



Freedericksz transitions in nematic liquid crystal
by Phillip Alexander Himmer

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in
Physics

Montana State University

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Abstract:

Liquid crystal macromolecules have many potential uses in various devices such as displays. These types of applications require liquid crystals with specific elastic constants in order to work effectively. The Freedericksz transition is one method of measuring these constants. In this experiment the Freedericksz transition for the bend geometry is studied in order to obtain the bend and splay elastic constants. Using the silane agent DMOAP a perpendicular orientation of the molecules was obtained at the cell boundaries. The gap thickness was measured using the He-Ne back reflection technique. The magnetic susceptibility for this particular liquid crystal was never measured and measuring it was not possible with the available equipment. Therefore a value which agreed within an order of magnitude of published values was used. This limits the accuracy of the fitted constants to an order of magnitude also. These constants were found to be 1.64×10^{-11} for K₃₃ and 8.64×10^{-12} for K₁₁

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APPROVAL

of a thesis submitted by

Phillip Alexander Himmer

This thesis has been read by each member of the thesis committee and has been found to be satisfactory regarding content, English usage, format, citations, bibliographic style, and consistency and is ready for submission to the College of Graduate Studies.

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ABSTRACT

Liquid crystal macromolecules have many potential uses in various devices such as displays. These types of applications require liquid crystals with specific elastic constants in order to work effectively. The Freedericksz transition is one method of measuring these constants. In this experiment the Freedericksz transition for the bend geometry is studied in order to obtain the bend and splay elastic constants. Using the silane agent DMOAP a perpendicular orientation of the molecules was obtained at the cell boundaries. The gap thickness was measured using the He-Ne back reflection technique. The magnetic susceptibility for this particular liquid crystal was never measured and measuring it was not possible with the available equipment. Therefore a value which agreed within an order of magnitude of published values was used. This limits the accuracy of the fitted constants to an order of magnitude also. These constants were found to be 1.64×10^{-11} for K_{33} and 8.64×10^{-12} for K_{11} .

CHAPTER 1

INTRODUCTION

Liquid crystals are macromolecules that have varying degrees of orientational and positional order. There are three basic phases that liquid crystals can form: isotropic, nematic, and smectic. The isotropic phase is the least ordered of the three with random orientational and positional order. The nematic phase has orientational order such that the molecules are pointing in the same direction on the average but it has no positional order. In the smectic phase there is positional as well as orientational order.

The physics of liquid crystals was initially discussed in 1933 by various scientists. The Fredericksz transition, in which an external field distorts the liquid crystal molecules from some prearranged geometry, was noticed at this time but little importance was attached to this phenomenon. Also during this time Oseen¹ presented a paper detailing a theory of liquid crystal elastic interactions. In 1958 a paper by Frank² expanded upon this original theory. The resulting formulation for the free energy is known as the Oseen-Frank free energy. The Fredericksz transition has since been done for, in the language of the theory, the bend, splay, and twist cases (Figure 1). Most of the work has been done with nematic liquid crystals since they are the simplest to describe and the data are easier to interpret. The theory assumes that the liquid crystal molecules are uniaxial which is a good assumption for most nematic liquid

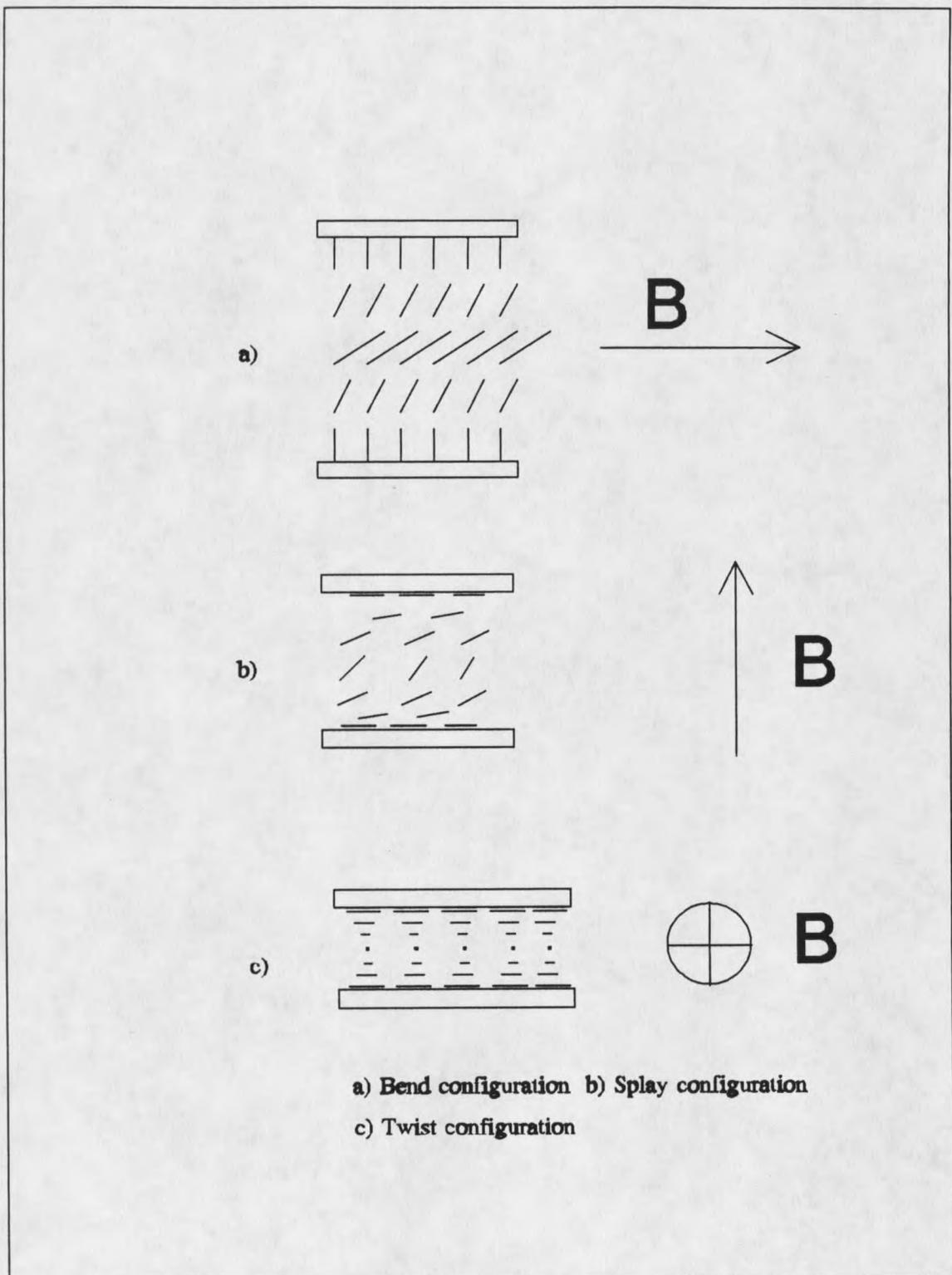


Figure 1. Alignment geometries.

crystals. In this thesis the nematic liquid crystal E-7, a type of cyanobiphenyl liquid crystal, made by BDH is studied with the goal of determining the splay elastic constant K_{11} and the bend elastic constant K_{33} . E-7 has one phase transition between isotropic and nematic at 60°C . The principal use for this material is in twisted nematic cells, such as would be used for watch displays.

CHAPTER 2

SAMPLE PREPARATION

In order to measure the bend and splay elastic constants by means of the Freedericksz effect I used a magnetic field perpendicular to the direction of the aligned liquid crystals (Figure 2). This gives the bend geometry as seen in Figure 1.

To make a sample, two pieces of optically flat glass, obtained from Edmunds Scientific, were used to form a gap that the liquid crystal will be inserted into. This glass was first cleaned with a 1M potassium hydroxide solution for approximately one hour in a water bath at 50° C. Then the glass was put into a solution of one part concentrated nitric acid, one part concentrated sulfuric acid, and two parts distilled water and allowed to soak for approximately one hour in a 60° C water bath. To remove any residue the glass was then put in isopropanol alcohol, soaking for at least 4 hours. The cleaning procedure called for a hot vapor of isopropanol condensing but the apparatus needed to do this was not available. Between each step of the procedure the glass was rinsed with distilled water³.

To align the liquid crystal the surface of the glass was treated with a silane bonding agent called N,N-dimethyl-N-octadecyl-3-aminopropyltrimethoxysilyl chloride (DMOAP) made by Dow Chemical. This silane agent adheres to the glass surface with a long trailing end pointing perpendicular to the glass surface. The cleaned glass was put in

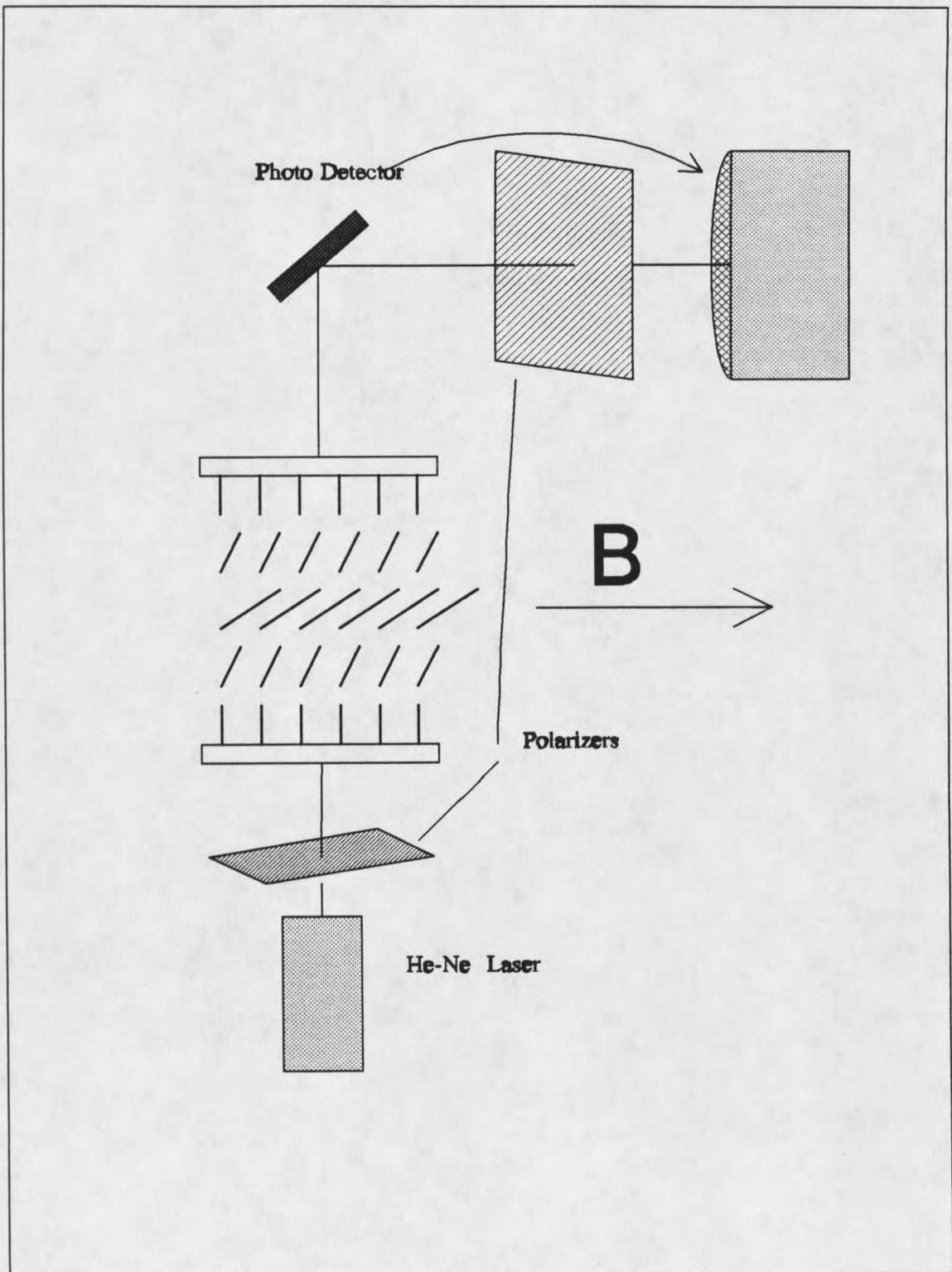


Figure 2. Experimental setup

a 0.1% (by volume) solution of DMOAP and distilled water and agitated for five minutes in an ultrasonic cleaner. The glass was then rinsed with distilled water and dried with nitrogen gas. To cure the coating the glass flats were heated under nitrogen for one hour at 110° C.⁴ Initially, alignment of the liquid crystal was attempted by rubbing the glass surfaces in two perpendicular directions with diamond paste but poor data resulted⁵. This could be due to the rubbing or to the fact that the glass flats used were microscope slides and not the optically flat glass finally used.

The glass flats were held by nylon set screws in aluminum plates separated by eight beryllium copper springs under compression (See Figure 3). The thickness was adjusted by tightening or loosening four brass screws which run through the center of four of the springs.

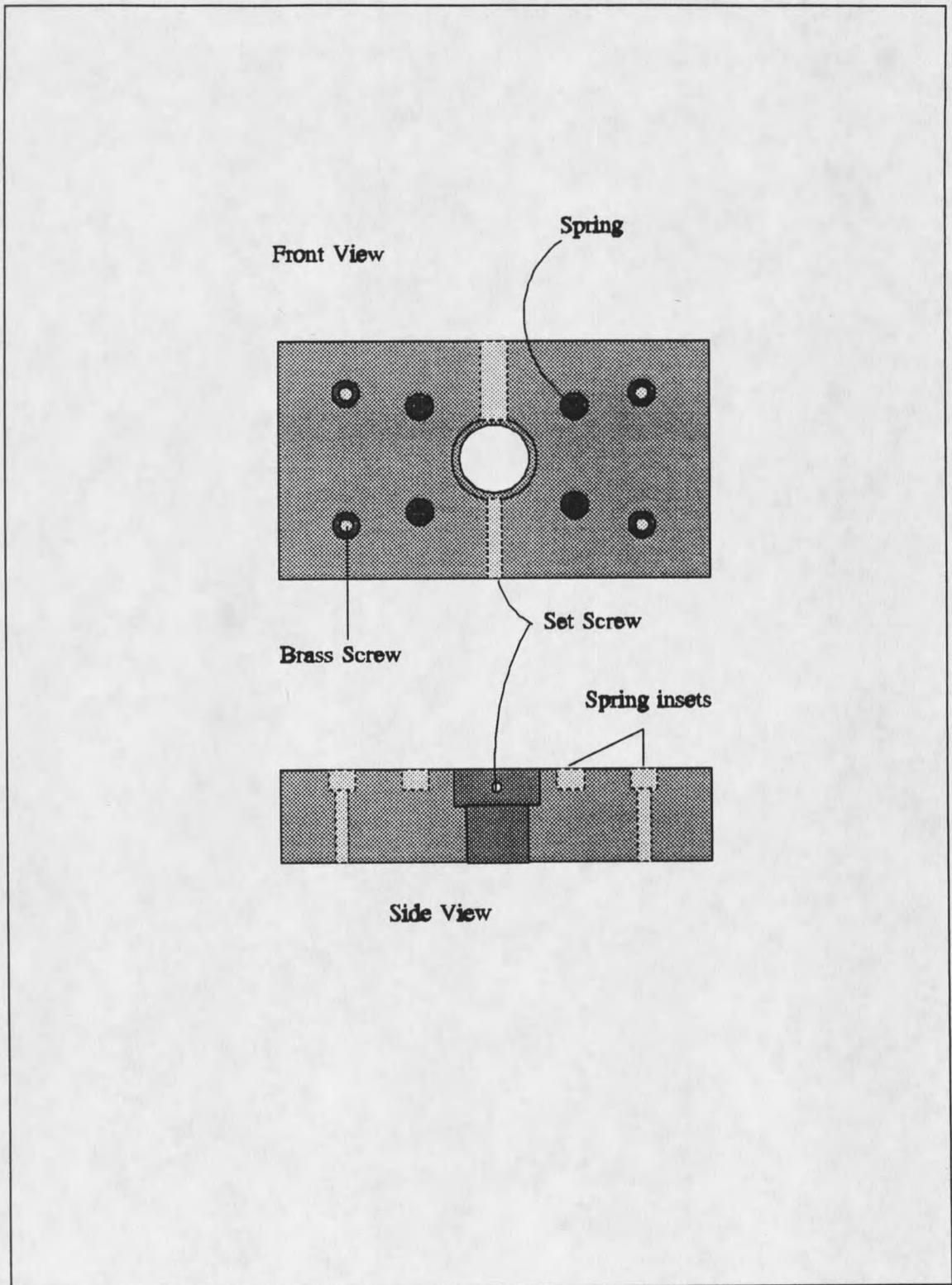


Figure 3. Sample holder

CHAPTER 3

EXPERIMENTAL TECHNIQUES

He-Ne Back Reflection Technique

To align the glass flats to a desired thickness and to set them parallel a He-Ne back reflection technique was used⁶. The cell was illuminated with He-Ne laser light that was passed through a pinhole, then collimated with a 250 mm focal length lens (See Figure 4). Four spots appeared from back reflections; one from each surface of the two glass flats. To see these spots clearly, two mirrors were used to reflect the beam allowing the small deviation, due to the fact that the surfaces of a flat were not exactly parallel, to separate the reflections. The two spots that represent the inside surfaces of the two glass flats could be found through trial and error. The interference pattern representing the gap changed more slowly than other interference patterns such as that from the outside surface of one flat and the inside surface of the other flat, because the gap was thinner. The cell was attached to an Aerotech 301R rotation table in order to accurately rotate the sample. As the cell was rotated through an angle one could observe interference fringes moving outward from the center of the combined spot. Starting at a known angle, typically three degrees, the fringes could be counted up to another known angle. From the equation

$$2d \cos(\theta) = (m)\lambda, \quad (2.1)$$

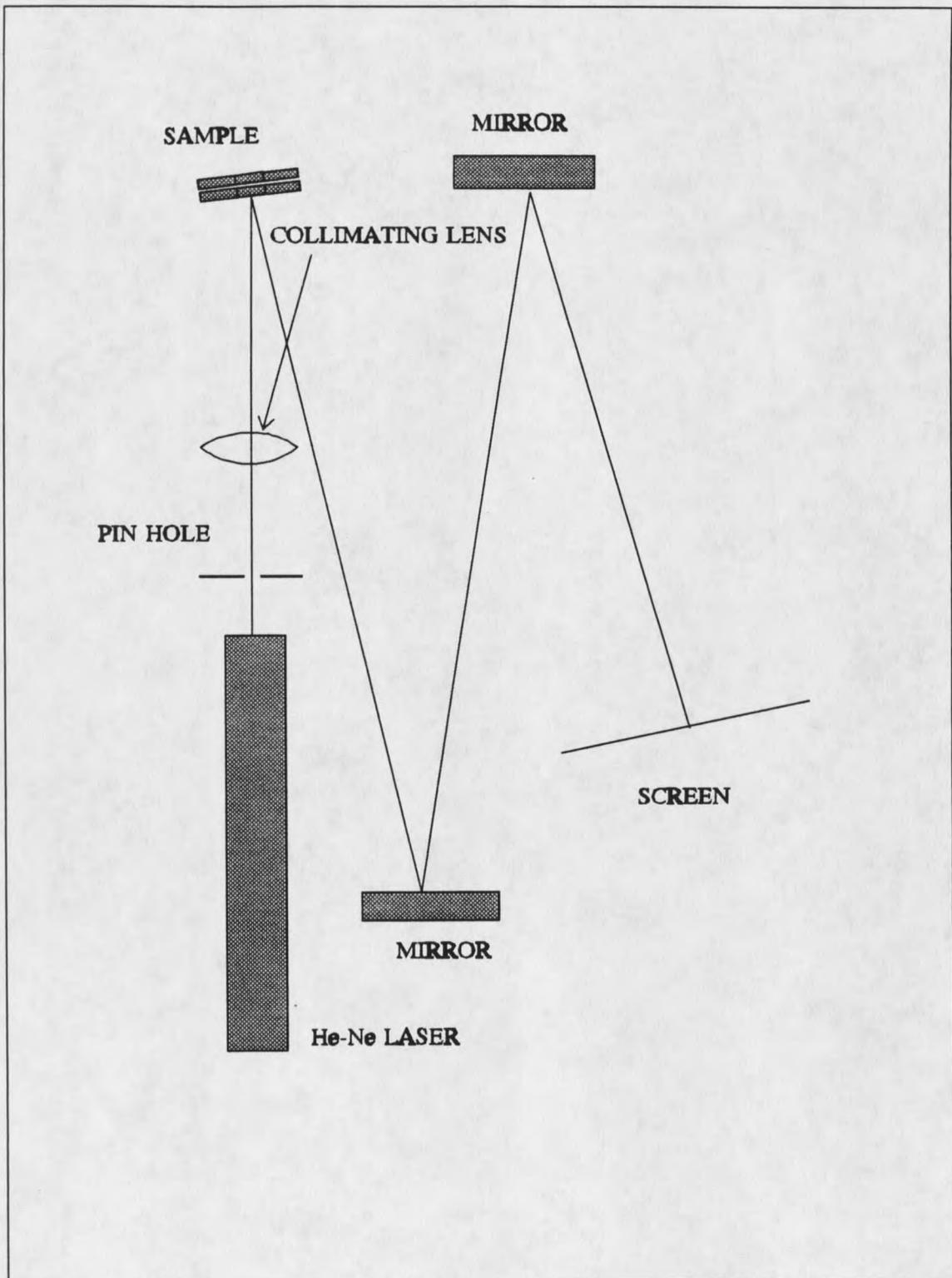


Figure 4. He-Ne back reflection apparatus

the number of fringes that one saw as the table was rotated from θ_1 to θ_2 , allowed the thickness of the sample to be calculated by taking the difference of the order number at the two different angles. To align $\theta=0$, the back reflection of the fixed plate was lined up onto the pinhole. Ideally one would see spots as with a Fabry-Perot interferometer but $\frac{1}{4}\lambda$ glass flats have too much variation to give spots, so an interference pattern was seen. This could be remedied by using better optical flats.

While inserting the liquid crystal into the gap of the cell, the liquid crystal should ideally be in the isotropic phase so that it can move more freely.³ I twice attempted to heat the liquid crystal into the isotropic phase after the liquid crystal was in the cavity, and then let it cool to room temperature, but poor data resulted each time. I suspect that it was due to a interaction between the liquid crystal and the DMOAP, or perhaps the sample holder became distorted. Therefore the liquid crystal was left in the room temperature nematic phase when it was inserted and was kept at room temperature for the duration of the experiment. After a day it appeared that the samples settled down so that the data were reproducible. In the future it would be nice to be able to insert the liquid crystal in the isotropic phase to reduce the time needed for the molecules to orient themselves and to insure better anchoring.

Data Acquisition

The data were taken with a Hewlett Packard 34401A multimeter and a Keithley 195A multimeter connected via GPIB ports to a Zenith Data Systems 286 computer.

I distinguish between the HP and Keithley because the software that read in the data assumed that the Keithley was connected to a Varian V-FR 2703 magnet with 5" poles and when the voltage at the Keithley was 15 volts the data file was closed and the program terminated. To take data, the cell was inserted into the holder, positioning it between the magnet poles, and the holder was adjusted so the beam entered the photodiode at the center. To keep the intensity below the saturation level of the photocell, two polarizers were placed on the laser and turned until the intensity was low enough. To polarize the beam 45 degrees from the magnetic field axis the two polarizers on the laser were rotated as a unit until the top polarizer was oriented at 45° with respect to the direction of the magnetic field. After the light passed through the cell, the polarizer in front of the photocell was turned so as to minimize the intensity. Thus the oscillations began from a minimum⁷.

The data was stored in the computer as an ASCII file. The program accepted twenty readings from the multimeters and averaged them to give a data point. This was done to help reduce random fluctuations in the voltages representing the magnetic field and the intensity. The number of data points taken ranged from 763 to 788 for a 50-minute scan. The variation occurred because the field sweep percent dial could not be started exactly at zero each time. The program used the voltage from the sweep circuit which varied from 0 to 15 volts to obtain the magnetic field, given the center field and the range of the field (Appendix A).

CHAPTER 4

THEORY

Oseen Frank Free Energy

The Oseen Frank free energy for liquid crystals is given by the expression

$$F_f = \frac{1}{2} \int [K_{11} (\nabla \cdot \hat{n})^2 + K_{22} (\hat{n} \cdot \nabla \times \hat{n})^2 + K_{33} (\hat{n} \times \nabla \times \hat{n})^2] d\tau \quad (3.1)$$

where \hat{n} is the direction of the director. The director is the average direction of the liquid crystal molecules. When the liquid crystal is put in a magnetic field an additional term given by

$$F_m = -\frac{1}{2} \frac{\Delta\chi}{\mu_o} \int (B \cdot \hat{n})^2 d\tau \quad (3.2)$$

is introduced⁸. For the magnetic field in the \hat{x} direction and the liquid crystal aligned perpendicular to the glass with the director \hat{n} pointed in the $+\hat{z}$ direction, \hat{n} will have the form $\hat{n} = \sin(\theta)\hat{x} + \cos(\theta)\hat{y}$. The free energy can then be written as

$$F_f + F_m = AK_{33} \int_0^{\frac{z}{d}} [(1 - \kappa) \sin^2(\theta) \left(\frac{\partial\theta}{\partial z}\right)^2 - \frac{\Delta\chi B^2}{\mu_o K_{33}} \sin^2(\theta)] dz \quad (3.3)$$

where

$$\kappa = 1 - \frac{K_{11}}{K_{33}}, \quad A = \text{Area of the sample, } d = \text{sample thickness,}$$

and θ is the angle between the director and the \hat{z} axis. Now it is necessary to find the function $\theta(z)$ that minimizes the free energy. This is done with variational calculus which says that the function $\theta(z)$ must satisfy the differential equation

$$\frac{d}{dz} \left(\frac{\partial \phi}{\partial \theta} \right) - \frac{\partial \phi}{\partial \theta} = 0 \quad (3.4)$$

where ϕ is the integrand of the integral representing the free energy. After making the substitution $U = \frac{\partial \theta}{\partial z}$ the resulting differential equation becomes separable.

Using the limits that θ goes from θ to θ_m and U goes from U to 0 one obtains

$$\frac{\partial \theta}{\partial z} = \left(\frac{\Delta \chi B^2}{\mu_0 K_{33} \kappa} \right)^{\frac{1}{2}} \left(1 - \frac{(1 - \kappa \sin^2(\theta_m))}{(1 - \kappa \sin^2(\theta))} \right)^{\frac{1}{2}} \quad (3.5)$$

Separating variables and integrating gives

$$\int_{\theta}^{\theta_m} \frac{(1 - \kappa \sin^2(\theta))^{\frac{1}{2}} d\theta}{(\sin^2(\theta_m) - \sin^2(\theta))^{\frac{1}{2}}} = \left(\frac{\Delta \chi B^2}{\mu_0 K_{33}} \right)^{\frac{1}{2}} \int_z^{\frac{d}{2}} dz. \quad (3.6)$$

Setting the lower limits on the integral to 0 gives an expression relating the magnetic field to the maximum angle θ_m . This expression can subsequently be used to find the

magnetic field for a given phase shift. To relate equation 3.6 to the observed phase shift an expression for the index of refraction vs. angle of the director is needed.

Index of Refraction Calculation

Using Maxwell's equations an expression for the index of refraction can be found.

$$\nabla \times \vec{E} = \mu_o \frac{\partial \vec{H}}{\partial t} \quad \nabla \times \vec{H} = \epsilon_o \frac{\partial}{\partial t} (\vec{\epsilon}_r \cdot \vec{E}) \quad (3.7)$$

where $\vec{\epsilon}_r = \begin{pmatrix} \epsilon_{ro} & 0 & 0 \\ 0 & \epsilon_{ro} & 0 \\ 0 & 0 & \epsilon_{re} \end{pmatrix}$, such that ϵ_{ro} is the dielectric constant perpendicular

to the director and ϵ_{re} is the dielectric constant along the director. Since the externally applied magnetic field is in the \hat{x} direction the extraordinary axis of the liquid crystal will be in the $\hat{x} \hat{z}$ plane. Assuming the laser beam is propagating in the \hat{z} direction the condition at the boundary is that the \hat{z} components of the displacement field at $z=0$ and at $z=d$ are zero. This comes from the assumption that the electric field is of the form

$$\vec{E} = \vec{E}_{eo} e^{i(kz - \omega t)} \quad (3.8)$$

so that the only spatial dependence is in the \hat{z} direction. Writing the displacement vector in terms of the \hat{x}' and \hat{z}' coordinates gives (See Figure 5)

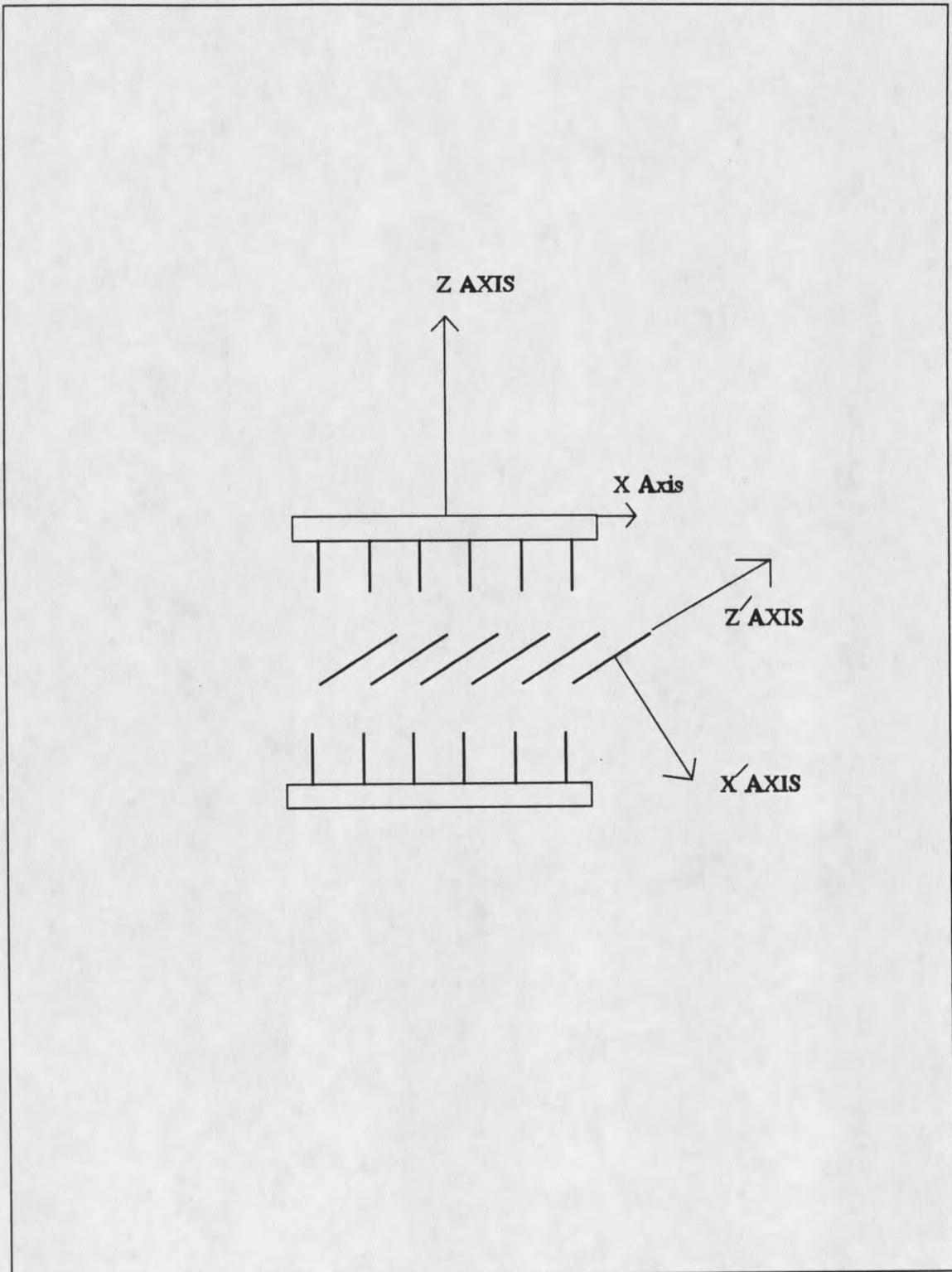


Figure 5. Coordinates for index of refraction calculation

$$\vec{\epsilon}_r \cdot \vec{E}_{eo} = \epsilon_{re} E_{eo} \sin(\theta - \alpha) \hat{z}' + \epsilon_{ro} E_{eo} \cos(\theta - \alpha) \hat{x}' \quad (3.9)$$

The boundary condition $\vec{D}_z = 0$ gives the relation

$$\tan(\theta - \alpha) = \frac{\epsilon_{ro}}{\epsilon_{re}} \tan(\theta) \quad (3.10)$$

After a bit of work the expression

$$\vec{\epsilon}_r \cdot \vec{E}_{eo} = \frac{E_{eo} n_o^2 n_e^2}{(n_e^4 \cos^2(\theta) + n_o^4 \sin^2(\theta))} \hat{x} \quad (3.11)$$

is found where n_e and n_o are the extraordinary and ordinary indices of refraction respectively. Putting equation 3.8 into the first of Maxwell's equations and then substituting the result into the second leads to the result

$$\vec{\epsilon}_r \cdot \vec{E}_{eo} = n^2(z) E_{eo} \cos(\alpha) \hat{x} \quad (3.12)$$

where $n(z)$ is the index of refraction at some distance z through the thickness of the sample. After rewriting $\cos(\alpha)$ in terms of θ the result

$$n(z) = \frac{n_e n_o}{(n_o^2 \sin^2(\theta(z)) + n_e^2 \cos^2(\theta(z)))^{\frac{1}{2}}} \quad (3.13)$$

is found. Taking the difference in the optical path length between the ordinary and extraordinary axis and integrating over half the thickness of the sample gives the expression³

$$\delta = \left(\frac{4\pi}{\lambda} \right) \int_0^{\frac{d}{2}} [n(z) - n_o] dz \quad (3.14)$$

Using equation 3.5 you can replace the integral over z with a integral over θ . This can then be numerically integrated to give the phase shift as a function of the magnetic field.

Intensity Modulation

Once the phase shift is known the intensity can be calculated by letting

$$\vec{E} = \frac{E_o}{\sqrt{2}} (\hat{I}_f e^{-i\omega t} + \hat{I}_s e^{-i\omega t}) \quad \text{at } z=0 \quad (3.15)$$

so that after passing through the sample the electric field along the \hat{I}_f axis undergoes a phase change of φ_f while the field along the \hat{I}_s undergoes a phase shift of φ_s . Letting $\varphi_f = \varphi_s + \delta$ and changing the axis to the \hat{x} and \hat{y} axis as defined in Figure 6 gives the equation

$$\vec{E} = \frac{E_o}{2} e^{-i(\omega t + \varphi)} (\hat{x}(1 - e^{-i\delta}) + \hat{y}(1 + e^{-i\delta})) \quad (3.16)$$

After passing through the polarizer which is in the \hat{x} direction and then squaring the complex conjugate the expression

$$I = \frac{E_o^2}{4} \cos^2(\omega t + \varphi_s) (1 - 2\cos(\delta) + \cos(\delta)^2) \quad (3.17)$$

