A LIGHT SCATTERING STUDY OF CORRELATIONS IN MOLECULAR ORIENTATION OF A NEMATIC LIQUID CRYSTAL

A Dissertation

Presented to

the Faculty of the Department of Electrical Engineering University of Houston

In Partial Fulfillment

of the Requirements for the Degree Doctor of Philosophy in Electrical Engineering

by

John James Nemec December, 1970

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ABSTRACT

Certain substances exhibit mesophases between the solid and isotropic liquid phases. In these mesophases the substance has anisotropic properties of the solid while simultaneously displaying fluid properties of a liquid. Such substances are called liquid crystals. The mesophases are of three types: smectic, nematic, and cholesteric, all of which appear in a variety of textures, depending on the environment and history of the substance. The fundamental difference between the mesophases is the type of ordered arrangement of the cigarshaped molecules. Optically these substances behave as positive uniaxial crystals when in the smectic or nematic mesophase.

Thermal agitation causes the molecules to fluctuate about their equilibrium positions, and since the molecules are asymmetric, fluctuations of twist, bend, and splay are present. These describe fluctuations in orientation of the molecules in a volume element with respect to the local molecular orientation direction. Splay is a fan-like expansion, the spread turning away from the equilibrium orientation axis.

Molecular motion of nematic para azoxyanisole is examined through light scattering techniques. Three correlation coefficients, a_1 , a_2 , and a_3 , corresponding to splay, twist, and bend fluctuations, respectively, are measured experimentally. They are found to be: $a_1 = 4.7 \times 10^{-6}$, $a_2 = 8.2 \times 10^{-6}$, and $a_3 = 2.32 \times 10^{-5} \text{ cm}^2/\text{xec.}$ at 125°C . The temperature variation of these parameters is determined throughout the nematic range. All three coefficients are found to increase, in general, with increasing temperature. The coefficient a_1 diverges at the nematic-isotropic transition temperature, T_m , according to the relation $A|T/T_m - 1|^{\gamma}$ where A is empirically found to be 2.5 x $10^{-6} \text{ cm}^2/\text{sec}$ and γ is -0.17. It is found that a_2 also diverges but at a temperature, T_o , approximately four degrees below T_m . This divergence follows $A|T/T_o - 1|^{\gamma}$ where below T_o , $A = 1.5 \times 10^{-6} \text{ cm}^2/\text{sec}$ and $\gamma = -0.44$, while above T_o , $A = 5.5 \times 10^{-6} \text{ cm}^2/\text{sec}$ and $\gamma = -0.1$. The coefficient a_3 is observed to increase at a rate of approximately 1.4 $\times 10^{-5} \text{ cm}^2/\text{sec}/^{\circ}\text{C}$.

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CHAPTER I

INTRODUCTION

Matter is generally found in the three states: solid. liquid, and gas, each having certain properties characteristic of only that particular phase. Solids, for example, are rigid, and may possess anisotropic mechanical and electromagnetic properties, a partial consequence of their three dimensional molecular order. Simple liquids and gases, on the other hand, are easily deformed and have isotropic mechanical and electromagnetic properties, a partial consequence of the random nature of their molecular position. Application of heat to a solid generally results in direct phase transitions, at specific temperatures, from solid to liquid, liquid to gas. There are, however, several exceptions to these laws. Three of these exceptions, which are the object of much presentday research, are the superfluidity phenomenon, the plasma state, and the liquid crystal phenomenon. The liquid crystal phenomenon has received comparatively less attention than the others.

Unlike usual substances, liquid crystals do not pass directly from solid to isotropic liquid and back to solid, but rather they exhibit mesophases between the solid and isotropic liquid states. The term mesophase comes from the Greek mesos meaning middle. In these mesophases, the liquid crystal

displays a definite structure as in the solid phase, but it has the rheologic properties of a fluid. More explicitly, the mechanical and electromagnetic properties of the mesophase are similar to those of a solid, i.e., the substance is anisotropic, while the substance is simultaneously fluid having a consistency between that of water and honey. It is these properties which make liquid crystals fruitful subjects of study for increasing our understanding of nature.

The many exotic properties of liquid crystals and their possible applications are numerous; however, only a few will be mentioned here. Some liquid crystals scatter large amounts of light when electric fields are applied.¹ Such properties are used in devices which electronically control light, and in optical display systems.²

When exposed to white light, certain liquid crystals scattered a preferred color dependent on their temperature. These properties have been successfully used in thermal mapping by associating the color of light scattered from an area with the local temperature.³

There are many other applications, but the lack of physical and optical data on a large number of known substances which exhibit mesophases has precluded easy selection of a substance for some particular application. The liquid crystal state is not rare as it occurs in approximately one of every two hundred organic compounds.⁴ Much information

about liquid crystals can be gained through the study of light scattered by these substances. It is this approach that will be taken in this study. There are, of course, other methods. The extent of ordering, expecially for liquid crystals in the nematic mesophase, is not sufficient to allow much significant information to be obtained through X-Ray diffraction studies, although some information has been obtained for liquid crystals in the solid and smectic states.⁵ Ultraviolet and infrared absorption studies were made, but abandoned in the early years due to the lack of precision equipment required to make such studies.⁶ It is probable that measurements using ultraviolet and infrared will be undertaken now that there is renewed worldwide interest in liquid crystals. Recently, NMR has been employed in the investigation of the internal molecular structure.⁷

The discovery of liquid crystals is credited to both Reinitzer and Lehmann working independently in 1888.⁸ They noted the existence of turbidity of a substance at temperatures just above the melting point. The turbidity, however, cleared at some higher temperature. Many discounted these first observations and attributed the strange behavior to impurities within the sample. After it was established that a new discovery had been made, other observers began the study of these compounds, and by the early 1900's as many as 250 substances exhibiting the liquid crystal behavior were discovered.

In 1922, Friedel succeeded in identifying the three mesophases characteristic of liquid crystal compounds.⁹

Following Friedel's mesophase identification, investigations turned to the classifications of the various textures of the mesophases. Different textures are observed under a microscope for different mechanical environments and preparations of the samples. The different textures are far too numerous to list; however, it should be noted that examination of these textures does provide enlightenment concerning the quasi-crystaline structures of liquid crystals.

After this period of great interest, the activity in this area of study declined, but was renewed at times. One effort resulted in an expression for the free energy density of a liquid crystal in terms of the molecular orientation. The analysis was done first by Oseen, then later critically analyzed by Frank.¹⁰ The work of these two individuals also categorized the types of curvature which the molecular orientation in a liquid crystal may experience: bend, twist, and splay.

Prior work is well summarized in the book by Gray,¹¹ published in 1962, and in the review articles by Brown¹² and Chistyakov¹³ published in 1957 and 1967, respectively.

Most of the early examinations of liquid crystals were made optically using a microscope, then later more advanced techniques using light scattering were employed. In 1948,

Chatelain made the first observations of angular dependence of the scattered light intensity and related his results to a theoretical analysis based on the "swarm theory".¹⁴ Work similar to that done by Chatelain was performed in the 1960's by Stein. Like Chatelain, Stein considered the angular dependence of the intensity of the scattered light and determined light scattering was produced primarily by fluctuations in molecular orientation.¹⁵

There is more information obtainable from the scattered light, however. Measurement techniques using light scattering have been developed in the study of liquids and solids, and among the most powerful of these is the analysis of the spectrum of the scattered light. Detailed investigation is usually made of a spectrally unshifted peak (Rayleigh lines) and two symmetrically shifted peaks (Brillouin lines) of scattered light of both polarized and depolarized components, and relating the findings to physical constants and nature of the scatterer. Significant is the technique advanced by Benedek and co-workers, which employs homodyne detection utilizing the square law properties of photoelectron emision in the determination of the fine structure of the Rayleigh peak.¹⁶ It is not difficult to see how such investigative procedures could be used in the study of liquid crystals, especially since liquid crystals yield a spectral distribution of scattered light similar to that of liquids.

These techniques were employed by a group of French researchers who, in 1969, measured the angular dependence of the width of the Rayleigh peak of the light scattered from nematic para azoxyanisole.¹⁷ A pure Lorentzian spectral density was observed whose bandwidth depended in a unique way on the scattering angle. Interpretation of such measurements is indeed difficult, however. The chief drawback is the complex anisotropic properties of liquid crystals, which are not, in general, homogeneous. A tensor character must be assigned to the electric susceptibility to account for these properties, and then a direct relation must be provided connecting the susceptibility to the orientation of the liquid crystal molecules. Thermally excited molecular orientation fluctuations can, in this way, be related to the spectral density of the anode current fluctuations of the light detecting photomultiplier tube. An analysis of this kind requires full examination of the equations of the motion of the liquid crystal and the mechanism of the light scattering, light detecting system.

The breadth of such an analysis encompasses two unique areas; moreover, each area requires discussion to considerable depth. In this thesis, separate chapters will be devoted to the following two subjects: dynamics of the thermally excited molecular orientation fluctuations, Chapter II; and, the theory of light scattering, Chapter III. These two

chapters provide the foundation for the interpretation of the results of our experimental investigation.

In Chapter II, the equations of motion of nematic liquid crystals are presented. They are then solved, using approximations which are motivated by particular experimental constraints, for the correlation in the director, a quantity describing the instantaneous, local molecular orientation. This correlation depends directly on certain viscosity and elasticity parameters of the liquid crystal. Chapter III provides the connection between the spectral density of the photomultiplier anode current fluctuations and the correlations in the susceptibility fluctuations, taking into account the finite line width of the laser light source and the quantum characteristics of the photodetector. The results of these two lengthy analyses are drawn on in Chapter IV, where a direct connection is made between the theoretical formalism and the experiment. Here it is shown that the autocorrelation in one component of the director is directly related to the spectral density of the anode current fluctuations of the photomultiplier tube. Therefore, a means is established for the determination of the liquid crystal parameters from the experimental data.

The depth of the investigation may now be increased to the measurement of temperature dependence of the elastic moduli and principle viscosities of the liquid crystal.

Experimentally, this implies a repetition of the procedure at each temperature, but the interpretation of the data is again a formidable task, since the thermodynamic theory of liquid crystal is not easily formulated.

A theory of the temperature dependence of the elastic moduli of nematic liquid crystals, based on a statistical molecular theory, was proposed by Saupe in 1960.¹⁸ The theory predicts a unique temperature variation in these coefficients through the molecular volume and a molecular ordering parameter. Verification of the theory has been made through direct measurement of the elastic moduli as a function of temperature for a magnetically oriented crystal.¹⁹ A somewhat similar approach was taken by Helfrich in his investigation of certain viscosity coefficients; unfortunately, he limited his discussion of the model to a comparison with experimental results at one temperature.²⁰ Nevertheless, his theory does predict a unique temperature dependence for the coefficients. Some viscosity coefficients have been experimentally studied throughout the nematic range by direct measurement, but they are not directly related to those defined by Helfrich.²¹ Our measurements can provide a quantitative determination of the temperature dependence of two of Helfrich's viscosities with the aid of independent data on the elastic moduli. A discussion in Chapter VI comparing our experimental results to these theories completes this

report on this study of liquid crystals in the nematic state.

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CHAPTER II

LIQUID CRYSTALS

NATURE OF LIQUID CRYSTALS

It has been brought out in the introduction that liquid crystals have certain properties which make them profuse light scatterers. Before presenting the theory of light scattering from these substances and, most important, before an attempt is made to interpret the data, the nature of the liquid crystal mesophase must be examined in greater detail. The discussion will be restricted to two main topics: first, a general description of the liquid crystal state will serve to define terminology and explain the general characteristics of liquid crystals; second, since the experiment deals with the light scattering properties of liquid crystals, the optical properties will also be discussed along with the mechanics of the thermally excited fluctuations which cause light scattering.

A detailed description of the liquid crystal mesophase is far beyond the scope of this paper. There are, however, certain salient features which, when presented, can give a relatively clear picture of this complicated state of matter. Between the amorphous solid state and the isotropic liquid state of certain special substances, there exist three possible mesophases: smectic, nematic, and cholesteric. Which

mesophase the substance assumes depends upon: 1) the substance itself, (the substance may exhibit only one or two of these mesophases); 2) the temperature, past and present; and 3) the electromagnetic environment. The temperature history may affect the mesophase as shown in Figure 2.1.²² There is no known substance which exhibits both a cholesteric and nematic mesophase.²³

Each mesophase may also appear in a variety of textures depending mainly upon the surfaces with which the liquid crystal is in contact and again on the history of the substance. The nature of the bounding surface may sometimes strongly affect the appearance of the mesophase, while in other cases the effect may be extremely weak. The textures, as they are called, are named for their appearance under a microscope. There are many similarities between certain textures of different mesophases and because of this, confusion sometimes arises. Each mesophase also has optical properties which are characteristic of that mesophase. In general, liquid crystals behave optically as uniaxial crystals; however, biaxial behavior has been reported.²⁴

The molecules are long, thin, and essentially ellipsoidal in shape. Van der Waals forces largely control the way in which the molecules arrange themselves to give rise to a particular mesophase. The shape itself has little to do with the liquid crystal phenomenon, for there exist substances



FIGURE 2.1. Three Possible Sequences in the Change of State of Thermotropic Liquid Crystals. The Arrows Indicate the Permissible Transition Directions. Temperature Increases to the Right.

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with long, thin molecules which exhibit no mesophases, and conversely, there exist substances with disk-like molecules which do exhibit types of mesophases.²⁵ In each mesophase, there is no regular three dimensional order as in a crystal, with the exception of the cholesteric mesophase. The smectic mesophase is characterized by side-by-side alignment of the molecules as shown in Figure 2.2. The molecular groups aligned side-by-side form layers (horizontal in the figure), but there is little correlation in the position of the molecules from layer to layer (vertically in the figure). There is quasi-crystalization in two dimensions and the adjacent layers may easily slide on one another. There are three textures associated with this mesophase and each texture has a markedly different appearance under a microscope. The nematic mesophase is characterized by end to end "attachment" of the molecules as shown in Figure 2.3. With reference to the figure's directions, there is correlation horizontally but little vertically and in the direction perpendicular to the page. There is quasi-crystalization in one dimension. The nematic mesophase has four textures associated with it. Lastly, the cholesteric mesophase is a special, but unique, variation of the nematic mesophase. This mesophase has a three dimensional order not found in any other texture of the other mesophases. Here the molecules are arranged end to end as in Figure 2.2 except successive planes (vertically in the figure) have



FIGURE 2.2. The Molecular Arrangement in the Smectic Mesophase. The Angle θ Characterizes Smectic Types

A, B, and C.



FIGURE 2.3. The Molecular Arrangement in the Nematic Mesophase.



FIGURE 2.4. The Twist in Successive Nematic-Like Planes of the Cholesteric Mesophase. their molecules rotated at some particular angle with respect to the plane of the page. This three dimensional structure is shown in Figure 2.4. This three dimensional order gives this particular texture high optical rotary power, and temperature dependent Bragg reflection properties. The cholesteric mesophase is not of interest here. For a more complete discussion, see the review by Chistyakov.

The ellipsoidal molecules of liquid crystals have the ability to be polarized by the action of an external electric field. The molecules appear to be symmetric with respect to the long axis of the molecule and the polarizability seems to share this symmetry. However, the axis of electric symmetry need not correspond to the axis of geometric symmetry of the molecule. This fact complicates the matter of relating the scattered light to the molecular motion. For simplicity in this discussion, it will be assumed that the geometric and electric symmetries coincide. The molecules are relatively large along the long axis of the molecule, thus any orienting force, such as an externally applied electric or magnetic field, can easily produce large torques on the molecule. The molecules can therefore be oriented by moderate electric or magnetic fields. When the molecules in a particular sample are all oriented in a preferred direction, the macroscopic polarizability is highly anisotropic, and this anisotropy exists even for optical frequencies. It is clear then, that

these optical properties along with the capability to change them through a change in molecular orientation by an external electromagnetic field make liquid crystals possible materials for use in electro-optic devices. Some of the properties of the liquid crystal which affect the motion of the molecules can be determined from the data obtained in this study.

The description of liquid crystals is exceedingly complicated, first, due to a lack of regular order in the molecular arrangement (a consideration making description of liquids difficult) and second, due to the additional degrees of freedom of the system introduced by considering the molecular structure. The development of a mathematical model which accounts for the character of liquid crystals has been the subject of research by those interested in mechanical analysis, and we draw on the results of these workers in arriving at equations of motion for an oriented nematic liquid crystal. These equations can then be solved for the autocorrelation in the molecular orientation. The development of the equations describing liquid crystals is far beyond the scope of this paper, and so , the major results of other authors will simply be quoted and used as a starting point for the following analysis.

Let us begin with a brief description of the basic deformations which a liquid crystal may experience. In addition to the behavior of a pure liquid, liquid crystals may

undergo changes in molecular orientation. These distortions, generally referred to as curvatures, fall into three classes: bend, twist, and splay.

Considering a unit vector d, which is parallel to the local molecular alignment, the curvature can be described by changes in d from the preferred orientation. For convenience, let the preferred direction be the x_3 direction. The curvature, as depicted in Figure 2.5, can then be described by six coefficients:²⁶

splay:
$$s_1 = \partial d_1 / \partial x_1$$
, $s_2 = \partial d_2 / \partial x_2$
twist: $t_1 = -\partial d_2 / \partial x_1$, $t_2 = \partial d_1 / \partial x_2$ (2.1)
bend: $b_1 = \partial d_1 / \partial x_3$, $b_2 = \partial d_2 / \partial x_3$.

It was postulated by Oseen, through a generalization of Hooke's law, that the free energy density must be a quadratic function of these curvatures.²⁷ Reducing the general form, through symmetry arguments, Oseen and Frank found the free energy density for nematic liquid crystals to be expressible in terms of three fundamental elastic moduli, each associated with a particular curvature: k_{11} , splay; k_{22} , twist; and k_{33} , bend. In an arbitrary coordinate system, for nematic liquid crystals, the Oseen-Frank equation reads:

 $2\rho F = k_{22} d_{i,j} d_{i,j} + (k_{11} - k_{22} - k_{24}) d_{i,i} d_{j,j}$

+ $(k_{33} - k_{22}) d_i d_j d_{k,i} d_{k,j} + k_{24} d_{i,j} d_{j,i}$ (2.2) where F is the free energy density, d_i is the i-th component of the unit vector \tilde{d} which describes the molecular orientation





BEND

.



SPLAY

FIGURE 2.5. The Three Curvatures of the Molecular Orientation in Liquid Crystals at point \vec{x} , and the k's are the elastic moduli.²⁸ The elastic modulus k_{24} is not independent and is zero for planar structures.²⁹ The notation $U_{,j}$ standard in continuum mechanics and means $\partial U/\partial x_j$. In this equation, and all others in this section, it is understood that repeated indices are to be summed over from 1 to 3 unless otherwise specified. For example, the quantity $U_{i,jj}$ is given by

$$U_{i,jj} = \sum_{j=1}^{3} \frac{\partial^2 U_i}{\partial x_j^2} .$$
 (2.3)

The form of the constitutive equations for liquid crystals was arrived at by Leslie in his study of anisotropic fluids.^{30,31} Leslie's description begins by letting x_i denote the position of a typical particle at the present time, t', and ξ_i denote its position at a previous time, t, where

$$\xi_{i}(t) = \xi_{i}(x_{1}, x_{2}, x_{3}, t, t), x_{i} = \xi_{i}(t),$$

-\overline < t \le t. (2.4)

The components of the velocity are defined by

$$v_{i}(t) = \frac{d}{dt} \varepsilon_{i}(t)$$
 (2.5)

where x_i and t' are kept fixed during the differentiation. In addition, Leslie associates with each particle a director, d_i, defined in a way similar to the particle position, and with a corresponding velocity given by

$$W_{i}(t) = \frac{d}{dt} d_{i}(t). \qquad (2.6)$$

With these definitions, the following equations are proposed for a nematic liquid crystal under the assumption that

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it is incompressible:

$$v_{i,i} = 0, \rho \frac{dv_i}{dt} = \rho F_i + \sigma_{ji,j}$$
 (2.7 a,b)

$$\rho_1 \frac{di}{dt} = \rho_1 G_i + g_i + \pi_{ji,j}$$
 (2.7 c)

where F_i is the external body force per unit mass, G_i is the external director body force per unit mass, ρ is the density, and ρ_1 is a constant. The stress tensor, σ_{ji} and the director stress tensor, π_{ii} , are given by

$$\sigma_{ji} = -P\delta_{ij} - \rho \frac{\partial F}{\partial d_{k,j}} d_{k,i} + \sigma_{ji}$$
(2.8)

and

$$\pi_{ji} = \beta_{j} d_{i} + \rho \frac{\partial F}{\partial d_{i,j}},$$

where F is the free energy density, P is the hydrostatic pressure, and the β_j are constants. The factor, δ_{ij} , is the Kronecker delta. The extra stress, $\hat{\sigma}_{ij}$, is given by

$$\hat{\sigma}_{ji}' = \mu_1 d_k d_p A_{kp} d_i d_j + \mu_2 d_j N_i + \mu_3 d_i N_j + \mu_4 A_{ij} + \mu_5 d_j d_k A_{ki} + \mu_6 d_i d_k A_{kj}$$
(2.10)

where μ_1 through μ_6 are constants which take the form of viscosity coefficients. The velocity gradients, A_{ij} and ω_{ij} , are defined by

$$A_{ij} = \frac{1}{2} (v_{i,j} + v_{j,i}), \quad \omega_{ij} = \frac{1}{2} (v_{i,j} - v_{j,i}). \quad (2.11)$$

The quantity, N_i , contains the term describing the viscous damping of the director, and is given by

$$N_{i} = \frac{d}{dt} d_{i} + \omega_{ki} d_{k}. \qquad (2.12)$$

The intrinsic director body force, g,, is determined from

$$g_{i} = \gamma d_{i} - \beta_{j} d_{i,j} - \rho \frac{\partial F}{\partial d_{i}} + \hat{g}_{i}'$$
 (2.13)

where

$$\hat{g}_{i}' = \lambda_{1} N_{i} + \lambda_{2} d_{j} A_{ji}$$
(2.14)

and γ is a constant. For convenience, the following quantities have been defined:

$$\lambda_1 = \mu_2 - \mu_3, \ \lambda_2 = \mu_5 - \mu_6. \tag{2.15}$$

The director, d_i, in these equations is restricted to be of unit length; this restriction does not, however, change any assumptions or restrictions concerning the liquid crystal, it merely causes a transfer of certain dependences to other variables.

This entire group of equations, (2.7) through (2.15), forms a complete set describing the motion of the liquid crystal. It is this set which is to be solved for the autocorrelation in d_i. Finding a general solution is a formidable task; however, the liquid crystal may be constrained in a manner which greatly simplifies the description, making possible the solution of the equations.

FLUCTUATION DYNAMICS OF THE MOLECULAR ORIENTATION IN A NEMATIC MELT

The equations of motion describing a nematic liquid crystal have been set forth in the preceding section. The object here is to solve these equations for the correlation in the director, while keeping in mind the experimental configuration. The experimental restrictions imposed on the crystal allow simplifying approximations to be made permitting solution of the equations.

In view of these restrictions (see Chapter V) it can be noted first that no body forces exist; thus F_i and G_i in (2.7) vanish. Second, the liquid crystal is oriented, therefore, in equilibrium, the director is fixed in a certain direction, d_0 , which is taken to be the x_3 direction in this analysis, and thermal agitation causes fluctuations, d_1 and d_2 , in the director from its equilibrium position. It shall be assumed that these fluctuations are small relative to unity. (These quantities are, of course, random variables.) This assumption is made in anticipation of neglecting certain nonlinear terms in the equations of motion.

Before making any approximations, however, let us concentrate on the entirety of Equation (2.7c). Making all the substitutions from the equations of the first section, (2.7c) becomes

$$\rho_{1} \frac{dw_{i}}{dt} = -(k_{33} - k_{22}) d_{k,i} d_{k,j} d_{j} + \lambda_{1} N_{i} + \lambda_{2} d_{j} A_{ji}$$

$$+ k_{22} d_{i,jj} + (k_{11} - k_{22} - k_{24}) d_{1, 1i}$$

$$+ (k_{22} - k_{24}) (d_{1,j} d_{j} d_{i,1} + d_{1} d_{j,j} d_{i,1}$$

$$+ d_{1} d_{j} d_{i,1j}) + \frac{1}{2} k_{24} (d_{i,jj} + d_{j,ij}) + \gamma d_{i} (2.16)$$

Note that the terms containing β_{i} do not enter into the above

equations. Considering now only the fluctuations, restrict the subscript i in (2.16) to only the values 1 and 2. Two simplifications can now be made. First, since the deflections are small, d_j in the equation may be replaced by δ_{j3} (where δ_{ij} is the Kronecker delta), as this is the equilibrium value of the director. Second, quadradic terms in the director and its gradients may also be neglected.

A third approximation may also be made based on an a priori knowledge of the final results. The experimental spectral density as examined in Chapter IV assumes the form of a single Lorentzian; thus the return of the director to equilibrium is purely relaxational. The inertial term, $\rho_1 dW_i/dt$, is therefore not too large, for if it were, the Lorentzian would not be centered about zero frequency. Moreover, if this term were indeed significant, yet not large enough to cause oscillatory molecular motion, the empirical spectral density would be expected to appear as the sum of two Lorentzians. It is assumed, therefore, that the inertial term in (2.16) is entirely negligible.

In view of the above three simplifications, (2.16) reduces to

 $\lambda_{1} N_{i} + \lambda_{2} A_{3i} + (k_{22} + \frac{1}{2}k_{24}) (d_{i,11} + d_{i,22}) + (k_{33} + \frac{1}{2}k_{24}) d_{i,33} + (k_{11} - k_{22} - \frac{1}{2}k_{24}) (d_{1,1i} + d_{2,2i}) = 0$ (2.17) i = 1, 2,

where

$$N_{i} = \frac{d}{dt} d_{i} + \omega_{3i}$$
 (2.18)

The equations (2.17) are two linear, coupled equations in the director fluctuations. Note, however, that the particle velocity also enters the equations through the velocity gradients, ω_{3i} , in N_i and A_{3i}. These terms must be investigated before (2.17) is investigated further; therefore the velocity equation of motion will now be considered.

Equation (2.7b) is the velocity equation of motion, which in its present form is far too complex with which to deal. Yet, the same approximations used above may be applied to (2.7b) to reduce the relation to a usable form. Upon doing this (2.7b) may be written

$$\rho \frac{dv_{3}}{dt} = -P_{,3} + \mu_{1} A_{33,3} + \mu_{3} (\dot{d}_{1,1} + \dot{d}_{2,2} + \omega_{31,1} + \omega_{32,2}) + \mu_{5} (A_{31,1} + A_{32,2} + A_{33,3}) + \mu_{4} (A_{31,1} + A_{32,2}) + (\mu_{4} + \mu_{5}) A_{33,3} (2.19) \rho \frac{dv_{i}}{dt} = -P_{,i} + \mu_{2} \dot{d}_{i,3} + \mu_{2} \omega_{3i,3} + \mu_{4} (A_{i,11} + A_{i,22}) + (\mu_{4} + \mu_{5}) A_{i,33}, i = 1,2. (2.20)$$

If the Fourier transform of these equations is taken by multiplying by $\exp(i\vec{q}\cdot\vec{x})$ and integrating over the volume of the liquid crystal, then the solution will be of the form

$$\tilde{v}$$
 $(\bar{q},t) \rightarrow e^{-\frac{\mu}{\rho}} q^2 t$ (2.21)

where

$$\tilde{v}(\vec{q},t) = \int_{\infty}^{\infty} v(\vec{x},t) e^{i\vec{q}\cdot\vec{x}} d^{3}x,$$
 (2.22)

provided that pressure gradients, P,i, and terms in the director and its derivatives are disregarded.

This temporal dependence corresponds to a spectrum in the frequency domain of width comparable to $2\mu/\rho$ centered about zero frequency. As shall be seen later, in a rigorous analysis, the director has a similar dependence, with a corresponding spectral width of $2k/\rho$. Taking the approximate values $k = 10^{-6}$ dyne, $\mu = 1$ centipoise, and $\rho = 1$ gram/cm³, it is found that the spectral width associated with the velocity fluctuations is of the order of one hundred times smaller than the width associated with the director fluctuations. Thus, in the time domain, the return of the molecular orientation to the equilibrium direction is much faster than the rate at which the velocity fluctuations relax to zero. Therefore, during the time in which the director returns to equilibrium, the velocity can be considered essentially constant in (2.17). The correlation $\langle d_i(\vec{x},t)v_{j,k}(\vec{x}',t')\rangle$ can then be considered to be zero.

Qualitatively then, it appears that the molecular orientation is strongly held to the equilibrium direction by large elastic restoring forces, whereas the linear motion of the molecule is associated with large inertial energy which is dissipated by weak viscous damping. It may also be surmised

that the molecular orientation fluctuations correlate over a relatively small volume, while the velocity fluctuations are correlated over a relatively large, massive molecular aggregate. It is clear that these ideas may be linked to the quasicrystaline nature of nematic liquid crystals.

Although this velocity correlation will be disregarded in the following analysis, it should be mentioned that this does warrant further investigation. A large amplitude noise spectrum appearing below about 100 Hz is observed experimentally; however, this spectrum may arise from a variety of causes (see for example Chapter III, Equation (3.28) and the discussion following). For spectral densities of the director correlation with width in the range of 1000 Hz., the preceding discussion predicts a spectral width associated with the velocity fluctuations to be of the order of 10 Hz. The presence of this spectrum has no effect on data taken above 100 Hz, consequently; it may be ignored hereafter.

In view of the previous discussion, the velocity terms in (2.17) can be deleted; then when this is done, two equations are obtained which assume the form of diffusion equations.

 $\frac{d}{dt}d_{1} + a_{1}d_{1,11} + a_{2}d_{1,22} + a_{3}d_{1,33} + bd_{2,21} = 0 \quad (2.23)$ $\frac{d}{dt}d_{2} + a_{1}d_{2,22} + a_{2}d_{2,11} + a_{3}d_{2,33} + bd_{1,12} = 0 \quad (2.24)$ where

$$\lambda_{1}a_{1} = k_{11}, \quad \lambda_{1}a_{2} = k_{22} + \frac{1}{2}k_{24}$$

$$\lambda_{1}a_{3} = k_{33} + \frac{1}{2}k_{24}, \quad \lambda_{1}b = k_{11} - k_{22} - \frac{1}{2}k_{24}. \quad (2.25)$$

Note that b is not independent and may be determined through

$$b = a_1 - a_2$$
 (2.26)

and, therefore, only three elastic constants are needed here to describe the nematic liquid crystal.

These equations are solved in the following way. They will be solved for the autocorrelation in the fluctuation d_2 since this is what is experimentally measured. Clearly though, the equations are symmetric in d_1 and d_2 . Multiplying (2.24) by $d'_2 = d_2(\vec{x}', t')$ and taking the ensemble average, the following differential equation is obtained for the correlation:

$$\frac{\partial}{\partial t} \left\langle \mathbf{d}_{2} \mathbf{d}_{2}^{\prime} \right\rangle + a_{1} \frac{\partial}{\partial \mathbf{x}_{2}^{2}} \left\langle \mathbf{d}_{2} \mathbf{d}_{2}^{\prime} \right\rangle + a_{2} \frac{\partial^{2}}{\partial \mathbf{x}_{1}^{2}} \left\langle \mathbf{d}_{2} \mathbf{d}_{2}^{\prime} \right\rangle$$
$$+ a \frac{\partial^{2}}{\partial \mathbf{x}_{3}^{2}} \left\langle \mathbf{d}_{2} \mathbf{d}_{2}^{\prime} \right\rangle + b \frac{\partial^{2}}{\partial \mathbf{x}_{1}^{2}} \left\langle \mathbf{d}_{1} \mathbf{d}_{2}^{\prime} \right\rangle = 0 \qquad (2.27)$$

where

$$\langle d_2 d_2 \rangle = \langle d_2(\vec{x},t) \ d_2(\vec{x}',t') \rangle,$$

and the brackets $\langle \rangle$ denote the ensemble average. Since the medium is homogeneous due to special sample preparation, the correlation $\langle d_2 d_2' \rangle$ can not depend on the origin of coordinates and must, therefore, depend only on the difference in the spatial arguments. Moreover, since the liquid crystal is not

in motion, the process is stationary and this correlation can not depend directly on time, but only on the time difference t - t = τ . Thus the correlation is a function only of $\vec{u} = \vec{x}' - \vec{x}$, and τ , so (2.27) becomes

$$\frac{\partial}{\partial \tau} \left\langle \mathbf{d}_{2} \mathbf{d}_{2}^{\prime} \right\rangle + a_{1} \frac{\partial^{2}}{\partial u_{2}^{2}} \left\langle \mathbf{d}_{2} \mathbf{d}_{2}^{\prime} \right\rangle + a_{2} \frac{\partial^{2}}{\partial u_{1}^{2}} \left\langle \mathbf{d}_{2} \mathbf{d}_{2}^{\prime} \right\rangle$$

$$+ a_{3} \frac{\partial^{2}}{\partial u_{3}^{2}} \left\langle \mathbf{d}_{2} \mathbf{d}_{2}^{\prime} \right\rangle + b \frac{\partial^{2}}{\partial u_{1}^{2} u_{2}} \left\langle \mathbf{d}_{1} \mathbf{d}_{2}^{\prime} \right\rangle = 0. \qquad (2.28)$$

In anticipation of taking the Fourier transform, it is desirable to incorporate the initial conditions of the problem into the differential equation, thereby eliminating any auxiliary conditions. Assume then, that the initial condition can be specified by substituting the quantity $C_{0} \delta(\vec{u}) \delta(\tau)$, where δ is the Dirac delta function, in place of zero on the right hand side of (2.28).³² Now, take the Fourier transform by multiplying this equation by $\exp \left[i(\vec{q} \cdot \vec{u} - \omega \tau)\right]$ and integrating over \vec{u} over the limits of the volume, and over τ from $-\infty$ to ∞ . The fact that, in this case, the volume of the liquid crystal is much greater than the correlation volume allows two approximations to be made. First, the limits of the spatial integration may be extended to infinity without seriously affecting the value of the integrals. Second, when integration by parts is performed, the integrated parts vanish since the correlation must vanish for $|u_i| = \infty$, or $\tau = \infty$. The resulting equation is algebraic, taking the form

$$(-\alpha(q) + i\omega) \left\langle d_2 d_2 \right\rangle - bq_1 q_2 \left\langle d_1 d_2 \right\rangle = C_0, \qquad (2.29)$$

where the tilde denotes the Fourier transformed quantity and α (q) is given by

$$\alpha(\mathbf{q}) = \sum_{i=1}^{3} a_{i} q_{i}^{2} . \qquad (2.30)$$

The correlation $\langle d_1 d_2 \rangle$ may be determined in a similar manner. By multiplying (2.23) by d_2 and taking the ensemble average, then following the same procedure that was used to obtain (2.29), assuming no initial correlation between d_1 and d_2 , one obtains the relation

$$(-\alpha(q) + i\omega) \left\langle d_1 d_2 \right\rangle - bq_1 q_2 \left\langle d_2 d_2 \right\rangle = 0.$$
(2.31)

Eliminating $\langle d_1 d_2 \rangle$ from (2.29) using (2.31), the Fourier transform of the desired correlation is found to be

$$\left< \vec{d}_2 \vec{d}_2 \right> = \frac{C_0}{-\alpha (q) + i\omega - \frac{(bq_1 q_2)^2}{-\alpha (q) + i\omega}}$$
 (2.32)

The second term in the denominator, $(bq_1q_2)^2/(-\alpha(q) + i\omega)$, represents the nonzero correlation between the fluctuation d_1 and the fluctuation d_2 . Although this correlation is important, it does not contribute, to a great extent, to the experimental measurements. In the first scattering configuration (see Chapter V, Figure 5.1), q_2 is identically zero, as fixed by this geometry; therefore, the second term in the denominator of (2.32) vanishes. In the second scattering configuration
(see Figure 5.2 of Chapter V), neither q_1 nor q_2 is zero. Nevertheless, since q_1 is of the order of 2.2 x 10^4 cm⁻¹ and q_2 does not exceed 1.2 x 10^4 cm⁻¹, and the coefficients a_1 and a_2 are of the order of 5 x 10^{-6} and 2.5 x 10^{-5} cm²/sec, respectively, then the second term in the denominator is considerably less than the first term. On these bases, then, the Fourier transform of the director correlation can be approximated by

$$\left\langle \dot{d}_{2}\dot{d}_{2}\right\rangle = \frac{C_{0}}{-\alpha (q) + i\omega}$$
(2.33)

where $\alpha(q)$ is defined in (2.30).

This relation will be discussed more in Chapter IV where it will be shown that the form of (2.33) implies a Lorentzian spectral density of the correlation in the photomultiplier anode current fluctuations. It will also be shown how the coefficients a_1 , a_2 , and a_3 are determined from the experimental data.

CHAPTER III

THEORY OF LIGHT SCATTERING

REVIEW OF LIGHT SCATTERING FROM LIQUIDS

This experimental study utilizes the effect of the motion of the molecules of the liquid crystal on the light passing through the sample. Systematic investigation of this perturbed light yields information about the scatterer. Before proceeding to investigate the scattering theory in liquid crystals, a brief review of light scattering from liquids will be presented. Liquids rather than solids are discussed because of the greater similarity of liquid crystals to pure liquids rather than solids. This discussion will serve to introduce the problem and to clarify terminology.

In a pure isotropic liquid not near a critical point, the condition for Bragg scattering can not be satisfied for light waves, implying therefore, no scattered light. This is obviously not the case and early experiments showed the presence of scattered light. Guided by a suggestion of Von Smoluchowski, Einstein calculated the scattered field and intensity due to fluctuations of the dielectric permittivity about an equilibrium value.³³ He then went on to relate the permittivity fluctuations to thermodynamic quantities by considering the permittivity as a function of density and temperature.

Explicitly, Einstein found the scattered field of wave vector \vec{k} at a distance \vec{R} from the scattering volume to be

$$\vec{E}(R,q,t) = -\vec{E}_{O}\left(\frac{\omega_{O}}{c}\right)^{2} \frac{\sin\phi}{4\pi} \stackrel{i(\vec{k}\cdot\vec{R}-\omega_{O}\tau)}{R} (2\pi)^{3/2} \delta\varepsilon(q,t)$$
(3.1)

where $\vec{q} = \vec{k}' - \vec{k}$, \vec{k} is the incident wave vector, and ϕ is the angle between the incident polarization and the direction of \vec{k}' . $\delta \epsilon(q,t)$ is the fluctuation in the permittivity. This result shows an intimate connection between the scattered field and the permittivity fluctuations. Since $\delta \varepsilon(q,t)$ is a scalar, the equation predicts the polarization of the scattered field to be the same as the polarization of the incident field. The average intensity is simply the average of the square of (3.1) and is proportional to $\langle |\delta \epsilon(q,t)|^2 \rangle$ where the brackets $\langle \rangle$ denote the average. Einstein evaluated $\langle |\delta \epsilon(q,t)|^2 \rangle$ in terms of temperature and isothermal compressability for $\vec{q} = 0$. His results were later extended by Ornstein and Zernike to give the dependence of $\left< \left| \delta \epsilon (q,t) \right|^2 \right>$ on \dot{q} . 34

Following this theoretical work, much experimental work was devoted to the study of light scattering by liquids. One of the more important contributors of that time was Gross whose careful observations revealed a triplet of lines in the spectrum of the scattered light.³⁵ The center line was unshifted in frequency with respect to the illuminating light frequency while the other two formed a pair of lines symmetrically shifted with respect to the center line. Gross' observation revealed the angular dependence of the shift of the displaced lines; the shift increased with increasing scattering angle. He explained this phenomenon in terms of thermally excited acoustic waves which propagated throughout the liquid. This confirmed the prediction made earlier by Brillouin.

In early terminology, the center line was called the Rayleigh line and the symmetrically spaced doublet was termed the "wings of the Rayleigh line". The group of three lines was also referred to as the Rayleigh triplet. Now it is more common to refer to the unshifted central peak as the Rayleigh line and the shifted components due to acoustic waves* as Brillouin lines.

The results of Gross' experiments were not borne out in Einstein's evaluation of $\delta \epsilon$ since the choice of the independent thermodynamic variables density and temperature did not allow identification of the Rayleigh and Brillouin components. The proper choice was made by Landau and Placzek.³⁶ Their choice of entropy and pressure allowed the identification and calculation of the intensity of the Rayleigh and Brillouin components. They argued that scattering due to local entropy fluctuations gave rise to the Rayleigh line since local entropy fluctuations do not propagate in normal liquids and the Brillouin lines are

*as opposed to shifted components of Raman scattering, a result of a change in the internal molecular energy.

a result of local pressure fluctuations which propagate throughout the liquid. (Quantum mechanically, it can be seen that a shift in frequency in scattered light can only be caused by a propagating acoustic wave (precluding Raman scattering) and no frequency shift implies no acoustic wave, only relaxational motion. This is all implied in the conservation of momentum relation $\vec{q} = \vec{k} \cdot - \vec{k}$ where $\vec{k} \cdot$ is the scattered wave vector, \vec{k} is the incident wave vector, and \vec{q} is the acoustic wave vector.)

All of the theory presented heretofore is not the complete picture. Early investigations by Gross and others revealed the presence of a depolarized field of scattered light having a spectral structure similar to that of the polarized component.³⁷ These results are obviously inconsistent with the previous theory which predicts a completely polarized scattered field. The presence of the depolarized field has been explained in the following way: although a liquid is macroscopically isotropic, its molecules have a definite structure and, in general, will not be isotropic. Thermal agitation not only causes local pressure and entropy fluctuations, but also local fluctuations in molecular orientation causing a depolarization of the scattered field. The presence of the Brillouin doublet in the depolarized field was theoretically investigated by Leontovich who predicted a coupling between the molecular orientation and acoustic shear waves. 38 The

depolarized Rayleigh component has been attributed to molecular motion of a purely relaxational nature. The same situation also exists in the spectrum of light scattered by liquid crystals except that the intensity of the depolarized component is of comparable magnitude to that of the polarized component. This is a consequence of the large molecular anisotropy and the quasi-crystaline nature of liquid crystals. Moreover, the amount of scattering is much greater in the case of liquid crystals than for pure liquids. These facts make the acquisition of data on these substances relatively easy through light scattering.

Frequently mentioned, but seldom discussed, is the presence of a broad continuous background of scattered light whose breadth extends beyond the Brillouin components and appears in both the polarized and depolarized fields. A recent investigation has suggested that molecular repositioning contributes to this broad background and to the other components as well.³⁹

The previous discussion has seemed to stress a connection between the scattered light and thermodynamic quantities. It is important to recognize other theories besides the thermodynamic approaches and to utilize them in obtaining information about molecular fluctuations. Such nonthermodynamic theories have been developed by Rytov and others and consider the statistics of the fluctuations in the permittivity.⁴⁰ Such

approaches find great utility in the investigations of light scattering by liquid crystals where thermodynamic quantities can not easily be connected to the fluctuations in orientation and position.

The seemingly complicated spectrum of light scattered by a liquid is summarized in Figure 3.1. The three peaks and broad background are present in both the polarized and depolarized fields. The central, unshifted Rayleigh peak is associated with purely relaxational molecular motion, while the symmetrically shifted Brillouin components are associated with propagating acoustic waves. (The spectrum does not show Raman lines which arise from changes in the internal states of the molecule. This type of scattering will not be considered in this study.)

Much information about the scattering liquid can be gained from studying the fine structure of the Rayleigh and Brillouin lines. For example, the width of the Brillouin line is directly related to the acoustic absorption at the frequency equal to the shift of the Brillouin line from the incident frequency. This fact has made the study of Brillouin scattering a popular tool in the study of hypersonic waves. The laser has made such studies possible since the laser linewidth is, in general, much less than the spacing of the Brillouin components. Such studies usually use a scanning Fabry-Perot interferometer.



FIGURE 3.1. The Spectrum of Light Scattered by a Pure Liquid. ω_{0} is the mean frequency of the incident light, ω_{B} is the mean frequency of the phonons causing the Brillouin scattering. This spectrum appears in both the polarized and depolarized components of the scattered field.

The Rayleigh line may be studied in the same way; however, a development of Benedek and coworkers has made analyzation of the Rayleigh line relatively easy.⁴¹ They have used a spectrum analyzer to obtain the spectral density of the current of a photomultiplier tube illuminated by the light scattered from a liquid. Benedek argues that the system operates because of the heterodyne action of the Fourier frequency components of the light with themselves in the photomultiplier (hence the name homodyne spectrometer). A careful theoretical analysis of this scheme was undertaken recently by Mandel in which the effect of the laser linewidth is considered. His analysis justifies the equations used by others in studying light scattering by analysis of photomultiplier currents, while simultaneously pointing out the consequences of assuming (erroneously) that the laser light is perfectly monochromatic. The spectrometer used in this experimental study is similar to that described by Benedek.

LIGHT SCATTERING FROM A SUBSTANCE HAVING AN ANISOTROPIC SUSCEPTIBILITY

From the previous introduction it is clear that light scattering has been a useful tool for many years in the study of liquids. The polarization and frequency shift of the scattered light have been associated with certain classes of molecular motion and quantitative results have been used to calculate sound velocity and absorption, and other properties

of the scattering medium. However, as previously mentioned, there is more information to be obtained from the scattered light than early technology allowed. One of the technological drawbacks was the lack of an intense monochromatic source of light which would enable, simultaneously, easy observation of the scattered light and perfect coherence of the incident light as assumed in the theory. A great advance, of course, came with the laser; however, the laser is not monochromatic as is sometimes assumed. Nevertheless, the use of this new device enables acquisition of more information than previously obtainable.

The object here is to relate information acquired about the statistics of the scattered light to the statistics of the molecular motion. With this end in view, the following analysis will relate the statistical quantities measured by the laboratory instruments to statistics of the molecular motion. The measurable quantity for the experimental technique used is the spectral density, $S(\vec{x}, \omega)$, of the correlation function of the light intensity taken at the same observation point \vec{x} , but at different times. The scatterer is represented by its susceptibility $\vec{x}(\vec{x},t)$, a tensor whose components are random functions of position in the scattering volume and time. The tensoral representation of the susceptibility reflects the fact that the molecules are not isotropic.

The analysis to follow parallels that given by Mandel in

a recent paper with a few exceptions:⁴² first is the tensoral rather than scalar characteristics of the susceptibility; second, the scattered light is passed through an analyzer which selects a particular polarization of the scattered field; third, the Fourier transform of the intensity correlation is taken since the photocurrent at frequency ω is measured.

If the incident laser field is $\vec{E}_{O}(\vec{x},t)$, then the induced polarization per unit volume dV is

 $\vec{P}(\vec{x},t) dV = \overleftrightarrow{\chi}(\vec{x},t) \vec{E}_{0}(x,t) dV$ (3.2) The susceptibility, $\overleftrightarrow{\chi}(\vec{x},t)$ may be written

 $\overleftrightarrow{\chi}(\vec{x},t) = \langle \overleftrightarrow{\chi} \rangle + \overleftrightarrow{\lambda}(\vec{x},t)$ (3.3)

where by $\langle \stackrel{\leftrightarrow}{\chi} \rangle$ we mean the tensor whose components (χ)_{ij} = $\langle \chi_{ij} \rangle$, where $\langle \rangle$ denotes the ensemble average. Since the liquid crystal is oriented, $\langle \stackrel{\leftrightarrow}{\chi} \rangle$ is the same for all points within the scattering volume and is also independent of time. This diffracted field resulting from the induced polarization $\langle \stackrel{\leftarrow}{\chi} \rangle \stackrel{\neq}{E}_{0}(\vec{x},t)$ is not of interest here. Of importance is the scattered field radiated by the induced polarization,

$$\dot{\Delta \chi}(\vec{x},t) \vec{E}_{\alpha}(\vec{x},t)$$
 (3.4)

The real laser field is represented by

$$\vec{E}_{o}(\vec{x},t) = \sum_{s} \int d^{3}k \vec{\epsilon} \left[v_{,s} e^{i(\vec{k}\cdot\vec{x} - ckt)} + c.c. \right]$$
(3.5)

where c.c. denotes the complex conjugate of the quantity on

the left in the brackets, $\vec{\hat{k}}$, is the unit polarization vector \vec{k} ,s of mode \vec{k} of polarization s, and v is the amplitude of that mode.

The scattered field may be calculated using the well known dipole formula 43

$$\vec{E}_{s} = -\frac{1}{c}\vec{A} - \nabla\phi \qquad (3.6)$$

where

$$\vec{A}(\vec{x},t) = \int_{V} \frac{1}{cR} \left[\vec{P} \right] dV$$
(3.7)

$$\phi(\vec{x},t) = \int_{V} \{ \left[\vec{P} \right] \cdot \nabla' \frac{1}{R} + \frac{\vec{R}}{cR^2} \cdot \left[\dot{\vec{P}} \right] \} dV' \qquad (3.8)$$

The dots above quantities indicate time differentiation; the bracket [] indicates the argument of the enclosed quantity is to be evaluated at the retarded time, t-R/c, where $\vec{R} = \vec{x} - \vec{x}'$ and $R = |\vec{x} - \vec{x}|$. The integrals are taken over the scattering volume; and $\vec{P}(\vec{x}',t) = \vec{\Delta}_{\vec{X}}(\vec{x}',t) \vec{E}_{0}(\vec{x}',t)$. (3.10)

Examination of the relative magnitudes of the terms involved shows that the only terms of significance are those involving spatial or temporal derivatives of $\vec{E}_0(\vec{x}',t - R/c)$ in the integrals. Retaining only these terms, it is found that

$$\vec{E}_{s}(\vec{x},t) = \int_{V} \frac{dV'}{V} \sum_{s} \int d^{3}kk^{2} \left[\overleftarrow{\Delta\chi}(\vec{x}',t-\frac{R}{c}) \vec{\epsilon} \\ \vec{k},s \right]$$

$$- \left[\overrightarrow{\rho} \cdot (\overleftarrow{\Delta\chi}(\vec{x}',t-\frac{R}{c}) \epsilon_{\vec{k},s}) \cdot \overrightarrow{\rho} \right] \left[v_{\vec{k},s} e^{i(\vec{k}\cdot\vec{x}'-ck(t-\frac{R}{c})+c.c.)} \right]$$

$$(3.10)$$

where $\vec{\rho} = \vec{R}/R \approx \vec{x}/R$, since the distance to the observation point will be much larger than the linear dimensions of the scattering volume. Note that $\vec{\rho}$ is a unit vector lying along the direction of the wave vector of the scattered light. This expression may be simplified further by noting that $\vec{\Delta \chi}$ operating on $\vec{\epsilon}_{k,s}$ reflects only a change in polarization in the far field component of the scattered light. Therefore,

$$\dot{\Delta} \cdot (\dot{\Delta}\chi(\dot{x}',t-\frac{R}{c}) \stackrel{\vec{e}}{\epsilon}) = 0$$
 (3.11)

and so

$$\vec{E}_{s}(\vec{x},t) = \int_{V} \frac{dV'}{R} \sum_{s} \int d^{3}kk^{2} (\vec{\Delta\chi}(\vec{x}',t-\vec{R}) \vec{\epsilon})$$

$$(v_{k,s} e^{i(\vec{k}\cdot\vec{x}'-ck(t-R/c))} + c.c.) .$$
(3.12)

For a single mode laser, \vec{k} is nearly a constant during the integration and may therefore be removed from under the integral provided it is replaced by the mean wave number of the mode, \vec{k}_{0} . The desired relation between the scattered field and incident laser field is

$$\vec{E}_{s}(\vec{x},t) = k_{o}^{2} \int \frac{dV'}{R} \quad \overleftarrow{\Delta\chi}(\vec{x}', t - \frac{R}{c}) \quad \vec{E}_{o}(\vec{x}', t - \frac{R}{c}). \quad (3.13)$$

It is desirable to express $\vec{E}_{s}(\vec{x},t)$ in terms of an analytic signal since a simple description of the photodetection process exists in terms of this quantity rather than $\vec{E}_{s}(\vec{x},t)$ itself.⁴⁴ The transition is carried out by writing $\vec{\lambda}\vec{\chi}$ and \vec{E}_{o} in terms of their Fourier transforms and supressing the negative frequencies of the entire transform, thus assuring a complete description of $\vec{E}_{s}(\vec{x},t)$ solely in terms of positive Fourier frequency components. Following this prescription we write

$$\vec{E}_{s}(\vec{x},t) = k_{o}^{2} \int_{V-\infty}^{\infty} \int \frac{1}{R} \overleftrightarrow{\chi}(\vec{x}',\omega') \overrightarrow{U}(x',\omega'')$$

$$e^{i(\omega' + \omega'')(t - R/c)} d\omega' d\omega'' dV' \qquad (3.14)$$

then, make the substitution $\omega' = \omega + \omega''$. This can be written

$$E_{s}(x,t) = k_{0}^{2} \int_{V} \frac{1}{R} \int_{-\infty}^{\infty} d\omega \int_{-\infty}^{\infty} d\omega' \int_{X}^{\infty} (x', \omega - \omega'') e^{i\omega(t - \frac{R}{c})} dV$$
(3.15)

where

$$\overleftrightarrow{\chi}(\vec{x},\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \Delta \chi(\vec{x}',t) e^{-i\omega t} dt$$
 (3.16)

and

$$\vec{U}(\vec{x}',\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \vec{E}_{O}(\vec{x}',t) e^{-i\omega t} dt. \qquad (3.17)$$

First, note that $\vec{U}(\vec{x}', \omega'')$ in the integral differs from zero only for values of ω'' large and positive, i.e., near the optical frequency of the laser. This fact allows disregarding negative ω'' in the integral. Second, note that the fluctuations $\vec{\Delta}_{\vec{X}}(\vec{x},t)$ are relatively slowly varying functions of time; therefore, $\vec{\chi}(\vec{x}', \omega - \omega'')$ differs appreciably from zero only for values of ($\omega - \omega''$) near zero. Therefore, negative values of ω may also be disregarded. The desired analytic signal is

$$\vec{\tilde{V}}_{S}(\vec{x},t) = k_{O}^{2} \int_{V} \frac{dV'}{R} \int_{0}^{\infty} d\omega \int_{0}^{\infty} d\omega'' \overleftrightarrow{\chi}(\vec{x}',\omega - \omega'')$$

$$\cdot \vec{\tilde{U}}(\vec{x}',\omega'') e^{i\omega(t - R/c)} \qquad (3.18)$$

Now, making the inverse transform $\omega = \omega' + \omega''$, this becomes

$$\vec{\hat{V}}_{s}(\vec{x},t) = k_{0}^{2} \int_{V} \frac{dV'}{R} \int_{-\omega'}^{\infty} d\omega' \int_{0}^{\infty} d\omega'' \chi(\vec{x}',\omega')$$

$$\cdot e^{i\omega''(t - R/c)} \vec{\hat{U}}(\vec{x}',\omega'') e^{i\omega''(t - R/c)} \qquad (3.19)$$

The facts mentioned above also allow extension of the integral over ω ' from $-\infty$ to ∞ . Recognizing the Fourier transform of $\overleftarrow{\lambda} \overrightarrow{\chi}$ and the integral over ω '' as the analytic signal representation of the incident laser field, the expression for the analytic signal of the scattered field can be written

$$\vec{V}_{s}(\vec{x},t) = k_{0}^{2} \int_{V} \frac{dV'}{R} \vec{\lambda} \vec{\chi}(\vec{x}',t-R/c) \vec{V}_{0}(x',t-R/c)$$
 (3.20)

where \vec{v}_{o} is the analytic signal representation of the incident laser field.

It is well known that

$$\vec{\nabla}_{o}(\vec{x},t) = \vec{\epsilon} I_{o}^{\frac{1}{2}} e^{i(\vec{k}_{o}\cdot\vec{x} - ck_{o}t + \beta(\vec{x},t))}$$
(3.21)

where I_0 is the laser light intensity and $\beta(\vec{x},t)$ is a random variable uniformly distributed between 0 and 2π . This expression reflects the constant intensity, quasimonochromaticity of the laser.⁴⁵ $\vec{\epsilon}$ is the unit polarization vector of the laser field. When this expression for \vec{V}_0 is placed in the

the previous expression for the scattered field, it can be approximated that $\beta(\vec{x'}, t - R/c)$ is almost constant during the integration provided the physical extent of the scattering volume is small compared to the coherence length of the inci-

dent laser light. Therefore, under these conditions, one may write

$$\vec{\tilde{V}}_{s}(\vec{x},t) = I_{o}^{\frac{1}{2}} k_{o}^{2} e^{i\beta(\vec{x}_{o},t-R_{o}/c)} \int_{V} \frac{dV'}{R} \vec{\tilde{\Delta}}_{X}(x',t-R/c)$$

$$\cdot \vec{\tilde{\epsilon}} e^{i(\vec{k}_{o}\cdot\vec{x}-ck_{o}(t-R/c))}$$
(3.22)

where \vec{x}_{0} is the mean position of the scattering volume and $R_{0} = |\vec{x} - \vec{x}_{0}|$.

The scattered light then passes through an analyser which selects the portion of the scattered light which lies parallel to the analyser axis, \vec{a} . The analytic signal arriving at the detector at point \vec{x} is then

$$V_{d}(\vec{x},t) = I_{o}^{\frac{1}{2}} k_{o}^{2} e^{i\beta(\vec{x}_{o},t-R_{o}/c)} \int_{V} \frac{dV'}{R} \mu(x',t-R/c)$$

$$\cdot e^{i(\vec{k}_{o}-\vec{x}'-ck_{o}(t-R/c))} \qquad (3.23)$$

where

$$\mu(\vec{x},t) = \vec{a} \cdot (\vec{\Delta \chi}(\vec{x},t) \vec{\epsilon}). \qquad (3.24)$$

Here μ can be any selected linear combination of the elements of $\Delta \chi$ by proper selection of \vec{a} and $\vec{\epsilon}$.

The intensity correlation function is

$$\left\langle I(\vec{x},t) | I(\vec{x},t+\tau) \right\rangle = \left\langle V_{d}^{*}(\vec{x},t) | V_{d}(\vec{x},t) | V_{d}^{*}(\vec{x},t+\tau) | V_{d}(\vec{x},t+\tau) \right\rangle$$

$$= I_{0}^{2} k_{0}^{8} \int_{V} \frac{dV_{1} dV_{2} dV_{3} dV_{4}}{R_{1} R_{2} R_{3} R_{4}}$$

$$\cdot \langle \mu(\vec{x}_{1}, t - R_{1}/c) \mu(\vec{x}_{2}, t - R_{2}/c)$$

$$\cdot \mu(\vec{x}_{3}, t - R_{3}/c + \tau) \mu(\vec{x}_{4}, t - R_{4}/c + \tau) \rangle$$

$$\cdot e^{-i} \vec{k}_{0} \cdot (\vec{x}_{1} - \vec{x}_{2} + \vec{x}_{3} - \vec{x}_{4})$$

$$\cdot e^{-i} k_{0}^{(R_{1} - R_{2} + R_{3} - R_{4})} \cdot (3.25)$$

Since $\overleftrightarrow{\lambda}_{\chi}$ is assumed to be a normal random variable, then μ is a normal random variable, also, and the Gaussian moment theorem may be applied to the above ensemble average.⁴⁶ This allows writing

$$\left\langle \mu \left(\vec{x}_{1}, t - R_{1}/c \right) \ \mu \left(\vec{x}_{2}, t - R_{2}/c \right) \ \mu \left(\vec{x}_{3}, t - R_{3}/c + \tau \right) \right. \\ \left. \left. \mu \left(\vec{x}_{4}, t - R_{4}/c + \tau \right) \right\rangle \\ = \left\langle \mu \left(\vec{x}_{1}, t - R_{1}/c \right) \ \mu \left(\vec{x}_{2}, t - R_{2}/c \right) \right\rangle \left\langle \mu \left(\vec{x}_{3}, t - R_{3}/c + \tau \right) \right. \\ \left. \left. \mu \left(\vec{x}_{4}, t - R_{4}/c + \tau \right) \right\rangle + \left\langle \mu \left(\vec{x}_{1}, t - R_{1}/c \right) \right. \\ \left. \left. \mu \left(\vec{x}_{3}, t - R_{3}/c + \tau \right) \right\rangle \left\langle \mu \left(\vec{x}_{2}, t - R_{2}/c \right) \right. \\ \left. \left. \mu \left(\vec{x}_{4}, t - R_{4}/c + \tau \right) \right\rangle + \left\langle \mu \left(\vec{x}_{1}, t - R_{1}/c \right) \right. \\ \left. \left. \mu \left(\vec{x}_{4}, t - R_{4}/c + \tau \right) \right\rangle + \left\langle \mu \left(\vec{x}_{2}, t - R_{2}/c \right) \right. \\ \left. \left. \mu \left(\vec{x}_{4}, t - R_{4}/c + \tau \right) \right\rangle \left\langle \mu \left(\vec{x}_{2}, t - R_{2}/c \right) \right. \\ \left. \left. \mu \left(\vec{x}_{3}, t - R_{3}/c + \tau \right) \right\rangle \right\rangle \right\}$$

$$(3.26)$$

If the scattering medium is homogeneous, the ensemble averages of the type $\langle \mu(\vec{x}_1, t - R_1/c) \ \mu(\vec{x}_2, t - R_2/c) \rangle$ can only depend

upon the relative position of points 1 and 2, that is upon the vector $\vec{x}_1 - \vec{x}_2$. Moreover, if the scattering material is in thermodynamic equilibrium, then the process is stationary. Therefore, these correlations can depend only on the difference in the arguments; more explicitly, one can write, for example,

$$\left< \mu(\vec{x}_1, t - R_1/c) \ \mu(\vec{x}_2, t - R_2/c) \right> = \sigma(\vec{x}_1 - \vec{x}_2, \frac{R_2 - R_1}{c}).$$

(3.27)

The slowly varying nature of $\overrightarrow{\Delta \chi}$ and μ have been brought out before; however, this property may be utilized again to justify neglecting the argument $(R_2 - R_1)/c$ in σ for small scattering volume. Making these approximations, the intensity correlation becomes

$$\langle \mathbf{I}(\vec{x},t) \ \mathbf{I}(\vec{x},t+\tau) \rangle = \mathbf{I}_{0}^{2} k_{0}^{8} \int_{V} \frac{dV_{1}}{R_{1}} \frac{dV_{2}}{R_{2}} \frac{dV_{3}}{R_{3}} \frac{dV_{4}}{R_{4}} \cdot \{\sigma(\vec{x}_{1} - \vec{x}_{2}, 0) \ \sigma(\vec{x}_{3} - \vec{x}_{4}, 0) + \sigma(\vec{x}_{1} - \vec{x}_{3}, \tau) + \sigma(\vec{x}_{1} - \vec{x}_{4}, \tau) \ \sigma(\vec{x}_{2} - \vec{x}_{3}, \tau) \} e^{-i\vec{k}} \circ \cdot (\vec{x}_{1} - \vec{x}_{2} + \vec{x}_{3} - \vec{x}_{4}) \cdot e^{-ik} \circ (R_{1} - R_{2} + R_{3} - R_{4})$$
(3.28)

Taking the Fourier transform of this expression gives the spectral density, $S(\vec{x}, \omega)$, of the intensity correlations. Note that the first term in the brackets {} does not depend on ω , therefore it contributes only at zero frequency. This term is not of interest here and will be disregarded. The spectral density for $\omega > 0$ is then,

$$S(\vec{x},\omega) = I_{0}^{2} k_{0}^{8} \int_{-\infty}^{\infty} \int_{V} \frac{dV_{1}}{R_{1}} \frac{dV_{2}}{R_{2}} \frac{dV_{3}}{R_{3}} \frac{dV_{4}}{R_{4}} \{\sigma(\vec{x}_{1} - \vec{x}_{3}, \tau) \\ \cdot \sigma(\vec{x}_{2} - \vec{x}_{4}, \tau) + \sigma(\vec{x}_{1} - \vec{x}_{4}, \tau) \sigma(\vec{x}_{2} - \vec{x}_{3}, \tau) \} \\ \cdot e^{-i\vec{k}_{0}} \cdot (\vec{x}_{1} - \vec{x}_{2} + \vec{x}_{3} - \vec{x}_{4}) e^{-ik_{0}(R_{1} - R_{2} + R_{3} - R_{4})} \\ \cdot e^{-i\omega\tau} d\tau.$$
(3.29)

This expression can be simplified further. First, note that R_1 through R_4 in the denominator are approximately equal to the mean distance from the scattering volume to the detector. These factors may, therefore, be replaced by this mean distance R_0 . Furthermore, the quantity in the exponent containing R_1 through R_4 may be approximated by

$$k_{o}R \approx k_{o}|\vec{x}| - k_{o}\vec{\rho} - \vec{x}'$$
 (3.30)

where, as before, $\vec{\rho} = \vec{x}/R$. Letting $\vec{k}' = \vec{k}_0$ (\vec{k}' is the wave vector of the scattered light), the spectral density is then

$$s(\vec{x},\omega) = \frac{I_{0}^{2} k_{0}^{8}}{R_{4}} \int_{-\infty}^{\infty} \int_{V} dV_{1} dV_{2} dV_{3} dV_{4} \{\sigma(\vec{x}_{1} - \vec{x}_{3},\tau) \\ \cdot \sigma(\vec{x}_{2} - \vec{x}_{4},\tau) + \sigma(\vec{x}_{1} - \vec{x}_{4},\tau) \sigma(\vec{x}_{2} - \vec{x}_{3},\tau) \} \\ \cdot e^{i(\vec{k}' - \vec{k}_{0})} \cdot (\vec{x}_{1} - \vec{x}_{2} + \vec{x}_{3} - \vec{x}_{4}) e^{-i\omega\tau} d\tau$$
(3.31)

For integration for the first term in the brackets, the substitutions $\vec{x}_a = \vec{x}_1 - \vec{x}_3$, $\vec{x}_b = \vec{x}_2 - \vec{x}_4$ can be made. Similarly, for the second term, one can substitute $\vec{x}_a = \vec{x}_1 - \vec{x}_4$ and $\vec{x}_b = \vec{x}_2 - \vec{x}_3$. Making these substitutions and performing some

integrals, the following expression is obtained for the spectral density:

$$S(\vec{x},\omega) = \frac{I_{o}^{2} k_{o}^{8}}{R_{o}^{4}} V^{2} \int_{-\infty}^{\infty} \int_{V} dV_{a} dV_{b} \sigma(\vec{x}_{a},\tau) \sigma(\vec{x}_{b},\tau)$$

$$\cdot e^{i\vec{q}\cdot(\vec{x}_{a}-\vec{x}_{b})} e^{-i\omega\tau}d\tau \{1+\frac{1}{V^{2}}\int_{V} e^{i2\vec{q}\cdot(\vec{x}_{3}-\vec{x}_{4})}$$

$$\cdot dV_{3} dV_{4}\} \qquad (3.32)$$

where $\vec{q} = \vec{k} \cdot - \vec{k}_0$. Since $\sigma(\vec{x},\tau)$ is a correlation function between two points in a homogeneous medium separated by \vec{x} , it is reasonable to assume $\sigma(\vec{x},\tau) = \sigma(-\vec{x},\tau)$. Also, if the detector is not placed too close to the axis, i.e., if \vec{q} is not too small, then the second term in the brackets is negligible compared to unity. Making these changes and approximations, then replacing \vec{x}_b by $-\vec{x}_b$, it is found that

$$S(\vec{x},\tau) = \frac{I_o^2 k_o^8 V^2}{R_o^4} \int_{-\infty}^{\infty} \left| \int_{V} \sigma(x',\tau) e^{i\vec{q}\cdot\vec{x}'} dV' \right|^2 e^{-i\omega\tau} d\tau.$$
(3.33)

What is actually measured is the square root of the absolute value of the above quantity, that is the output of the spectrum analyser is proportional to

$$\left\{ \left| \int_{-\infty}^{\infty} \right| \int_{V} \sigma(\vec{x}',\tau) e^{i\vec{q}\cdot\vec{x}'} dV' \right|^{2} \exp(\omega\tau) d\tau \right\}^{\frac{1}{2}}$$
(3.34)

the proportionality constant including the square root of the product of the quantum efficiency and gain of the photomultiplier tube. It is sufficient to note here that the spectral density $S(\vec{x}, \omega)$ is related to the correlation function

$$\sigma(\vec{x},\tau) = \langle \vec{a} \cdot (\vec{\Delta \chi}(x_1,\tau)\vec{\epsilon}) | \vec{a} \cdot (\vec{\Delta \chi}(\vec{x}_1 + \vec{x},\tau + \tau)\vec{\epsilon}) \rangle \qquad (3.35)$$

through a four dimensional space-time Fourier transform. It is possible to find this correlation function by knowing the absolute value of the spectral density of the scattered light.

CHAPTER IV

LIGHT SCATTERED FROM AN ORIENTED NEMATIC LIQUID CRYSTAL AND THE SPECTRUM OF THE

PHOTOMULTIPLIER ANODE CURRENT FLUCTUATIONS

The results of the preceding two chapters permit a direct connection between the spectral density of the photomultiplier anode current fluctuations and physical constants of the liquid crystal provided that a quantitative relation exists between the director, d, and the dielectric susceptibility, $\overleftarrow{\chi}$. The purpose of this chapter is to formulate an explicit relation between the parameters of the liquid crystal and the experimental data. To do so, the relation between the fluctuations in the director and the susceptibility will be established. It is convenient to also use this chapter for a general examination of the experimental results and the theory in order to first, justify the assumptions made in the previous chapters, and, second, to point out some general features of the observations. This will be done later in the chapter where examples of the observed Lorentzian spectral density and q² dependence of the Lorentzian linewidth will be given.

To provide the relation between d and $\overleftrightarrow{\chi_{f}}$ return to the model of a nematic liquid crystal as proposed in Chapter II. It is assumed that the director lies along the long axis of

the molecule and the molecule has cylindrical symmetry about this axis. Moreover, it is assumed that the molecular polarizability shares this same symmetry and that the susceptability can be represented by the tensor

$$\stackrel{\leftrightarrow}{\chi} = \begin{bmatrix} \chi_2 & 0 & 0 \\ 0 & \chi_2 & 0 \\ 0 & 0 & \chi_1 \end{bmatrix}$$
 (4.1)

in a coordinate system in which the x_3 axis lies along the director.

When thermal agitation causes a deviation in the local molecular orientation from the preferred orientation direction, the susceptibility can no longer be represented by the above tensor in a coordinate system fixed to the preferred orientation direction. A representation of $\stackrel{\leftrightarrow}{\chi}$ in this latter coordinate system may be found by performing a transformation on $\stackrel{\leftrightarrow}{\chi}$ (as given in (4.1)) which constitutes a coordinate rotation. The transformation may be uniquely determined in terms of the components of $\stackrel{d}{d}$. As a first step in using Euler angles, it is found that 47

$$\begin{bmatrix} d_1 \\ d_2 \\ d_3 \end{bmatrix} = \begin{bmatrix} \sin \psi \sin \theta \\ \cos \psi \sin \theta \\ \cos \theta \end{bmatrix}$$
(4.2)

The Euler angle, ϕ , is not defined by this relation; however, it is eliminated by requiring that when $d_1 = d_2 = 0$, the x_1 and x₂ axes of the coordinate system fixed to the molecule coincide with the corresponding axes of the system fixed to the preferred molecular orientation direction. Carrying out the transformation, using Euler angles as an intermediate step, it is found that the change in susceptibility due to a local change in orientation from that of the preferred direction is given by

$$\dot{\Delta}_{X}^{\star} = \Delta P \begin{bmatrix} d_{1}^{2} & d_{1}d_{2} & d_{1}d_{3} \\ d_{1}d_{2} & d_{2}^{2} & d_{2}d_{3} \\ d_{1}d_{3} & d_{2}d_{3} & 1 - d_{3}^{2} \end{bmatrix}$$
(4.3)

in the coordinate system fixed to the preferred orientation direction of the liquid crystal. Here ΔP is equal to the difference $\chi_1 - \chi_2$. Restricting \tilde{d} to be of unit length and considering small fluctuations, the following approximations can be made:

$$\hat{\Delta}_{X}^{2} = \Delta P \begin{bmatrix} d_{1}^{2} & d_{1}d_{2} & d_{1} \\ d_{1}d_{2} & d_{2}^{2} & d_{2} \\ d_{1} & d_{2} & d_{1}^{2} + d_{2}^{2} \end{bmatrix}$$
(4.4)

where the x_3 axis is taken to coincide with the equilibrium director direction. This is the desired result. The susceptibility fluctuations are uniquely related to the fluctuations, d_1 and d_2 , in the director through (4.4).

The preceding work has connected the results of Chapters II and III; therefore, some salient features of the experimental results may now be examined which justify the approximations and assumptions made in the theoretical development. We begin by reiterating the results of Chapters II and III and examining more closely the significance of the equations. Consider the correlation $\langle d_2(\vec{x},t) \ d_2(\vec{x}',t') \rangle$ since this is, in fact, the correlation which is measured in the experiment. The results of Chapter II imply that the Fourier transform of this quantity is given by

$$\left\langle d_{2}(\vec{x}',t' \ d_{2}(\vec{x}' + \vec{x},t + \tau) \right\rangle = \frac{C_{0}}{-\alpha(q) + i\omega}$$
(4.5)

where α is given by (as in Chapter II)

$$\alpha(q) = a_1 q_1^2 + a_2 q_2^2 + a_3 q_3^2 \qquad (4.6)$$

where \vec{q} is the Fourier wave vector and a_1 through a_3 are the constants describing the behavior of the liquid crystal (cf. Chapter II):

The susceptibility fluctuation selected by the experimental geometry is

 $\Delta \chi_{\text{measured}} = \Delta P d_2 \tag{4.7}$

and then, the parameter, σ , of chapter III becomes

$$\sigma(\vec{x},\tau) = (\Delta P)^2 \left\langle d_2(\vec{x}',t) \ d_2(\vec{x}' + \vec{x},t + \tau) \right\rangle.$$
(4.8)

Therefore, the spectral density of the photomultiplier anode current fluctuations reduces to (as calculated in Chapter III)

$$S(\vec{q},\omega) = \text{const } x \int_{-\infty}^{\infty} \left| \langle d_2(\vec{x}',t) | d_2(\vec{x}' + \vec{x}, t + \tau) \rangle e^{i\vec{q}\cdot\vec{x}} d^3x \right|^2$$
$$\cdot e^{-i\omega\tau} d\tau \qquad (4.9)$$

The quantity $\langle d_2 d_2 \rangle$, as derived in Chapter II, is already in a Fourier transform form, but it may be inverted in its temporal dependence, permitting substitution into (4.9). The quantity within the absolute value symbols in the above expression is, then, equal to

$$\int_{-\infty}^{\infty} \left\langle d_{2}(x',t) \ d_{2}(\vec{x}' + \vec{x},t + \tau) \right\rangle e^{i\omega\tau} d\omega = e^{-|\alpha(q)\tau|} \quad (4.10)$$

from (4.5). Placing this in the integral for the spectral density, it is found that (4.9) assumes the form

$$S(\vec{q},\omega) = \frac{f}{(2\alpha(q))^2 + \omega^2}$$
(4.11)

where f is a function of q, but not of ω . Thus, the spectral density of the anode current fluctuations has the form of a Lorentzian spectral distribution with a half-width, $\omega_{\rm HW}$, given by

$$\omega_{HW} = 2 |\alpha(q)|.$$
 (4.12)

Measurement of this width then yields data necessary to determine $\alpha(q)$.

Now that the theoretical formalism has been directly related to the experimental procedure, our attention can turn to some examples of the empirical spectral density and its q dependence. Figure 4.1 is typical of the spectra recorded on the recording wave analyzer. The dots along the curve follow a perfect Lorentzian curve as generated by a computer fit to the experimental data. The curves exhibited here are,



FIGURE 4.1. An Output Spectrum of the Wave Analyzer.

in actuality, square roots of Lorentzians since the rectifier in the wave analyzer is a linear full-wave detector which provides an output proportional to the square root of the input power spectrum.⁴⁸

The width of the Lorentzian spectrum is a function of $\dot{\vec{q}}$ through equations (4.12) and (4.6), and has a q^2 dependence, where, as defined in Chapter II, \vec{q} is the difference between the wave vector of the scattered light and the wave vector of the incident light, both in the scattering medium. Figure 4.2 shows a typical example of the dependence of the Lorentzian width on the Fourier wave vector \vec{q} . The solid lines are computer generated curves which give a best fit of $\alpha(q)$ to the data. The two parts of the figure are for the two different scattering geometries used in the experimental investigation. Examination of this dependence then allows determination of the parameters a_1 , a_2 , and a_3 . Note that the form of $\alpha(q)$ permits the determination of these parameters without the need of exploring all of q space. It is only necessary to vary q over two orthogonal planes to completely determine $\alpha(q)$. The correlation coefficients a1, a2, and a3 may, of course, be associated with the elastic and viscosity coefficients in Leslie's equations and in the Oseen-Frank equation. This shall not be done here, however, since it is more convenient to discuss only a1, a2, and a3. The next major concern is the temperature dependence of these quantities. This will be



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discussed in Chapter VI.

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CHAPTER V

THE EXPERIMENT

SELECTION OF THE SCATTERING GEOMETRIES

In Chapters II and III, expressions were obtained for the correlation function of the molecular orientation and the relation between the statistics of the scattered light intensity and the susceptibility. These results have been tied together in Chapter IV in order to provide a means for interpreting the results of the experimental investigation. The task now is to select scattering configurations which provide the connections between the scattered light and the molecular orientation fluctuations which correspond to the theory. In the following paragraphs, two scattering configurations will be described which permit this.

The basis for the selection of a scattering geometry is the equation from Chapter III:

$$\sigma(\vec{x},\tau) = \left\langle \vec{a} \cdot (\vec{\Delta \chi}(\vec{x}',\tau)\vec{\epsilon}) \ \vec{a} \cdot (\vec{\Delta \chi}(\vec{x}' + \vec{x},t + \tau)\vec{\epsilon}) \right\rangle. \quad (5.1)$$

The vectors \vec{a} and \vec{e} describe the direction of the analyzer and the incident polarization, respectively. It must be noted that the position of the detector determines uniquely the Fourier vector, \vec{q} , and the position of the analyzer, \vec{a} . The description of the analyzer in the above equation must be referred to the coordinate system fixed to the preferred direction of the liquid crystal. However, for experimental

convenience, \vec{a} is usually described by its position with respect to the detector. Since the detector position changes, \vec{a} is likely to change also; yet, certain scattering geometries allow changing the scattering angle (i.e., changing \vec{q}) without changing the description of the analyzer that must be used in (5.1). Two such geometries will now be described.

The first scattering configuration is shown in Figure 5.1. The x_3 axis is aligned with the preferred orientation direction, \vec{d}_0 , of the liquid crystal and x_1 lies along the wave vector of the incident light, \vec{k}_0 . The scattering plane is the x_1 x_3 plane and \vec{k}_s , \vec{k}_0 , \vec{q} , and $\vec{\epsilon}$ lie in this plane. The analyzer direction is chosen perpendicular to the scattering plane, i.e., in the x_2 direction, and is clearly independent of the position of the detector. Clearly then, for this configuration, the relation for σ reduces to

$$\sigma(\vec{x},\tau) = (\Delta P) \left\langle d_2(\vec{x}',t) \ d_2(\vec{x}' + \vec{x},t + \tau) \right\rangle$$
 (5.2)

and $\alpha(q)$, as defined in Chapter II, can be determined for any q_1 and q_3 , but with q_2 equal to zero. Thus, the correlation coefficients, a_1 and a_3 , may be determined from measurements made using this geometry.

The second scattering configuration is shown in Figure 5.2. This is the same as the configuration just described except the scattering plane is now the $x_1 - x_2$ plane, $\vec{\epsilon}$ is in the scattering plane in the x_2 direction, and the analyzer is in the x_3 direction. Clearly, \vec{a} , referred to the coordinate



FIGURE 5.1. The First Scattering Geometry.



FIGURE 5.2. The Second Scattering Geometry.

system which is fixed to the preferred orientation direction of the liquid crystal (the system shown in the figure) always remains in the x_3 direction. For this configuration, the relation for σ reduces to

$$\sigma(\vec{x},\tau) = (\Delta P) \left\langle d_2(\vec{x}',t) \ d_2(\vec{x}' + \vec{x},t + \tau) \right\rangle$$
 (5.3)

which is the same as before, except the vector, \vec{q} , is different. In this case, $\alpha(q)$ can be determined for any q_1 and q_2 , but for q_3 equal to zero; therefore, the correlation coefficients a_1 and a_2 can be determined from measurements taken using this scattering geometry.

Note that in both cases, the correlation in d_2 is measured regardless of the value of \vec{q} , provided \vec{q} is restricted to the proper plane in q space. The quantity of interest, d_2 , has thereby been isolated from the geometrical factors of the measurement, and no correction need be made nor scattering angle limitations imposed. These two scattering geometries are the ones used in the experimental measurements.

GROWTH OF ORIENTED NEMATIC LIQUID CRYSTALS

The experimental study performed here requires a preferred molecular orientation throughout the scattering volume since the interest here is in the fluctuations in molecular orientation about some known equilibrium direction. To fix this preferred direction, the sample of liquid crystal to be studied is prepared in a special way. The method that will be described has not been found to work with all liquid crystals; experiments with cholesteryl nonanoate indicate that the molecules can not be made to align parallel to a contacting surface; however, the method works well with para azoxyanisole.

The azoxyanisole samples used in this experiment are held between a specially prepared glass microscope slide and coverslip. After the glass and coverslip are prepared, the coverslip is placed on top of the glass slide with the treated faces in contact. The sizes are selected so that the coverslip is slightly smaller than the slide so that part of the glass slide is not covered by the coverslip. It is on this portion of the slide that the solid liquid crystal is placed. This ensemble is then placed in the scattering cell and heated to the desired temperature. When the liquid crystal melts, it is drawn into the space between the slide and coverslip by This aids in filtering out large foreign capillary action. particles which may be present in the unmelted solid. It also seems to provide a more uniform sample than if the liquid crystal were allowed to melt while between the slide and the coverglass.

To prepare the slide and coverslip so that the crystal will be oriented parallel to the glass, the microscope slide and coverglass are, first, cleaned using acetone or some similar agent. The glass and coverslip are handled only with forceps during this cleaning. The glass is then allowed to

No other chemical cleaning is done. Next, the glass and dry. coverslip are rubbed in one direction on a piece of typewriter paper. To insure that the rubbing is uniform and in one direction only, the paper is placed on a flat, smooth, hard surface and the glass slide or coverglass is moved back and forth on the paper with one edge forced firmly against a straight guide. A convenient guide is a piece of glass held firmly down, securing the paper beneath it. Forty or fifty up and back strokes is more than adequate to prepare the surface. During the rubbing, the rubbed glass is held through a tissue to prevent grease from the hands from contaminating the surface. After the rubbing operation is completed, the rubbed surfaces of the slide and coverglass are placed in contact with each other, taking care to align the directions of the rubbing. The solid crystal is placed on the glass as described above and then melted. A nematic melt of para azoxyanisole prepared in this way will have its molecules parallel to the glass and the direction of rubbing.

Allowing the liquid crystal to return to the solid state will tend to deteriorate the aligning effects of the surface; therefore, if the sample is allowed to cool to the solid state, a new sample must be prepared and the old one discarded. New glass slides and coverslips are used for each newly prepared sample, thereby insuring that no effect of the previous preparation procedure will alter the new sample. Alignment of
the nematic melt is checked by viewing the crystal through two polaroids at various angles in white light.

THE EXPERIMENTAL PROCEDURE

The scattering geometries required to select the desired components of the susceptibility tensor have been described in Section 2.1. These descriptions, along with that of the light detection scheme of Benedek (see Chapter III), form a complete prescription for the experimental arrangement. The light source for our study is a Spectra-Physics Model 122 He-Ne laser. Light from this source passes through a temperature controlled scattering cell, which contains the liquid The scattered light exits the cell in the forward crystal. direction and is intercepted by a screen which contains a pinhole aperture. In this way, only the light scattered at a particular angle is passed through to the analyzer and photomultiplier tube. Fixing the aperture position uniquely determines the Fourier wave vector, \vec{q} . The anode current of the photomultiplier, an RCA 1P21, is observed by monitoring the voltage which appears across the anode load resistor. The spectrum of this noise voltage is then measured by a General Radio 1910A recording wave analyser, set at 10 Hz. bandwidth.

The requirements on the design of the scattering cell are stringent in that the cell must provide a constant temperature environment for the liquid crystal, while simultaneously

allowing the passage of light in and out of the cell. The cell is machined from solid brass and has two cavities, one for the liquid crystal with apertures front and back to allow the passage of light, and another for the electric heating element. The front, and larger access to the cavity for the liquid crystal is sealed off using electrically heated conducting glass, while the rear, and small access hole is sealed by a microscope coverglass. The cell temperature is controlled by an automatic electronic device which supplies the heating element with a corrected voltage proportional to the error in resistance of a resistance wire thermometer from a predetermined value.

DATA PROCESSING

After the essential data has been acquired, it must be reduced to a form permitting relation to the quantities in the equations set forth in Chapter II and III. The three major steps in the data reduction are as follows: first, \vec{q} inside the scattering volume must be determined through knowledge of the pinhole aperture position, the incident polarization, and the analyzer direction; second, the Lorentzian half-width must be computed from the whole of the spectrum recorded on the wave analyzer; and third, the parameters in α (q) must be determined from the \vec{q} dependence of the spectral width.

In the calculation of the vector $\vec{q} = \vec{k}_s - \vec{k}_o$, the values

of \vec{k}_{s} , the scattered wave vector, and \vec{k}_{o} , the incident wave vector, must be corrected for inside the scattering medium; for although only single scattering has been assumed in Chapter III, both the incident and scattered fields experience an average susceptibility $\langle \vec{x} \rangle$, throughout the scattering volume through which they propagate. Therefore, \vec{k}_{s} and \vec{k}_{o} must be corrected using knowledge of the refractive index of the ordinary or extraordinary waves and the components of these wave vectors outside the scattering volume. Envoking Snell's law and the condition that the incident and refracted wave vectors and the interface normal are coplanar, it is found that

$$\vec{k}_{11n} = \vec{k}_{11}$$
 (5.4)

and

$$k_{\perp n}^{2} + k_{o}^{2} = k_{\perp}^{2} + k_{o}^{2} n^{2}$$
 (5.5)

where k_0 is the mean free space wave number of the incident laser light, n is the index of refraction of the liquid crystal for the polarization of interest, and the subscript, n, indicates those quantities within the liquid crystal volume. Those quantities without the subscript n are outside the scattering volume. In addition, the subscripts 11 and \perp indicate those components which are parallel and perpendicular, respectively, to the interface plane between the liquid crystal and the surrounding space. The indices of refraction used in these equations are determined, through linear interpolation, from the refractive index data of Chatelain, for the polarization, temperature, and wavelength of interest.⁵⁰

Having the knowledge of q, the next requirement is to determine the Lorentzian half-width from the spectral data. The recorded spectrum of the photomultiplier anode current is not normalized and may contain a small amount of white noise. The data is fit, by the least mean square error criterion, to the square root of a normalized Lorentzian by numerically minimizing the function

$$F(\omega, A, B) = \frac{\sum_{i=1}^{n} \{D(\omega, f_{i}) - (AV_{i} - B)\}^{2}}{\{\sum_{i=1}^{n} D(\omega, f_{i})\}^{2}}$$
(5.6)

with respect to the unknown parameters, ω , the Lorentzian half-width, A, the normalization factor, and B, the noise level. The summations in (5.6) are over all data points: the recorder voltages, V_i at frequency f_i, where f is in Hertz for convenience. The function D(ω_{HW} , f) is the Lorentzian form

$$D(\omega_{HW}, f) = \left\{ \frac{\omega_{HW}}{\pi \left[(2\pi f)^2 + \omega_{HW}^2 \right]} \right\}^{\frac{1}{2}}.$$
 (5.7)

The normalization constant and noise level are determined analytically and uniquely for a particular ω through

$$\frac{\partial F}{\partial A} = 0$$
 and $\frac{\partial F}{\partial B} = 0$

respectively; thus the computer need only search along a line

(ω) to determine the minimum of F in (5.6). The denominator of this function is included to prevent the computer from drifting to $\omega \rightarrow 0$, A $\rightarrow 0$, or $\omega \rightarrow \infty$, A $\rightarrow 0$ and overlooking the proper minimum. After the minimization is complete, numerical values for ω_{HW} , A, and B are obtained for the particular \vec{q} and temperature at which the spectrum was observed. Similar data reduction techniques are used to determine a_1 , a_2 and a_3 through the empirical values of ω_{HW} as a function of \vec{q} at some specified temperature.

CHAPTER VI

EMPIRICAL TEMPERATURE DEPENDENCE OF THE CORRELATION COEFFICIENTS

INTRODUCTION

The theory of the dynamics of the fluctuations in molecular orientation has been derived from Leslie's equations and the Oseen-Frank equation. These equations contain elastic moduli and viscosity coefficients which are functions of temperature. However, the theories consider macroscopic behavior; consequently no investigation is made of the temperaature dependence of these parameters. In proposing a model for such an investigation, one must view the liquid crystal on a microscopic level describing, in some way, the intermolecular forces. A statistical molecular theory was developed in this way by considering primarily dipole-dipole interaction. This theory predicts a unique temperature dependance of the elastic moduli k_{11} , k_{22} , and k_{33} . Explicitly, it is found (both in the theory and in the experimental verification) that each elastic modulus follows the form^{51,52}

$$k = \frac{s^2}{\sqrt{7/3}} C_k$$
 (6.1)

where V is the mole volume, C_k is a constant, and S is an ordering parameter which depends on V and the temperature through an implicit relation. The ratio of the elastic moduli

is then independent of temperature and is empirically found to fit (for para-azoxyanisole)

$$k_{22} : k_{11} : k_{33} = 1.0 : 1.6 : 3.8$$
 (6.2)

A statistical approach was also taken by Helfrich in his study of certain viscosity coefficients.⁵³ Taking a model of the molecular interaction as osculating ellipsoids, the theory predicts λ_1 to follow

$$\lambda_1 = \frac{T^2}{V^2} C_{\lambda} \tag{6.3}$$

where T is the temperature in degrees Kelvin, and C_{λ} is a constant. Unfortunately, Helfrich limited the comparison of his theory with the measured values to one temperature, inferring the value of λ_1 from dielectric measurements on flowing, magnetically oriented para-azoxyanisole.⁵⁴ Further checks made on the theory indicate that (6.3) predicts the proper trend. Saupe's and Helfrich's theories, therefore, provide a reasonably verified theoretical dependence of the ratio k/λ_1 , (where k is k_{11} , k_{22} , or k_{33}) on temperature.

It is unfortunate that no data is available on k_{24} . While it does appear in the theory, Frank mentions that it is zero for "planar structures". Some have asserted that this parameter has no meaning and was included by Frank through an oversight, while others ignore k_{24} entirely.⁵⁵ Although there is confusion concerning this elastic modulus, the purpose in mentioning it is not to attempt to resolve the issue, but rather to point out that if k_{24} is indeed nonzero, then the theory, for our purpose, is incomplete. This shall be discussed later. First, it is desirable to discuss results at some specified temperature.

VALUES OF a1, a2, AND a3 AT 125°C

There have been experimental measurements taken which allow the determination of the parameters k_{11} , k_{22} , k_{33} , and λ_1 (either directly or by inference). We wish to compare these results to the values of a_1 , a_2 , and a_3 obtained in this study. This comparison shall be made at 125°C. Values of the elastic moduli have been obtained by Saupe⁵⁶ and by Zwetkoff⁵⁷ while λ_1 may be inferred from the dielectric anisotropy of a flowing, oriented nematic melt.⁵⁸ Table 1 is a summary of the data on k_{11} and λ_1 and includes values of a_1 calculated from this data. For comparison, the value of a_1 obtained by direct measurement is also included.

	k ₁₁	^λ 1 [*]	a _l calc.	a _l meas.
	x10 ⁷	x10 ²	x10 ⁵	x10 ⁵
Saupe	6.08		1.81	
		3,35		0.466
Zwetkoff	4.5		1.34	•

*Anisotropy data of Marinin and Zwetkoff yia the theory of Helfrich

TABLE I

The measured value is about one third to one fourth the value calculated from the published data. Although agreement is fair, it is most likely that if an error exists in the published data, the value of λ_1 is the most doubtful since it has not been as extensively verified as the elastic moduli.

There is another alternative to the comparison. From Saupe's elastic moduli data and our a_1 , one finds that $\lambda_1 =$ 13.0 centipoise. Then taking $k_{24} = 2.3 \times 10^{-6}$ dyne, we find that $a_2 = 1.2 \times 10^{-5}$ and $a_3 = 2.0 \times 10^{-5}$. These values are in reasonably good agreement with the measured values $a_2 =$ 0.82×10^{-5} and $a_3 = 2.32 \times 10^{-5}$ cm²/sec. The comparison is not as good if k_{24} is taken to be zero.

From this presentation, it can be concluded that the results of this experimental study compare favorably with those of other investigators at 125° C. The next concern is of the temperature dependence of the parameters a_1 , a_2 , and a_3 . This interest is primarily of the form of the variation with temperature rather than the actual magnitude of the coefficients.

TEMPERATURE DEPENDENCE OF a1, a2, AND a3

The theory predicts that the values of these coefficients should monotonically decrease with increasing temperature. In addition, it is noted that this temperature dependence is followed by a_1 , a_2 , and a_3 as calculated from the empirical values of the elastic moduli and the dielectric anisotropy measurements. Yet, the dependence observed in this study is, in general, an increase in these parameters with increasing temperature; a direct contrast to the expected variation. Moreover, the coefficients are observed to experience an anomalous change near 128° C. At this temperature a_3 reverses its trend, and above 128° C it decreases with increasing temperature. The parameter a_2 experiences what appears to be a discontinuity, diverging to large values at this same point. Divergence of the coefficients is also observed as the nematic-isotropic transition is approached--a trend indicated in the published data but not fully investigated by these authors. Let us begin the detailed presentation by examining the temperature dependence of a_1 .

It has been mentioned previously that a_1 increases with increasing temperature and, as the nematic-isotropic transition is approached, this parameter diverges to large values. Figure 6.1 displays the variation in a_1 with temperature throughout the entire nematic range. The solid line in the figure is a plot of f(T) fitted to the data, where f(T) is given by

$$f(T) = A |T/T_m - 1|^{\gamma}$$
 (6.4)

The melting point temperature, T_m , is taken to be 132.0°C. It is found from this fit that γ is approximately equal to -0.17. Note how closely a_1 follows this assumed curve over the entire nematic region; the fit to a straight line when $\ln(a_1)$ is plotted versus $\ln(T_m - T)$ is remarkably good, especially for values within a few degrees of the melting point.



FIGURE 6.1. The Temperature dependence of a1.

It can be seen from this curve that although a_1 does not follow the predicted dependence, a smooth, upward trend in a_1 with increasing temperature is indicated.

The dependence of a_3 shares a similar trend, as shown in Figure 6.2, with the exception of a change in slope near 128°C. Unfortunately, the data obtained for a_3 does not make obvious a likely analytic form for the temperature dependence of this quantity. Nevertheless, some qualitative observation can be made. It is clear from the figure that a_3 increases, in general, with increasing temperature. This trend continues up at a rate of approximately 1.4 $\times 10^{-5}$ /°C to approximately 128°C, above which a possible downward trend is indicated. The upward trend of a_3 apparent here is again in contrast with the expected temperature variation. Little else can be said concerning a_3 at the present time.

The quantity a_2 has a completely anamalous, yet consistent behavior. Above the solid-nematic transition temperature, a_2 experiences an increase with increasing temperature. However, a divergence of this parameter is observed near 128°C; a_2 tends to large values as this temperature is approached from either side. This behavior is indeed present at a temperature below the nematic-isotropic transition temperature since the values of a_1 taken in conjunction with a_2 follow those taken in conjunction with a_3 . The measured quantity common to both scattering configurations, a_1 , varies smoothly



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FIGURE 6.2. The Temperature Dependence of a₃

through $128^{\circ}C$, diverging at the higher transition temperature. This indicates the existence of the anomaly at approximately four degrees below the nematic-isotropic transition temperature. The divergence of a_2 at this temperature, which we now denote as T_{o} , is assumed to follow

$$a_{2}(T) \rightarrow A | T/T_{O} - 1 |^{\gamma}$$
(6.5)

Figure 6.3 displays the temperature dependence of a_2 , with the solid lines being, as usual, the fitted curve following the assumed form of the variation with temperature. Below T_0 , it is found that A is approximately equal to 1.5 x 10^{-6} cm²/sec and γ is approximately -0.44, while for above this temperature, A is approximately 5.5 x 10^{-6} cm²/sec and γ is -.10. For the best fit of the assumed curves, T_0 is found to be $128.7^{\circ}C$. This striking difference in the temperature dependence of a_2 from the expected variation seems to indicate that these measurements reveal more character of the liquid crystal than is discernible through less direct measurement methods.

DISCUSSION AND CONCLUSION

Several marked differences are noted between the results obtained in this study and in the theoretical and experimental results obtained by others. It is the purpose here to discuss these differences and suggest both experimental and theoretical areas in need of further investigation. First, the anomaly at temperature T_o will be considered.



FIGURE 6.3. The Temperature Dependence of a2.

The observed variation of a2 exhibits marked divergence at T_0 , with the divergence fitting $A|T/T_0-1|^{\gamma}$. Moreover, the trend of a₃ indicates a possible change in slope at this same temperature. Since T is within the nematic range, it must be concluded that a type of second order phase transition occurs at this temperature. This transition is categorized as a "type" of second order transition since the divergence of a₂ at T₀ is not common to the other coefficients. Observations made by others on the temperature dependence of the scattered light spectrum for temperatures above the nematic isotropic transition indicate that a second order transition does take place at a temperature slightly below the nematicisotropic phase transition.⁵⁹ It must be noted that the theory of Saupe does not predict a second order phase transition in the range in which the liquid crystal is nematic. The possibility of such transitions should be considered in the light of the results of this experiment.

Experimental results of other authors to which we have previously referred indicate that a_1 , a_2 , and a_3 decrease rather than increase as the temperature is raised. Yet, the measurements on λ made by these researchers necessitates a flowing melt. Since the flow through parallel plates or capillary tubes can not be expected to be with uniform cross-sectional velocity, it is apparent that the substance under study is not in thermodynamic equilibrium. Although bulk continuum

properties were measured in these experiments, it seems unlikely that they bear a connection to fundamental thermodynamic properties of the nematic melt. It is also possible that, if second order phase transitions do take place, they would be difficult to observe under such circumstances. Light scattering measurements, like those made in this study, provide the means to determine these latter properties.

It is, of course, expected that the parameters a1, a2, and a₃ will experience a discontinuity at the nematic-isotropic transition temperature. This is apparent in the data of a₁ which diverges to large values at the transition point following $A|T/T_m-1|^{\gamma}$. It is less obvious in the trend of a_3 and to an even lesser extent in a2. Examination of Figure 6.3 reveals that the temperature dependence of a, is dominated by the second order transition; thus details of the nematicisotropic transition are not discernible in this figure. The same conditions also apply in Figure 6.2; however, a trend to small values of a₃ at the isotropic transition may be indicated. Finally, it may be said that, although the temperature dependence of a₃ is rather vague, the behavior of a₁ and a₂ are clearly indicated in the results presented in Figures 6.1 and 6.3. As has been indicated, these results are unique and warrant further study.

In conclusion, it is desirable that some comments be made about further experimental investigation. The method of data

acquisition used in this study requires a relatively long measurement time at one temperature. This has two undesirable features. First, for example with a_3 , approximately fifty hours of spectra recording are required to take the data displayed in Figure 6.2. Clearly, changes could take place during this time which obscure the true trend of the measured parameters. Second, the taking of a plethora of data which may be averaged is precluded, thus no reasonable estimate of the experimental error can be determined. Part of the solution is obtaining the correlation given in (4.10) in real time, a process taking fractions of a second as opposed to many minutes. Real time correlation should be the next step in any continued research. Such procedures would allow greater detail of the temperature variation of a_1 , a_2 and a_3 to be determined.

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