k} \cdot \vec{E})\vec{k} = -\mu_e c^2 \vec{D}. \]  
\text{Eq. B. 7}

The next step is to simplify this vector equation by rewriting it only for each vector's \( i \)th component. For notational convenience, the vector dot products are written as the sum over a separate index, \( j \). The quantity \( \vec{k} \cdot \vec{k} \) is simply
\( n^2 \), and the quantity \( \vec{k} \cdot \vec{E} \) can be rewritten as \( \sum_j \vec{k}_j E_j \). Also, the displacement field can be written as \( \vec{D} = \varepsilon \vec{E} \), such that its \( i \)th component is: \( D_i = \varepsilon_0 \sum_j \varepsilon_{ij} E_j \), where \( \varepsilon_0 \) is the dielectric permittivity of free-space and \( \varepsilon_{ij} \) is the permittivity or dielectric constant for the crystalline material. With these substitutions, the combined Maxwell equation takes on the final form:

\[
\sum_j (\varepsilon_{ij} + \vec{k}_i \vec{k}_j) E_j = n^2 E_i.
\]

Eq. B. 8

This is the final eigen-equation for describing the propagation of light in an anisotropic medium. In this equation, the \( E_i \)'s are the eigenvectors while the \( n^2 \)'s are the eigenvalues. For propagation along one principal axis, the eigen-equation is diagonalized, the eigenvectors lie in the direction of the other two axes, and the eigenvalues are the diagonal elements. However, for propagation in an arbitrary direction, the solutions are a bit more complex as will be demonstrated presently.
Example #1-B: Uniaxial Crystal with Propagation Along a Principal Axis

Consider a uniaxial crystal with the wavevector directed along the x-axis:

![Uniaxial Crystal Diagram]

Figure B - 1: Uniaxial Crystal with the Wavevector along the x-axis

In such a system, the relevant quantities are:

\[ \epsilon_{ij} = \begin{bmatrix} \epsilon_{xx} & 0 & 0 \\ 0 & \epsilon_{xx} & 0 \\ 0 & 0 & \epsilon_{zz} \end{bmatrix} \]  

Eq. B. 9

\[ \vec{k}_i = \vec{k}_j = \vec{k}_x = n \hat{k}_x \quad \text{thus} \quad \vec{k}_i \vec{k}_j = n^2 \hat{k}_x \hat{k}_x = \begin{bmatrix} n^2 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \]  

Eq. B. 10

\[ n^2 = \begin{bmatrix} n^2 & 0 & 0 \\ 0 & n^2 & 0 \\ 0 & 0 & n^2 \end{bmatrix} \]  

Eq. B. 11
Thus, the eigenequation (Eq. B. 8) becomes:

\[
\begin{bmatrix}
\varepsilon_{xx} & 0 & 0 \\
0 & \varepsilon_{xx} - n^2 & 0 \\
0 & 0 & \varepsilon_{zz} - n^2
\end{bmatrix}
\begin{bmatrix}
E_x \\
E_y \\
E_z
\end{bmatrix} = 0.
\]

Eq. B. 12

As with any eigenequation of this form, the solution for the eigenvalues \( n^2 \), can be obtained by setting the determinant of the matrix equal to zero. The resulting solutions are:

**Solution #1:**
- **eigenvalue:** \( \varepsilon_{xx} = 0 \)
- **eigenvector:** \( E_x \)
  - (i.e. a non-physical, longitudinal wave)

**Solution #2:**
- **eigenvalues:** \( n_1^2 = \varepsilon_{xx} \) and \( n_2^2 = \varepsilon_{zz} \)
- **eigenvectors:** \( E_x \) and \( E_z \) (with \( E_y = 0 \))
  - (i.e. transverse waves)

Thus, for the simple example described above, if the field is polarized along the z-axis, the crystalline refractive index is the "extraordinary" refractive index while for polarization along the y-axis, the crystalline refractive index is the "ordinary" refractive index.
Example #2–B: **Uniaxial Crystal with Propagation Along an Arbitrary Direction**

Consider a uniaxial crystal with the wavevector in the yz-plane:

Figure B – 2: Uniaxial Crystal with the Wavevector along an Arbitrary Direction

In this system, the only important change from the previous example is in the form of the wavevector $\vec{k}$:

$$\vec{k} = \begin{pmatrix} 0 \\ n \sin \theta \\ n \cos \theta \end{pmatrix} \rightarrow \vec{k}_{\theta} = \begin{pmatrix} 0 & 0 & 0 \\ n^2 \sin^2 \theta & n^2 \sin \theta \cos \theta \\ n^2 \sin \theta \cos \theta & n^2 \cos^2 \theta \end{pmatrix}$$  \hspace{1cm} \text{Eq. B. 13}

Hence, the eigenequation (Eq. B. 8) has the form:

$$\begin{bmatrix} \varepsilon_{xx} - n^2 & 0 & 0 \\ 0 & \varepsilon_{xx} - n^2 \cos^2 \theta & n^2 \sin \theta \cos \theta \\ 0 & n^2 \sin \theta \cos \theta & \varepsilon_{xx} - n^2 \sin^2 \theta \end{bmatrix} \begin{bmatrix} E_x \\ E_y \\ E_z \end{bmatrix} = 0.$$  \hspace{1cm} \text{Eq. B. 14}
which again can be solved by setting the matrix determinant equal to zero; the eigenequation becomes:

\[ \{\varepsilon_{\alpha\alpha} - n^2\}\{(\varepsilon_{\alpha\alpha} - n^2\cos^2 \theta)(\varepsilon_{\alpha\alpha} - n^2\sin^2 \theta) - n^4\sin^2 \theta \cos^2 \theta\} = 0. \quad \text{Eq. B. 15} \]

The solutions are:

**Solution #1:**  \( n_1^2 = \varepsilon_{\alpha\alpha} \)

*eigenvector:* \( \vec{E} = E_0(1,0,0) \)

(i.e. transverse wave)

**Solution #2:**  \( \frac{1}{n_2^2} = \frac{\cos^2 \theta + \sin^2 \theta}{\varepsilon_{\alpha\alpha}} = \frac{\cos^2 \theta}{n_o^2} + \frac{\sin^2 \theta}{n_r^2} \)

*eigenvectors:* \( \vec{E} = E_0(0,\cos \psi,-\sin \psi) \), where \( \psi \) is slightly different from \( \theta \).

(i.e. quasi-transverse wave in the yz-plane)

Thus, to summarize the calculations for a uniaxial crystal, the crystalline index is specified by the direction of \( \vec{k} \). For \( \vec{k} \) along a principal axis, the \( x \)-axis for example, one wave is a non-physical longitudinal wave with eigenvalue \( \varepsilon_{\alpha\alpha} = 0 \) and eigenvector \( E_z \). The other two transverse waves have eigenvalues \( n_1^2 = \varepsilon_{\alpha\alpha} \) and \( n_2^2 = \varepsilon_{\alpha\alpha} \) with eigenvectors along the axes perpendicular to the propagation axis. For propagation at an arbitrary angle \( \theta \) with respect to the \( z \)-axis, the solutions result in a transverse wave with
\( n_i^2 = \varepsilon_{\alpha\beta} \) and eigenvector perpendicular to the plane containing \( \vec{k} \) and the z-axis. Also, the system is solved by a quasi-transverse wave with the eigenvector in the kx-plane and \( n_2^2 \) given by a geometric combination of \( \varepsilon_{\alpha\alpha} \) and \( \varepsilon_{\alpha\beta} \). This latter solution was the one utilized in the light scattering configurations B and C.
Example #3-B: Biaxial Crystal with Propagation along an Arbitrary Direction

Consider a biaxial crystal with the wavevector in the xz-plane:

Figure B – 3: Biaxial Crystal with the Wavevector along an Arbitrary Direction

In this system, the solutions to the eigenequation are quite tedious and complicated to derive. Instead, only an interesting result will be presented. In biaxial crystals, the middle index is designated by \( n_y \), such that \( n_x < n_y < n_z \). Clearly, with \( \vec{k} \) lying in the xz-plane, one crystal index (i.e. eigenvalue) will correspond to the index \( n_y \), regardless of the direction of \( \vec{k} \). However, the other crystal index will range in value from \( n_x \) to \( n_z \), depending entirely on the direction of \( \vec{k} \). At some angle, denoted by \( (\beta/2) \), which corresponds to propagation along an optical axis, this index will assume the value \( n_y \), since \( n_y \) is chosen to be the intermediate index. Hence, at \( (\beta/2) \) and \( (\pi/2) - (\beta/2) \), the two crystal indices will have the same value and the crystal is said to have
two optical axes. The reason these crystals are called biaxial is that there are two directions of propagation in which birefringence disappears. The optic angle $\beta$, though complicated to derive, is given by:

$$\tan \beta = \sqrt{\frac{n_i^2(n_i^2 - n_e^2)}{n_e^2(n_i^2 - n_o^2)}}.$$  

Eq. B. 16
APPENDIX C: AUTOCORRELATOR COUNTING ROUTINE

The method by which the Brookhaven 136-channel digital autocorrelator processes data is a somewhat interesting routine worthy of separate mention. For the experiments described in this thesis, scattered light from a nematic sample enters a photomultiplier tube whose instantaneous current is passed through a pulse amplifier/discriminator circuit, and fed into the autocorrelator. The job of the autocorrelator then, is to count the scattered light pulses in such a way as to build-up the intensity-intensity autocorrelation function \( \langle I(0)I(\tau) \rangle \).

In order to achieve this, the autocorrelator stores data in three separate registers which, for convenience, will be denoted as: the total-register, the active-register, and the present-count-register. Let \( \tau \) denote the sample time per channel (in microseconds) as inputted by the user. Thus, the total decay time, ignoring delay channels, will extend over a time interval of \((136*\tau)\) microseconds. The active- and total-registers are divided into 136 bins with each bin separated in time by an interval \( \tau \), while the present-count-register is a single bin register containing the number of pulses detected in the last \( \tau \) microseconds. The model BI-2030AT autocorrelator is equipped with a 4–bit processor which means that it can detect up to 16 (i.e. \( 2^4 \)) pulses per channel ranging from 0 to 15. Hence, in the first \((137*\tau)\)
microseconds of data acquisition, the active-register will fill its 136 bins with the number of counts detected every $\tau$ microseconds; the present-count-register will fill its single bin with the most recently detected number of pulse counts; and the total-register’s bins will temporarily remain completely unfilled. An example of such data processing is schematically represented below:

**Present Time:** $t$

**Time Elapsed:** $136\tau + \tau$

**Total-Register**

```
#1  #2  #3 ................................................................. #136
0   0   0   0   0   0   0   0
```

**Active-Register**

```
2  14  3  0  7  8  15  10
```

**Present-Count-Register**

```
4
```

**Figure C – 1: Autocorrelator Counting – First step in the counting procedure.**

The correlator then fills each of the total-register’s bins with the product of the present-count-register and the corresponding bin in the active-register. Hence the first total-register bin is occupied by the value of the product of the present-count-register and the first active-register bin. If $n$ represents the bin number of the total-register, the result of the multiplication just described is
that each bin now contains the product \( I(t) \times I(t-n\tau) \):

**Present Time:** \( t \)  
**Time Elapsed:** \( 136\tau + \tau \)  

after multiplication, bin \#135 in the total-register contains the value \( I(t) \times I(t - 135\tau) \)

<table>
<thead>
<tr>
<th>Total-Register</th>
<th>8</th>
<th>56</th>
<th>12</th>
<th>0</th>
<th>28</th>
<th>32</th>
<th>60</th>
<th>40</th>
<th>20</th>
<th>36</th>
<th>44</th>
<th>12</th>
</tr>
</thead>
<tbody>
<tr>
<td>#1</td>
<td>#2</td>
<td>#3</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Active-Register</th>
<th>2</th>
<th>14</th>
<th>3</th>
<th>0</th>
<th>7</th>
<th>8</th>
<th>15</th>
<th>10</th>
<th>5</th>
<th>9</th>
<th>11</th>
<th>3</th>
</tr>
</thead>
</table>

<table>
<thead>
<tr>
<th>Present-Count-Register</th>
<th>4</th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
</table>

bin \#135 in the active-register contains the value \( I(t - 135\tau) \)

the present-count-register contains the value \( I(t) \)

**Figure C-2: Autocorrelator Counting – Second step in the counting procedure.**

Immediately following this multiplication, the value residing in the present-count-register is removed and placed in the first bin, bin \#1, of the active-register. All values in the active-register are subsequently shifted one bin to the right with the value of bin \#136 being discarded and replaced by the former value in bin \#135. Meanwhile, after another time elapse of \( \tau \) microseconds, a completely new value is placed into the present-count-register depending on the number of counts detected from the scattered light:
Time Elapsed: $136\tau + 2\tau$

**Total-Register**

<table>
<thead>
<tr>
<th>8</th>
<th>56</th>
<th>12</th>
<th>0</th>
<th>28</th>
<th>32</th>
<th>60</th>
<th>40</th>
</tr>
</thead>
<tbody>
<tr>
<td>#1</td>
<td>#2</td>
<td>#3</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>20</th>
<th>36</th>
<th>44</th>
<th>12</th>
</tr>
</thead>
</table>

**Active-Register**

<table>
<thead>
<tr>
<th>2</th>
<th>14</th>
<th>3</th>
<th>0</th>
<th>7</th>
<th>8</th>
<th>15</th>
</tr>
</thead>
</table>

<table>
<thead>
<tr>
<th>5</th>
<th>9</th>
<th>11</th>
</tr>
</thead>
</table>

former value of the present-count-register is placed into bin #1 of the active-register

previous value in bin #136 is discarded

new value enters the present-count-register

---

**Figure C – 3: Autocorrelator Counting – Third step in the counting procedure.**

Finally, in order to obtain the desired autocorrelation function $\langle I(0)I(\tau) \rangle$, the multiplication operation is repeated; however, note that the multiplicative result does not replace the values in the total-register. Instead, the result is added to the previous value residing in each total-register bin. In other words, just as before, the value in the present-count-register is multiplied by each bin in the active-register. The result is then added to the value currently occupying the corresponding bin in the total-register.

Consider the present example represented in the previous diagrams. The
present-count-register contains the value 7 which is multiplied by the value in bin #1 of the active-register 4. The result \((4 \times 7 = 28)\) is then added to the value previously in bin #1 of the total-register 8, giving the total \(8 + 28 = 36\). Thus, the value 36 is placed into bin #1 of the total-register:

\[
\text{Time Elapsed: } 136\tau + 2\tau
\]

### New Total-Register

<table>
<thead>
<tr>
<th>36</th>
<th>70</th>
<th>110</th>
<th>21</th>
<th>28</th>
<th>81</th>
<th>116</th>
<th>145</th>
<th>48</th>
<th>71</th>
<th>107</th>
<th>89</th>
</tr>
</thead>
</table>

\#1 \#2 \#3 \hline

\text{(7 \times 4) + 20 = 48}

### Previous Total-Register

<table>
<thead>
<tr>
<th>8</th>
<th>56</th>
<th>12</th>
<th>0</th>
<th>28</th>
<th>32</th>
<th>60</th>
<th>40</th>
<th>20</th>
<th>36</th>
<th>44</th>
<th>12</th>
</tr>
</thead>
</table>

### Active-Register

<table>
<thead>
<tr>
<th>4</th>
<th>2</th>
<th>14</th>
<th>3</th>
<th>0</th>
<th>7</th>
<th>8</th>
<th>15</th>
<th>4</th>
<th>5</th>
<th>9</th>
<th>11</th>
</tr>
</thead>
</table>

### Present-Count-Register

| 7 |

Each cell is filled by the formula:

\[
\text{new total-register} = ([\text{present-count-register}] \times [\text{active-register}]) + [\text{previous total-register}]
\]

**Figure C – 4: Autocorrelator Counting – Final step in the counting procedure.**

At this point, one iteration of the autocorrelator's algorithm for constructing the intensity-intensity autocorrelation function is complete. The autocorrelator will continue this procedure until a total duration time \(t_{\text{curr}}\) again
measured in microseconds, is reached. This duration time can be entered by the user and is chosen, usually by a somewhat trial-and-error method, to be long enough to result in a "smooth" autocorrelation function. Obviously, the autocorrelator is required to execute its counting method a total of \( \frac{t_{\text{dur}}}{\tau} \) times during the entire experimental acquisition time.
APPENDIX D:
DISTORTIONS ASSOCIATED WITH MOTION
ALONG THE UNIT VECTORS \( \hat{e}_1 \) AND \( \hat{e}_2 \)

In Chapters 2 and 3, the unit vector \( \hat{e}_1 \) was introduced as a direction which corresponds to a mixture of periodic deformations of the splay and bend nematic distortions. Likewise, \( \hat{e}_2 \) was introduced as a direction corresponding to a mixture of periodic deformations of the twist and bend nematic distortions. The connection between the direction of the unit vectors and the resulting nematic deformations was never fully developed. It is a useful exercise, therefore, to visualize the various types of deformations occurring along these unit vectors. A heuristic development of this connection is now presented. An illustration will be made for a specific light scattering geometry and the results generalized for the other geometries used in this study.

Consider the following light scattering geometry, corresponding to configuration C of the experimental light scattering set-ups:
Figure D – 1: Configuration C Light Scattering Geometry

In this particular geometry, the quantities of interest have the following values:

\[ \hat{n} = (-1,0,0), \quad \hat{i} = (0,0,1), \quad \hat{j} = (\sin \phi \cos \phi,0), \]
\[ \vec{k}_{in} = k_o n_o (1,0,0), \]
\[ \vec{k}_{out} = k_o n_{ef} (\cos \phi, -\sin \phi, 0), \]
\[ \vec{q} = k_o (n_{ef} \cos \phi - n_o - n_{ef} \sin \phi, 0). \]  \hspace{1cm} \text{Eq. D. 1} \]

Thus, the unit vectors \( \hat{e}_1 \) and \( \hat{e}_2 \) are given by:

\[ \hat{e}_2 = \frac{\hat{n} \times \vec{q}}{|\hat{n} \times \vec{q}|} = (0,0,1), \quad \hat{e}_1 = \frac{\hat{e}_o \times \hat{n}}{|\hat{e}_2 \times \hat{n}|} = (0,-1,0). \]  \hspace{1cm} \text{Eq. D. 2} \]

With the various vectors well-defined, the scattering geometry can be schematically depicted using a slightly different representation:
Now, with $\hat{e}_1$ and $\hat{e}_2$ explicitly drawn, the nematic distortions associated with these unit vectors can be qualitatively discussed. The unit vectors will be treated individually:
• **Motion associated with \( \hat{e}_2 \):**

To understand which type of deformation corresponds to motion along the direction of the \( \hat{e}_2 \) unit vector, the component of the nematic director fluctuations in the \( \hat{e}_2 \) direction, along the parallel and perpendicular components of the scattering vector \( \vec{q} \), must be examined. Nematic fluctuations whose motion has a component along the direction defined by \( \hat{e}_2 \) are clearly those fluctuations occurring *out* of the scattering plane (i.e. along the z-axis). Mathematically, let \([\delta n(x,y)]\) denote the nematic distortion directed along \( \hat{e}_2 \) (i.e. \( \hat{z} \)). Thus, \((\nabla \times \hat{n})\) will lie in the scattering plane, with components along the x- and y-axes. The resulting deformations can be summarized as:

\[
\begin{align*}
\delta \hat{n} &= \delta n(0,0,1), & \nabla \times \hat{n} &= \left( (\partial \delta n/\partial y), (\partial \delta n/\partial x), 0 \right), \\
\nabla \cdot \hat{n} &= 0 & \rightarrow & \text{splay component}, \\
\hat{n} \cdot (\nabla \times \hat{n}) &= -\frac{\partial \delta n}{\partial y} & \rightarrow & \text{twist component}, \\
\hat{n} \times (\nabla \times \hat{n}) &= -\frac{\partial \delta n}{\partial x} & \rightarrow & \text{bend component}.
\end{align*}
\]

Eq. D. 3

Since, by definition, \( q_\perp \) is perpendicular to the nematic director, out-of-plane motion along \( q_\perp \) will correspond to a twist deformation of the nematic director; recall that the twist deformation corresponds, mathematically, to the formulation: \( \vec{q} \) parallel to the direction of \((\nabla \times \hat{n})\) [i.e. \( \partial \delta n / \partial y \)]. On the other hand, out-of-plane motion along a direction parallel to the nematic director (i.e. \( q_\parallel \)) will correspond to a bend deformation; such a distortion corresponds, mathematically, to the formulation: \( \vec{q} \) perpendicular to the direction of \((\nabla \times \hat{n})\) [i.e. \( \partial \delta n / \partial x \)]. These distortions are perhaps better understood by the depiction below:
Bend and Twist Deformations Occurring for Fluctuations along $\hat{e}_2$

fluctuations with a component in the direction of $\hat{e}_2$, will undergo a **BEND** deformation along the $q_\parallel$ component of the scattering vector.

fluctuations with a component in the direction of $\hat{e}_2$, will undergo a **TWIST** deformation along the $q_\perp$ component of the scattering vector.

*Figure D – 3: Twist and Bend Deformations Occurring for Nematic Director Distortions along $\hat{e}_2$*
• **Motion associated with \( \hat{e}_i \):**

Nematic fluctuations whose motion has a component along the
direction defined by \( \hat{e}_i \) are clearly those fluctuations occurring *in* the scattering
plane, specifically along the (-y)-axis. Mathematically, let \( \delta n(x,y) \) denote the
nematic distortion directed along \( \hat{e}_i \) (i.e. along -\( \hat{y} \)). Thus, \( (\nabla \times \hat{n}) \) will project
out of the scattering plane, directed along the z-axis. The resulting
deformations can be summarized as:

\[
\delta \hat{n} = \delta n(0,1,0), \quad \nabla \times \hat{n} = (0,0,\left(\partial \delta n/\partial x\right))
\]

\[
\nabla \cdot \hat{n} = \frac{\partial \delta n}{\partial y} \quad \rightarrow \text{splay component},
\]

\[
\hat{n} \cdot (\nabla \times \hat{n}) = 0 \quad \rightarrow \text{twist component},
\]

\[
\hat{n} \times (\nabla \times \hat{n}) = \frac{\partial \delta n}{\partial x} \quad \rightarrow \text{bend component}.
\]

**Eq. D. 4**

This change in fluctuation direction significantly alters the resulting
deformation possibilities. Since \( q_\perp \) is perpendicular to the nematic director,
in-plane motion along \( q_\perp \) will correspond to a splay deformation of the
nematic director; recall that the splay deformation corresponds,
mathematically, to the formulation: \( (\nabla \cdot \hat{n}) \neq 0 \) [i.e. \( \partial \delta n/\partial y \)]. On the other
hand, similar to the discussion concerning fluctuations along \( \hat{e}_i \), in-plane
motion along a direction parallel to the nematic director (i.e. \( q_\parallel \)) will once
again correspond to a bend deformation since \( \bar{q} \) is directed perpendicular to
the direction of \( (\nabla \times \hat{n}) \) [i.e. \( \partial \delta n/\partial x \)]. These distortions are illustrated below:
Bend and Splay Deformations Occurring for Fluctuations along $\hat{e}_1$

fluctuations with a component in the direction of $\hat{e}_1$, will undergo a **BEND** deformation along the $q_s$ component of the scattering vector

fluctuations with a component in the direction of $\hat{e}_1$, will undergo a **SPLAY** deformation along the $q_s$ component of the scattering vector

**Figure D – 4**: Splay and Bend Deformations Occurring for Nematic Director Distortions along $\hat{e}_1$
In summary, a bend deformation of the nematic director occurs for fluctuations both in and out of the scattering plane. For splay distortions, however, the nematic fluctuations must occur in the scattering plane while twist distortions occur only for nematic fluctuations out of the scattering plane. (Note that twist deformations can occur for director distortions in the scattering plane, but the associated momentum transfer will be out of the scattering plane and therefore not observed.) Thus, by explicitly defining two orthogonal unit vectors, one in the scattering plane (i.e. $\hat{e}_1$) and one perpendicular to the scattering plane (i.e. $\hat{e}_2$), the nematic deformations are completely characterized along these two directions: $\hat{e}_1$ corresponds to a periodic distortion which is a mixture of pure splay and bend, while $\hat{e}_2$ describes a periodic distortion which is a mixture of pure twist and bend.
References


Chapter 1


Chapter 2


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Chapter 3


Chapter 4


Chapter 5


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Appendices
