LIGHT SCATTERING STUDIES OF ORIENTATIONAL ORDER IN LIQUID CRYSTALLINE TETRAPODES AND LYOTROPIC CHROMONIC LIQUID CRYSTALS

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CHAPTER 1
INTRODUCTION: LIQUID CRYSTALS AND THE SCOPE OF THIS DISSERTATION

Liquid crystals, or LCs, are phases of molecular matter whose degree of orientational and/or positional order lies intermediate between crystalline solids and isotropic liquids. The most common liquid crystalline phases remain fluid-like; they flow and can take the shape of a container. They are cloudy, indicating structural correlations or dynamical fluctuations at optical wavelengths (i.e., orders of magnitude above the constituent molecular size). The molecules of LCs, which are called as mesogens, exhibit three basic classes of ordering in the bulk: orientational order, positional order, and bond-orientational order. The orientational order is characterized by breaking of a continuous rotational symmetry; in the simplest case (the uniaxial nematic phase), the long axis of rod-like molecules is on average parallel to a well defined spatial direction, described by a unit vector known as the director, \( \hat{n} \). In the case of the more highly ordered smectic phase, continuous translational symmetry is broken in at least one-dimension, producing a layered structure. On the other hand, bond-orientational order is characterized by a bond which is defined as a line in space joining center of masses of two adjacent molecules; this type of order develops when the orientation of the bonds is preserved over
a long range. It typically develops in the layer planes of one-dimensionally layered smectics.

The credit for the discovery of the liquid crystalline state goes to an Austrian botanist named Friedrich Reinitzer. In 1888, Reinitzer observed two melting points of a substance related to cholesterol--one from solid to an optically anisotropic fluid (LC phase) and the other from the LC to an isotropic liquid. Otto Lehmann, a professor in Germany, first labeled such substances as “liquid crystals” and performed the first detailed optical characterization. Interest in LC research increased after World War II. Glenn Brown, an American chemist, pioneered the modern era of LC research. He founded the Liquid Crystal Institute in Kent State University and organized the first of a continuing series of International LC conferences. Steady development of industrial and consumer applications of LCs, combined with basic studies of structure and phase transitions in condensed matter, has promoted dramatic growth in LC research in recent decades.

LCs are widely known these days because of their application in liquid crystal displays, or LCDs. LCDs are used in flat screen TV and computer monitors, as well as in smaller formats (cameras, watches, signage etc). Related examples of LC technology include switchable windows, thermometers and other sensors, and electronic-books. Progress in understanding LC phases also aids the understanding of more complex soft materials, such as the cell membrane, and of natural processes – e.g., certain diseases such as sickle-cell anemia. DNA, certain viruses and bacteria also exhibit LC phases.
Typical LCs are formed from organic molecules consisting of rigid aromatic core of benzene rings and flexible end groups. The cores can be straight or bent-shaped. Straight core LCs are referred to as rod-like or calamitic, while bent-core LCs are described as “banana”-shaped or bowl-like. Some other types of LCs include discotics, disc-like mesogens; sanidic, brick-like or plank-like mesogens; and main or side-chain polymer liquid crystals. The mesogenic entities can be single molecules or a group or aggregate of molecules. LCs can be lyotropic or thermotropic. Thermotropic LCs are formed from pure compounds or neat mixtures as the temperature is lowered from the isotropic fluid state. A second major class, lyotropic LCs, typically develop on dissolving sufficient amounts of small molecules with hydrophilic/hydrophobic ends, or rod-like polymers, in aqueous solvents. At certain (fairly high) concentrations [1], the free energy of these mixtures favors LC phases, which may occur in the form of orientational ordering of anisotropic aggregates (lyotropic nematic) or as planar bilayers of molecules (lamellar phases analogous to a thermotropic smectic).

1.1 THERMOTROPIC LIQUID CRYSTALS

The most common thermotropic LCs are calamitic LCs composed of small molecules (mesogens) with the anisotropic shape of elongated ellipses or cigars; a typical length and diameter are ~25 Å and ~5 Å, respectively. Common calamitic molecular structure and two basic, illustrated by the two LC compounds 5CB, and MBBA, is shown in Figure 1.1. As the temperature is changed, thermotropic mesogens start to order
Figure 1.1 Typical molecular structure of calamitic LCs, and two common calamitic LCs: 5CB and MBBA.
forming a myriad of partially ordered phases through temperatures that may range from ~200 to ~0°C.

By far the most well-known thermotropic liquid crystal phase is the nematic ($N$) phase, obtained on cooling from the isotropic ($I$) liquid. There are two basic types of nematic phase: a uniaxial nematic, $N_u$, and a biaxial nematic, $N_b$. In thermotropics, the observed phase is almost exclusively uniaxial; it is characterized by a long range orientational order along a single axis (typically the average long axis of the molecules), termed the director $\hat{n}$. The system is invariant to any rotations about $\hat{n}$ and to inversion of $\hat{n}$. The degree or magnitude of local order may be described by an orientational order parameter defined as $\langle \frac{3}{2} \cos^2 \theta - \frac{1}{2} \rangle$, where $\theta$ is the angle between a specific molecular axis (e.g., long axis of a calamitic) and the director $\hat{n}$. The angled brackets refer to a local average over the molecular axis orientation. This quantity measures the average degree of molecular alignment with respect to the director [2]; it vanishes in the $I$ phase where $\langle \cos^2 \theta \rangle = \frac{1}{3}$, and is unity when the director $\hat{n}$ is equivalent to the long molecular-axis and $\langle \cos^2 \theta \rangle = 1$ or equal to $-\frac{1}{2}$ when $\hat{n}$ is defined by the short molecular axis and $\langle \cos^2 \theta \rangle = 0$. (Recall the director is the symmetry axis; thus it need not always correspond to the long molecular axis.) A simpler order parameter – e.g., $\langle \cos \theta \rangle$ – cannot be used due to the requirement of inversion symmetry in $\hat{n}$.

The phase transition from $I$ to $N_u$ is first order with a discontinuity in the order parameter and the presence of latent heat. A schematic illustration of the $N_u$ and $I$ phases
of a thermotropic is shown in Figure 1.2. The biaxial $N_b$ phase will be discussed in detail in the next section.

The introduction of a chiral molecule, a molecule having its mirror image different from itself, into an achiral nematic system produces a helical distortion of the director. The phase so formed is known as the cholesteric phase. In the cholesteric phase, the local director rotates (or twists) about an axis periodically in space. The period of rotation is defined as the pitch; it is typically much longer than the molecular size and is of the order of an optical wavelength.

Typically, as the temperature of a thermotropic is lowered from $N_a$ phase, a one-dimensional positional ordering, characterized by the formation of planar layers, may develop; together with the long range nematic orientational order, this forms a smectic, $Sm$, phase. The simplest smectic, smectic $A$ phase or $SmA$, is shown in Figure 1.2. It consists of a layered structure with 1D quasi-long range positional order exhibited along the layer normal. The long axis of calamitic molecules is on average normal to the layers with short range bond-orientational order within the layer. Quasi-long range order is characterized by an algebraic decay of interlayer positional correlations, and is a feature of positional order in 1D. The direction along the normal to the smectic layers is conventionally chosen as $\hat{z}$; the $SmA$ phase is invariant under the transformation of $\hat{z}$ to $-\hat{z}$.
Figure 1.2 Crystalline phase, different LC phases, and an isotropic liquid phase of calamitic molecules. \( \hat{n} \) represents the orientational direction of the molecules.
In the Smectic \( C \) phase, \( SmC \), as shown in Figure 1.2, the molecules are tilted at an angle with respect to \( \hat{z} \); the \( \hat{z} = - \hat{z} \) symmetry is consequently broken. The \( SmC \) phase is orientationally biaxial -- broken translational symmetry along the layer normal introduces broken rotational symmetry along it leading to biaxiality. The chiral smectic \( C \), \( SmC^* \), features a helical precession of the tilted molecules about \( \hat{z} \), with a pitch greater than the interlayer spacing. Locally the \( SmC^* \) has a net polarization along a two-fold rotation axis parallel to the layers and perpendicular to the tilt plane; thus this phase is ferroelectric within layers (and “helielectric” over length scales along \( z \) comparable or greater than the pitch).

At lower temperatures, long range bond orientational order develops, followed by long-range positional order, within the layers, resulting in a cascade of higher-order (lower symmetry) smectic phases, eventually ending with a 3D molecular crystal. These differ from conventional solid-state, atomic crystals in that the molecules can still undergo limited rotational diffusion.

An interesting LC phase formed by disk-like mesogens is the columnar phase. This phase, characterized by orientational and 2D positional order, is obtained when columns consisting of discs stacked one on top of the other pack closely in the plane perpendicular to the column axis. The columns arrange into a 2D, typically hexagonal, lattice. However, there is no positional order of molecules along the columnar axes.
1.1.1 BIAXIAL NEMATIC LIQUID CRYSTALS

Freiser in 1970 [3], through the generalization of the Meier Saupe theory of the nematic phase in thermotropic liquid crystals, predicted a biaxial nematic (\(N_b\)) phase – an anisotropic fluid possessing two orthogonal axes of orientational order characterized by a uniaxial director, \(\hat{n}\), and a (perpendicular) biaxial director, \(\hat{m}\) (so that \(\hat{m} \cdot \hat{n} = 0\)). There are also two corresponding scalar order parameters - in the language of molecular orientational averages, these are \(\left\langle \frac{3}{2} \cos^2 \theta - \frac{1}{2} \right\rangle\) (the uniaxial order parameter introduced earlier) and \(\left\langle \sin^2 \theta \cos 2\phi \right\rangle\) to describe biaxial order. Here \(\phi\) may be defined as the angle between the director \(\hat{m}\) and projection of longest molecular axis (\(\hat{z}\) axis) on the plane perpendicular to \(\hat{n}\), and the angled brackets refer to a local average over \(\theta\) and \(\phi\) [4-7]. Figure 1.3 shows a schematic of the \(N_b\) phase for systems of different mesogens; here the third axis \(\hat{l} = \hat{m} \times \hat{n}\) is automatically ordered due to the ordering of \(\hat{n}\) and \(\hat{m}\). In contrast to the \(N_u\) phase, the \(N_b\) phase is anisotropic in the plane perpendicular to \(\hat{n}\). Thus, there are three principal directions along which the plane polarization of electromagnetic waves is preserved, with corresponding phase velocities given by \(v_i = c / \sqrt{\epsilon_i} \) \((i = 1,2,3)\), where \(\epsilon_i\) are principal values of the dielectric tensor, versus two in a \(N_u\) phase, \(v|| = c / \sqrt{\epsilon||}\) and \(v\perp = c / \sqrt{\epsilon\perp}\). (Here || refers to the direction of \(\hat{n}\).) Since most of the physical properties (mechanical, electrical, optical) of the \(N_b\) phase are still
Figure 1.3 Upper left: biaxial nematic phase of plank-like molecules; upper right: main (uniaxial) director, $\hat{n}$, and the secondary (biaxial) director, $\hat{m}$. Lower right: biaxial nematic phase of bent-core molecules; and lower left: biaxial nematic phase of a mixture of rods and discs [8].
dominated by \( \hat{n} \); \( \hat{n} \) is sometimes called the main director and \( \hat{m} \) is called a secondary or minor director.

The \( N_b \) phase has attracted much attention because of its interesting static and dynamic properties and possible device applications. It is predicted that the \( N_b \) phase could improve current display technologies and open a new avenue for LCD development [9, 10]. As shown in Figure 1.4 today’s LC devices rotate cylindrical molecules around the short axis by an applied electric field. In the \( N_b \) devices, an in-plane field could be used to rotate the molecules around the long axis, providing a new electro-optical degree of freedom and additional, potentially useful optical states for a display. Moreover, it has been suggested that the rotation of minor director \( \hat{m} \) could be as much as 100 times faster than the rotation of the main director \( \hat{n} \) [10-13]. This may lead to potentially faster and low power consuming new types of electro–optical devices [14]. The use of the \( N_b \) phase in the zenithally bistable family of devices that utilize defects may also produce improved switching properties. Additionally, novel optical compensation films may be based on the \( N_b \) phase.

After Freiser’s prediction, a flurry of both theoretical and experimental works were performed over the ensuing decade, culminating in the experimental demonstration of a \( N_b \) phase in a lyotropic mixture of KL-1-decanol-D\(_2\)O in 1980 by Yu and Saupe [15]. They observed the \( N_b \) phase between two uniaxial nematic phases, one composed of rod-shaped micelles and the other of disk-shaped micelles. The two uniaxial nematic phases are designated as \( N_C \) and \( N_L \), respectively. For 68 wt.% of D\(_2\)O concentration, the phase on heating and cooling were observed as \( N_L \Leftrightarrow N_b \Leftrightarrow N_C \). Convincing evidence of
Figure 1.4 Upper left: a twisted nematic cell in the absence of electric field. Upper right: the switching of molecules in the \( N_u \) phase due to applied electric field. Lower panel: proposed biaxial nematic device using in-plane fields to rotate the long axis of the molecules.
biaxiality was subsequently found in certain polymer nematics [16, 17]. However, nematic biaxiality in low molecular weight thermotropics proved elusive for nearly another 25 years.

Alben [18] first argued theoretically the possibility of the $N_b$ phase by mixing prolate (rods) and oblate (discs) mesogens. Over a certain range of compositions, there is a combined preferential alignment of rods in one direction and the discs along other direction perpendicular to the direction of alignment of rods. The possibility was investigated by different methods [19, 20]. However, the experimental research has been hampered due to the lack of fully miscible rod and disc shaped mesogens [10, 21-25]. Computer simulations [26] and mean-field calculations [27] have shown that the difficulty in producing such a biaxial mixture is due to its instability with respect to the decomposition into two uniaxial nematic phases--one rich in rods and the other rich in discs. A schematic representation of a $N_b$ phase formed by a mixture of rods and discs is shown in Figure 1.3.

The first systematic attempt to obtain the $N_b$ phase in low molecular weight thermotropic compounds concentrated on bridging the gap between rod-like and disk-like mesogens by combining their morphologies in a single molecule. Malthete et al. [28] in 1986 reported the observation of the optical texture expected of the $N_b$ phase in spoon like molecules $4-[3,4,5-\text{tris}(4\text{-dodecyloxybenzyloxy})\text{benzoyloxy}]-4'(4\text{-dodecyloxybenzoyloxy})-1',1'\text{-biphenyl}$ (Figure 1.5 (i)). Chandrashaker et al. [29] reported the conoscopic observation of the $N_b$ phase in cross shaped molecules of a copper complex (Figure 1.5 (ii)) in 1988. Similarly, in 1990 Praefcke et al. [30] reported the
Figure 1.5 Some molecules reported to form a thermotropic biaxial nematic phase.
conoscopic observation of biaxiality in a disk shaped molecule 2,3,4-trihexyloxycinnamic acid (Figure 1.5 (iii)). Chandrashaker et al. in 1996 [31, 32] again reported evidence of the $N_b$ phase in 4,4"(p-terphenyl)-bis[2,3,4-tri(dodecyloxy)benzal]imine (Figure 1.5 (iv)) by DSC, optical textures, conoscopy, and optical transmittance.

However, these earlier experimental searches for biaxiality in low molecular weight thermotropic compounds were not free from artifacts attributable purely to surface effects [10, 11] (as opposed to a true thermodynamic broken symmetry). Surfaces can induce an apparent biaxiality in optical microscopy even if the bulk sample is uniaxial: this is because the director $\hat{n}$ may be tilted with respect to the surface normal. Deuterium NMR spectroscopy, which is largely free from the influence of surface forces on the director, could provide a more definitive identification of biaxiality. In deuterium NMR spectroscopy the LC sample is rotated perpendicular to a magnetic field. Above a certain critical speed of rotation, for the positive diamagnetic anisotropy, the director $\hat{n}$ is observed to be randomly distributed in a plane perpendicular to the spinning axis [33]. For the $N_a$ phase the NMR spectra consists of two pairs of quadrupolar splitting: an outer pair of lines associated with the $\hat{n}$ director parallel to the magnetic field and an inner pair of lines associated with the $\hat{n}$ director orthogonal to the magnetic field. For the $N_a$ phase, the ratio of the outer and inner quadrupolar splitting is equal to 2:1 while it deviates from 2:1 for the $N_b$ phase. Deuterium NMR spectroscopy applied to the compounds in Figure 1.5 (i, iii, iv) found no detectable bulk biaxiality [34, 35], which made the issue of a thermotropic $N_b$ phase a highly controversial subject.
In the early 2000s, researchers conjectured the possibility of a stable thermotropic $N_b$ phase in recently-synthesized bent-core (also known as banana, boomerang, bow-like, or V-shaped) mesogens, using computer simulations [10, 11, 36] (Figure 1.3). The explosion of interest in bent-core LCs originally arose with the observation of ferroelectricity [37] in certain smectic phases of achiral bent-core molecules. Bent-core LCs are generally composed of five aromatic rings with a meta-substituted central ring, linking groups, and terminal chains (Figure 1.6 (i)). The properties--such as core opening angle, polarity, transition temperature etc--of a bent-core mesogen can be altered by altering the substitutions to the general formula [38-40]. Theory has indicated that the stability of the $N_b$ phase of bent-core mesogens should depend on the anisotropy of the two arms and the angle between them [22]. Lubensky and Radzihovsky have predicted a myriad of exotic nematic variants along with the $N_b$ phase for the bent-core molecules [41]. Acharya et al. [42, 43] and Madsen et al. [8, 44] first observed the existence of the $N_b$ phase in bent-core compounds by X-ray diffraction and deuterium NMR spectroscopy, respectively. One such compound, derived from 2,5-bis-(p-hydroxyphenyl)-1,3,4-oxadiazole, is shown in Figure 1.6 (ii). Madsen et al. have suggested that strong electrostatic forces are crucial, at least for these materials, in stabilizing the $N_b$ phase. A quantitative study of the biaxial order parameter in a bent-core compound has also recently been done by Raman scattering [45].
Figure 1.6 (i) Schematic diagram of bent-core liquid crystal- X, X', Y, and Y' represent the linkage groups; R and R' represent the terminal chains; and R₂, R₄, R₅, R₆, A, and B represent lateral substituents [46], (ii) a bent-core molecule reported to show biaxial nematic phase [42], and (iii) left: 3-ring Si-core LC tetrapode and right: plank-like morphology of the tetrapode as suggested from X-ray scattering [4, 47].
In the last several years, the search for the $N_b$ LCs has also focused on thermotropic molecules having a plank-like or a quasi-flat platelet-shaped morphology. In the so-called LC tetrapodes, rod-like mesogens are tethered to a single atom (Ge or Si) core through four flexible siloxane spacers, thereby forming a quasi-flat platelet [48, 49] (Figure 1.6 (iii)). A conceptual picture of a $N_b$ phase of plank-like mesogens is shown in Figure 1.3. Theoretical studies using different techniques have suggested the presence of the $N_b$ phase in such molecules [5, 6, 50, 51]. For LCs in general, phenomenological theories predict different ways of reaching the $N_b$ phase: a direct, first order $I$ to $N_b$ phase transition or a first order $I$ to $N_u$ transition followed by a first or second order $N_u$ to $N_b$ transition, with the possibility of a tricritical point. The complete phase diagram can be elaborated in terms of a mean field model of Sonnet et al. [5]. Merkel et al. [4] has calculated the phase diagram for tetrapodes in terms of shape anisotropy of the biaxial dielectric susceptibility, $\lambda$, and reduced temperature, $1/\beta$ ($\beta = U_o/k_B T$, $U_o$ is the interaction energy between nematogenic molecules) which is shown in Figure 1.7. Hindrance of molecular rotations due to the mesogen-core linkages, or to interdigitation of mesogens connected to different cores, is expected to promote biaxial order [4, 47].

Experimental studies from different techniques – including infrared (IR) absorbance spectroscopy, dichroism (anisotropic optical absorption), and Deuterium NMR – have supported the existence of the $N_b$ phase in tetrapodic compounds [4, 52-54]. Merkel et al. have reported results that imply the presence of the $N_b$ phase below the $N_u$ phase; their conclusion is based on IR absorbance measurements on both 3- and 4-ring tetrapodes. Specifically, on cooling, Merkel et al observe a weak first-order transition.
Figure 1.7 Theoretical phase diagram showing the dependence of reduced temperature $1/\beta$ on the molecular shape biaxiality parameter $\lambda$. Solid and broken lines, separating different color regions, represent first- and the second order transitions, respectively. The point where these lines meet is the tricritical point. The vertical dotted lines give corresponding values of $\lambda$ inferred from experiments on two Si tetrapodes [4, 5].
Figure 1.8 (i) Order parameters for the 3-phenyl ring Si core tetrapode [4]. Solid lines are fit predicted by mean field model [1]; (ii) asymmetry parameter $\eta \equiv \left( Q_{xx} - Q_{yy} \right) / Q_{zz}$ as a function of temperature [52]; and (iii) textures (top) and conoscopy (bottom) [4, 54] for a free standing film of 3-phenyl ring Si core tetrapode: (a) biaxial nematic phase, (b) phase transition between uniaxial and biaxial nematic phase, and (c) uniaxial nematic phase.
from $I$ to $N_u$ phase followed by a second-order transition to the $N_b$ phase in a Si-core 3-phenyl-ring tetrapode (Figure 1.8(i)). These results are supported by observations from conoscopy and texture (Figure 1.8 (iii)). They also investigated the 4-ring homolog in an unpublished study, and claimed observation of a uniaxial to biaxial transition but did not directly determine the order of the transition. An indirect analysis, however, places it on the first order side of the tricritical point in Fig. 1.7. Finally, this group also studied the same compounds with the Si core atom replaced by Ge. They report that the 3- and 4-ring Ge compounds give the same qualitative behavior for the $I$ to $N_u$ and $N_u$ to $N_b$ transitions as the Si-core compounds. (The Ge compounds were the materials made available for our study; they are discussed further in Chapter 3.)

Figueirinhas et al. [52] have independently reported a Deuterium NMR study which probed the molecular order exhibited by the same 3-ring compound studied by Merkel. This study provides further experimental evidence for the existence of the biaxial nematic phase in the tetrapodes. They reported (Figure 1.8 (ii)) high values, well above experimental error, for the asymmetry parameter $\eta = (Q_{xx} - Q_{yy})/Q_{zz}$ (where $Q$ is the symmetric and traceless second rank tensorial quantity describing nematic order) at the lower end of the nematic range as an unambiguous signature of a biaxial nematic phase.

High resolution calorimetry on the tetrapodes has only recently been performed. The single available study [55] reports no specific heat anomaly in the 3-ring tetrapode at the uniaxial to biaxial nematic transition, over the temperature range where it was detected by the IR dichroism and NMR techniques, and places an upper bound of 1 mJ/g on the specific enthalpy of the transition. This indicates that the transition could be
second-order, as was suggested from the dichroism data [52]. Since the calorimetry also found that the isotropic-uniaxial nematic transition is very weakly first order, with a latent heat of \( \sim 200 \text{ mJ/g} \) (remarkably small compared to values measured in typical thermotropics), it would not be so surprising that, even if the uniaxial-biaxial transition is first-order, the heat released, associated with a much subtler symmetry breaking than isotropic-nematic, could be minute and below the detection limit of the experiment.

1.2 LYOTROPIC LIQUID CRYSTALS

Lyotropic LCs are generally formed by dissolving anisotropic organic molecules in a suitable solvent [1]; the LC phases are exhibited as a function of concentration, with temperature playing a secondary role. We will briefly review the more common, surfactant-based LCs and then focus on the system of interest for this dissertation, the lyotropic chromonic LCs [56, 57].

1.2.1 SURFACTANT-BASED LYOTROPIC LIQUID CRYSTALS

These are conventional lyotropic LCs composed of surfactant (amphiphilic) molecules having a hydrophilic head and a hydrophobic tail, such as the common soap, sodium dodecyl sulfate, dissolved in water. In solution, the surfactant molecules tend to arrange in such a way that the polar heads are in contact with a polar solvent (water), and the non-polar tails are in contact with a non-polar co-solvent or simply packed together.
The aggregates (called micelles) are typically small (of order twice the surfactant length) and spherical, but depending on composition, may assume anisotropic shapes (cylinders or disks). Several phases such as isotropic micellar phase, nematic micellar phase, columnar phase, lamellar (or layered) phase, and inverted phases may be formed on varying the concentration of the surfactant molecules.

At low concentrations, the solution looks like any other particles of solute distributed randomly in the solvent. For concentration above a critical concentration, the molecules form micelles (Figure 1.9) with a size usually between 2 nm to 5 nm [58]. The surface of micelles consists of polar heads and the inner side consists of hydrophobic tails screened from the water. A hexagonal columnar phase is formed when cylindrical micelles (Figure 1.9 (b)) are arranged parallel to each other in a hexagonal array (Figure 1.9 (c)). At higher concentrations, the amphiphilic molecules may arrange into planar bilayer membranes forming a lamellar phase (Figure 1.9 (e)). At high concentration, the surfactants may assemble with the hydrophobic tails pointing outwards, trapping the solvent in interior pores or pockets and forming an inverted phase [59] (Figure 1.9 (d)).

1.2.2 LYOTROPIC CHROMONIC LIQUID CRYSTALS

Lyotropic chromonic liquid crystals, LCLCs, represent a novel type of lyotropic mesophases [56, 57, 60, 61] based on aqueous solutions of different complex organic materials including, principally, dyes but also encompassing nucleic acids and even
Figure 1.9 Structural organization of surfactant molecules in water: (a) a spherical micelle, (b) a worm-like micelle, (c) hexagonal columnar phase formed by worm-like micelles, (d) inverted micelle, and (e) bilayer membrane.
antibiotics [56]. In the most well-identified LCLCs, the constituents generally have disk-shaped or plank-shaped aromatic rings that are functionalized at the periphery with ionic or other hydrophilic groups for solubility in water. In aqueous solutions, these mesogens self-organize with a face-to-face arrangement of the aromatic cores, usually resulting in cylindrical stacks with molecular planes being more or less perpendicular to the axis of the aggregate (“stack of coins”). The main molecular mechanism for self-association comes from short-range attractions between aromatic rings containing delocalized charges, rather than the hydrophobic effect [62]. The term “chromonic” was derived from the bischromone structure of one of the early LCLC-forming compounds, disodium cromoglycate or DSCG, which is used as an anti-asthmatic and is known as Cromolyn.

The geometry of the basic structural unit in LCLCs is thus very different from micelles and bilayers formed by surfactant molecules. Unlike the amphiphilic lyotropic system, cromolyn molecules aggregate even in a very dilute solutions showing no minimum concentration required for the aggregation [60]. In contrast to closed micelles of conventional lyotropic LCs, the LCLC aggregates do not have a clearly defined size. They show “isodesmic” behavior [56, 57, 60, 61, 63]. For isodesmic behavior the addition of each chromonic molecule to the columnar aggregates is accompanied by a constant free energy increment.

LCLC can be formed from different self-assembling disk-like compounds such as xanthone derivatives, dyes including benzopurpurin 4B, Sunset Yellow, acid red 266, Violet 20, Blue 27 ([64] and references in it), but the most characterized system is DSCG.
When dissolved in water, DSCG forms two mesomorphic phases: a uniaxial lyotropic nematic (for concentrations \( \sim 10 – 18 \) wt\%) (Figure 1.10) and a columnar phase (for concentrations \( \sim 21 – 35 \) wt\%) [56, 57, 60, 65-77], designated \( M \). The \( I \) and \( N_u \) phases coexist over a relatively wide temperature range of about 3 °C. X-ray studies [68] indicate that the DSCG molecules are arranged in cylindrical aggregates with their core regions being basically perpendicular to the axis of the cylinder. In the \( M \) phase, the aggregates are parallel to each other and arranged into a hexagonal lattice. In the \( N_u \) phase, the column-like aggregates align parallel to each other on average but without positional order. The scalar orientational order parameter in the nematic phase of DSCG aggregates is substantial – in the range \( S = 0.76–0.97 \) [72], depending on concentration. The internal or cross-sectional structure of the aggregates is still not known with certainty.
[73, 74]. Different possible geometries of aggregation are enriched by the fact that the molecular planes can in principle adopt different orientation with respect to the aggregate axes and may be altered significantly with salt additives. Hartshorne and Woodard [68] first proposed that the aggregates are simple columns or stacks of single molecules.

Lydon [61] conjectured more complex aggregates, including a hollow square chimney shape formed by four molecules linked by electrostatic salt bridges. It has even been argued [75, 78, 79] that the aggregate structure could be similar to that of regular micelles. The birefringence of the $N_u$ phase is small (typically the refractive index anisotropy $\Delta n = n_\parallel - n_\perp = 0.02$) at optical wavelengths. This is consistent with the formation of columnar aggregates in which the molecular axis with the largest index of refraction is perpendicular to the long axis of the column [68, 80, 81].

It has recently become evident that LCLCs can be of practical use because of their mesomorphic properties. Different research groups have explored the possibility of using dye-based LCLCs in the fabrication of polarizing [77, 82-91] and optical compensating elements [83, 92-95]. The main feature allowing such an application is that when water evaporates, the resulting dry film still preserves an orientational order and thus the anisotropic optical properties over macroscopic length scales. Preserved in-plane long-range orientational order has been demonstrated not only for films of micron thickness but also for nanofilms comprised of just one or a few stacked LCLC monolayers and fabricated by an electrostatic layer-by-layer deposition technique [92, 95].

In recent years there is a growing interest in using LCLCs in biological sensors [80, 85, 96-103]. The idea of biological sensors is to amplify the antibody-antigen
binding and visualize the growth of immune complex through director distortions and in formation of nanostructure monolayers with long-range in-plane orientational order [95]. In the latter case, the bundles of LCLC rodlike molecular aggregates can be observed with an atomic force microscope, after depositing the molecular monolayers of LCLCs on a suitably charged substrate. Unlike thermotropic LCs which are often toxic [104, 105], LCLCs, which are nontoxic [104], water-based, and nonsurfactant-containing [56, 57], provide a more viable physiological environment for the microbes. They can be aligned with standard rubbed polyimide films.

1.3 DISSERTATION OUTLINE

This dissertation is focused on the study of two relatively novel nematic LCs – the tetrapodes, where our emphasis will be biaxiality and the \( N_u \) to \( N_b \) phase transition previously reported in these systems by other techniques, and the lyotropic chromonic nematic, where we will concentrate on measurements of orientational elastic constants and viscosities – using the well established technique of Dynamic Light Scattering (DLS). This dissertation is organized as follows.

Chapter 2 discusses the relevant theory of photon correlation spectroscopy that is the basis of our dynamic light scattering technique; reviews theoretical results for the \( I \), \( N_u \), and \( N_b \) phases and the transitions between them, based on Landau-deGennes phenomenological models; and describes the optical selection rules applicable to the \( N_u \) and \( N_b \) phases to detect the signature of biaxial order parameter and biaxial director
fluctuation. Chapter 3 deals with the general light scattering experimental set-ups used in our investigations; more specific details of scattering geometries will be discussed in Chapter 4 (for the biaxial nematic phase) and Chapter 5 (chromonic nematic phase). Chapter 4 presents the results of light scattering on two Germanium-based tetrapodes, the Ge 4-ring and Ge 3-ring (similar to the structure shown in Fig. 1.6 with the Si atom replaced by Ge), which possess the $N_b$ phase below the $N_u$ phase. In particular, we describe the observation of a nonhydrodynamic mode in the $N_u$ phase in both the tetrapodes, distinct from the $\hat{n}$ director and uniaxial order parameter modes, which has a dispersion and critical behavior consistent with biaxial order parameter fluctuations. The critical slowing down of this mode indicates a first order $N_u - N_b$ phase transition in the 4-ring tetrapode and second order transition in the 3-ring tetrapode. Through the temperature dependence of the intensity scattered by director fluctuations in selected scattering geometries, we have also separated out the signature of biaxial ($\hat{m}$) director fluctuation in the 4-ring tetrapode in the lower temperature ($N_b$) phase. Chapter 5 presents results for viscoelastic coefficients and their temperature dependence in the lyotropic chromonic nematic phase of DSCG in water. Absolute measurements of elastic constants and orientational viscosities are reported and compared with prior results from the somewhat analogous system of lyotropic polymer nematics. The temperature dependence of LCLC orientational elastic constants is analyzed with a simple available model developed by Meyer, which provides us important information associated with the length of the aggregates and the scission energy to break them. A conclusion (Chapter 6) provides a summation of our results and prospects for future, related studies.
REFERENCES


CHAPTER 2
THEORETICAL BACKGROUND: ORIENTATIONAL FLUCTUATIONS IN
UNIAXIAL AND BIAXIAL NEMATIC LIQUID CRYSTALS

This chapter develops the theoretical formulation we will use to interpret the experiments performed in this dissertation. The theory of light scattering, photon correlation spectroscopy, and hydrodynamics of the relevant liquid crystal phases are discussed. In particular, hydrodynamic and Goldstone modes associated with the director fluctuations are explained in detail for both the uniaxial and biaxial nematic liquid crystals. Important optical selection rules to single out order parameter or different director modes of uniaxial and biaxial nematic liquid crystals are developed for specific cases.

2.1 HYDRODYNAMICS

Light scattering is used to probe matter at length scales of the order of an optical wavelength (~400 – 700 nm) or greater – much longer than typical molecular dimensions. In this case, a continuum approach is suitable to study the hydrodynamics of the system.
A detailed and comprehensive hydrodynamic theory of both normal fluids and liquid crystals has been done by Martin, Parodi, and Pershan [1].

Hydrodynamic modes are collective fluctuations of a many particle system that are characterized by an angular frequency, and wavevector relations of the form $\text{Re}(\omega) \sim q^n$ and $\text{Im}(\omega) \sim q^m$. The former refers to a propagating mode, while the latter describes damping of a mode. In simpler terms, hydrodynamic modes have zero frequency (energy) when the fluctuation is uniform in space. For example, if all the molecules of a system are simply displaced by the same amount (i.e., $q \to 0$), there is no change in internal energy and no internal restoring force; thus, $\omega \to 0$. There are two basic categories of hydrodynamic modes in condensed systems. One type of mode is governed by a conservation law (e.g., mass, momentum, or energy) and the other type of mode, called a Goldstone mode, is associated with broken symmetry at a phase transition. Examples include acoustic waves in a crystal and orientational (director) fluctuations in a liquid crystal.

In general, any disturbances of a system from equilibrium relax back towards equilibrium in microscopic times and over microscopic distances except when the fluctuations involve a local variable governed by a conservation law. For any such variable $A$, the macroscopic conservation law can be written as

$$\frac{\partial A}{\partial t} + \nabla \cdot \vec{J}_A = \sigma_A \equiv 0$$

(2.1)

where $\vec{J}_A$ is the current density or flux of $A$ and $\sigma_A$ is a source of $A$. When the system fluctuates thermally about an equilibrium state, one has
\[
\frac{\partial}{\partial t} \delta A(\vec{r}, t) + \vec{\nabla} \cdot \vec{\delta J}_A(\vec{r}, t) = \delta \sigma_A(\vec{r}, t) \equiv 0 \tag{2.2}
\]

For conserved quantities, \(\delta \sigma_A(\vec{q}, t) \equiv 0\). Then taking the time-space Fourier transform of equation (2.2) [i.e., assuming \(A, J_A \sim \exp(i\vec{q} \cdot \vec{r} - i\omega t)\)] gives

\[
\omega \delta A(\vec{q}, t) = \vec{q} \times \delta \vec{J}_A(\vec{q}, t) \tag{2.3}
\]

In the limit \(|\vec{q}| \to 0\) (long wavelength limit since \(|\vec{q}| \propto \frac{1}{\lambda}\)) and for a finite amplitude \(\delta A\), we see that \(\omega(\vec{q}) \to 0\). A hydrodynamic mode for which \(\text{Re}(\omega) \neq 0\) is called a propagating mode. If \(\text{Re}(\omega) = 0\), the mode is purely diffusive. For the isotropic fluid, there are two propagating modes (longitudinal sound waves) and three diffusive modes (thermal conduction and two transverse shear waves). For a nonconserved quantity \(\sigma_A(\vec{q}, t) \neq 0\) and generally \(\omega \neq 0\) as \(\vec{q} \to 0\). The fluctuations of nonconservative quantities therefore have finite lifetime as \(\vec{q} \to 0\).

The uniaxial nematic phase is characterized by the director \(\hat{n}(\vec{r})\) which describes the average direction of alignment of anisotropically shaped molecules. According to Goldstone theorem [2, 3], there should be two new variables \(\delta n_x\) and \(\delta n_y\) (assuming average \(\vec{n} = \hat{z}\)) corresponding to independent rotations of the director, which give rise to two hydrodynamic modes. One can view the fluctuations \(\delta n_x\) and \(\delta n_y\) as trying to restore the rotational symmetry broken by the existence of \(\vec{n}\). Therefore, in total, there are seven hydrodynamic modes in uniaxial nematic liquid crystals: five of them are the same as in
the isotropic fluid and the remaining two are the Goldstone modes corresponding to the director fluctuations.

The biaxial nematic phase is characterized by two directors: the uniaxial director, \( \hat{n}(\vec{r}) \) and the biaxial director, \( \hat{m}(\vec{r}) \). The rotational symmetry around \( \hat{n} \) is broken in the biaxial nematic liquid crystals due to the development of \( \hat{m} \) perpendicular to \( \hat{n} \). This introduces one new Goldstone mode resulting in a total of three Goldstone modes, corresponding to rotations of the directors about \( x, y, \) and \( z \) axes respectively.

As Goldstone modes are associated with symmetry breaking transitions between different phases, they are a good source of information during phase transitions. Fluctuations in the degree or magnitude of order (order parameter modes) are generally non-hydrodynamic; such modes in the limit \( \vec{q} \to 0 \) still correspond to a change in symmetry (and a non-zero restoring force). This dissertation is focused on the use of light scattering to study both Goldstone and order parameter modes in the bulk and near to the phase transition in isotropic, uniaxial, and biaxial nematic phases.

2.2 THEORY OF LIGHT SCATTERING SPECTROSCOPY

The electric field component of light incident on matter exerts a force on the charges of the medium and thereby produces an oscillating polarization. The oscillating charges then radiate light in all directions in space. The scattering volume can be considered as composed of coherent subregions of volume small compared to the cube of the incident light wavelength. Light scattered from a coherent laser at any point in space
is the sum of the wavelets from all the subregions. A schematic diagram for the typical light scattering experiment is shown in Figure 2.1.

![Diagram of light scattering experiment](image)

Figure 2.1 Light of incident polarization $\hat{i}$ and wave vector $\vec{k}_i$ is scattered in all directions from a transparent medium and arrives at the detector at position $\vec{r}$ with respect to the center of the illuminated volume with wave vector $\vec{k}_f$, polarization $\hat{f}$, and scattering vector $\vec{q} = \vec{k}_f - \vec{k}_i$. The total radiated field at the detector is the superposition of the fields radiated from all infinitesimal volumes $d^3r'$ at positions $\vec{r'}$ with respect to the center of the illuminated volume.

There are two basic limits of the light scattering technique: inelastic Raman or Brillouin scattering and quasi-elastic Rayleigh scattering. Raman scattering is primarily associated with the rotational or vibrational excitations of individual molecules, or with translational collective modes (phonons). In Rayleigh scattering, on the other hand, the frequency of the incident light is broadened (but not shifted) by local fluctuations of the dielectric constant (or dielectric constant tensor) of the medium [4], including both the orientational order parameter and the director modes in liquid crystals.
To analyze the Rayleigh scattering from liquid crystals, consider an incident plane polarized electromagnetic wave \( \mathbf{E}_i(\mathbf{r}, t) = i E_0 \exp\left(i (k_i \cdot \mathbf{r} - \omega t)\right) \); of amplitude \( E_0 \), propagating vector \( k_i \), and angular frequency \( \omega \); polarized along \( \hat{i} \), is propagating through a nonconducting, nonmagnetic, and nonabsorbing medium with an average dielectric constant \( \varepsilon \) (and refractive index \( n = \sqrt{\varepsilon} \)). Assume the medium undergoes anisotropic fluctuations in dielectric properties expressed by

\[
\varepsilon(\mathbf{r}', t') = \varepsilon \mathbf{I} + \delta\varepsilon(\mathbf{r}', t')
\]  

(2.4)

where \( \delta\varepsilon(\mathbf{r}', t') \) represents fluctuations in the second rank dielectric tensor describing an optically anisotropic material at a position \( \mathbf{r}' \) and time \( t' \), and \( \mathbf{I} \) is the identity tensor.

The electric field of light scattered by the dielectric fluctuations at a position \( \mathbf{r} \) outside the sample (where \( r \) is assumed much larger than any dimension of the illuminated sample volume) and at a time \( t \), polarized along the analyzer direction \( \hat{f} \), is given by [5]

\[
E_s(\mathbf{r}, t) = -\frac{k_i^2 E_0}{4\pi \varepsilon_0 r} e^{i(k_i \cdot \mathbf{r}' - \omega t)} \int_{r'} \mathbf{d}^3 r' \hat{f} \times \hat{k}_j \times \delta\varepsilon(\mathbf{r}', t') \mathbf{e}^{-i\mathbf{q} \cdot \mathbf{r}'}
\]

(2.5)

where \( \mathbf{q} = \hat{k}_j - k_i \), \( \omega_j \) is replaced with \( \omega \) (for elastic scattering), and, since the time scale of the fluctuations of the dielectric tensor are much slower than the time it takes for light to propagate from the sample (\( r' \)) to the detector (\( r \)), \( t' \) in \( \delta\varepsilon(\mathbf{r}', t') \) is replaced by \( t \).

Using the identity

\[
-\hat{f} \cdot \left\{ \hat{k}_j \times \left( \hat{k}_j \times \delta\varepsilon \mathbf{i} \right) \right\} = \hat{f} \cdot \delta\varepsilon \mathbf{i} = \delta\varepsilon_{ij} \mathbf{i}
\]

the scattered field simplifies to
Equations (2.5) and (2.6) assume negligible multiple scattering of light within the sample; this is generally justified for thin, non-turbid samples, such as utilized in our experiments.

In dynamic light scattering experiments, the time correlation function of the scattered intensity \( I_s \) is defined as

\[
\langle I_s(0)I_s(\tau) \rangle = \lim_{T \to \infty} \frac{1}{T} \int_0^T I_s(t)I_s(t+\tau)dt
\]

\[
= \langle E_s^*(0)E_s(0)E_s^*(\tau)E_s(\tau) \rangle
\]

where \( \tau \) is the time delay between measurements of \( I_s \), and the ensemble average \( \langle \cdots \rangle \) is equivalent to a time average in the limit that the scattering process is ergodic [6]; practically, this means that the sample fluctuates about a thermodynamic equilibrium state. If, in addition, the scattering is collected from a large number of statistically independent (uncorrelated) subvolumes, the scattering may be described as a Gaussian Random Process [5] and the “four-point” field correlation reduces to a combination of “two-point” correlations,

\[
\langle E_s^*(0)E_s(0)E_s^*(\tau)E_s(\tau) \rangle = \langle |E_s(0)|^2 \rangle \langle |E_s(\tau)|^2 \rangle + \langle |E_s(0)|^2 \rangle \langle |E_s(\tau)|^2 \rangle
\]

To calculate the intensity correlation function, we then need to calculate the time correlation of the scattered electric field

\[
\langle E_s(\vec{r}_1,t_1)E_s(\vec{r}_2,t_2) \rangle = \frac{k^4}{4\pi \epsilon_0} \int d^3 r'^* \int d^3 r'' \int d^3 r' \int d^3 r'' \langle \delta \vec{E}_{\gamma}(\vec{r}_1,t_1) \delta \vec{E}_{\lambda}(\vec{r}_2,t_2) \rangle e^{-i\vec{q} \cdot (\vec{r}' - \vec{r}'')} e^{-i\omega t_1 e^{i\omega t_2}}\]

\[
(2.9)
\]
The statistical process describing the fluctuations is stationary [5] and spatially homogeneous. So the correlation function depends only on $\tau = |t_2 - t_1|$ and $\vec{r} - \vec{r}'$, and one of the integrals over the illuminated volume $V$ can be done immediately. This gives

$$\langle E^*_i(\vec{r},0)E_j(\vec{r},\tau) \rangle = \frac{k^4|E_0|^2}{(4\pi \varepsilon_0)^2} \frac{V^2}{r^3} \langle \delta \varepsilon_{ij}^*(\vec{q},0)\delta \varepsilon_{ij}(\vec{q},\tau) \rangle e^{-i\omega \tau} \quad (2.10)$$

where

$$\langle \delta \varepsilon_{ij}^*(\vec{q},0)\delta \varepsilon_{ij}(\vec{q},\tau) \rangle = \frac{1}{V} \int d^3r' \langle \delta \varepsilon_{ij}^*(0,0)\delta \varepsilon_{ij}(\vec{r}',\tau) \rangle e^{-i\vec{q}\cdot \vec{r}'}$$

and $\vec{r}$ is a point on the detector. The problem now becomes the calculation of $\langle \delta \varepsilon_{ij}^*(\vec{q},0)\delta \varepsilon_{ij}(\vec{q},\tau) \rangle$ relevant to different liquid crystal phases. We will treat the cases of uniaxial and biaxial nematics in subsequent sections.

### 2.3 DYNAMIC LIGHT SCATTERING

In dynamic light scattering (DLS), the scattered light collected at the detector is converted into a time series of electrical current pulses, which are then digitized and correlated in real time (either by electronic hardware or in software in a sufficiently fast CPU) to obtain a measurement of $\langle I_s(0)I_s(\tau) \rangle$. Thus, time-domain DLS is also known as Photon Correlation Spectroscopy (PCS).

There are two types of PCS: autocorrelation and cross correlation. Autocorrelation is used to find the similarity of a signal with itself at later times. Cross correlation calculates the correlation of two different signals. A form of cross correlation,
in which scattered light collected from a single illuminated volume and at the same scattering vector \( \vec{q} \) is evenly split between two detectors, is used in our experiments. It has key advantages over autocorrelation at short delay times. Autocorrelation is limited by the finite resolving time for two photons closely spaced in time and by “afterpulses” generated by reflections of photoelectrons cascading through the pulse amplification section of the photodetectors. The typical resolving time (usually called “dead time”) is on the order of tens of nanoseconds. Below this time measured autocorrelation functions drop abruptly to zero. Afterpulsing produces a large spurious autocorrelation at times corresponding to transit times within the photomultiplier (~50 ns to ~1 \( \mu \)s). Cross correlation of two independent photomultipliers essentially avoids these problems, because separate photons arriving at separate detectors within the dead time of a detector can still be accurately resolved, and because afterpulses between two independent detectors are uncorrelated.

For either type of PCS, one may define the normalized correlation functions

\[
g^{(1)}(\tau) = \frac{\langle E_s^*(0) E_s(\tau) \rangle}{\langle |E_s(0)|^2 \rangle}, \quad \text{and} \quad g^{(2)}(\tau) = \frac{\langle I(0) I(\tau) \rangle}{\langle I(0) \rangle^2} \tag{2.11}
\]

From equation (2.8), we get the Siegert relation

\[
g^{(2)}(\tau) = 1 + \beta \left( g^{(1)}(\tau) \right)^2 \tag{2.12}
\]

Here the spatial coherence factor \( \beta = 1 \) when the field is scattered coherently and purely from fluctuations (as assumed in equation (2.8)). In the case where static scattering from sample defects or inhomogeneities in the substrates or alignment layers surrounding the
sample contribute, $\beta < 1$ in equation (2.12). $\beta$ may also be less than unity if the light admitted onto the detector decoheres significantly over the area of the admitting aperture. The concept of “coherence area” is therefore important to the signal-to-background ratio in light scattering experiments. It may be estimated as [5]

$$A_{coh} \approx \frac{\lambda^2}{\Omega} \quad (2.13)$$

where $\Omega$ is the solid angle subtended by the illuminated sample volume at the detector and $\lambda$ is the illuminating wavelength. In cases where strong nematic director scattering was sampled, we optimized the light collection aperture and minimized stray scattering so that, typically, $\beta > 0.9$; this is referred to the “homodyne” limit.

In an actual experiment light collected at the detector is converted into a stream of digital pulses by the photodetector and amplifier/discriminator electronics are used to compute the correlation function. In practice, the number of photons $n(t)$ arriving at the detector during interval $\Delta t$ is counted by the correlator, and the correlation function of these photocounts is calculated as

$$\langle n(0)n(t) \rangle = \langle n(0)n(j\Delta t) \rangle \equiv \lim_{N \to 0} \frac{1}{N} \sum_{i=1}^{N} n_i n_{i+j} \quad (2.14)$$

where $t = j\Delta t$ and $n_i = n(i\Delta t)$. The photo count rate is proportional to scattered field by $n(t) \propto |E_s(t)|^2$. Thus, $\langle n(0)n(t) \rangle \propto \left| E_s(0) \right|^2 \left| E_s(t) \right|^2$ and

$$\frac{\langle n(0)n(\tau) \rangle}{\langle n(0) \rangle^2} \propto \frac{\langle I(0)I(\tau) \rangle}{\langle I(0) \rangle^2} \quad (2.15)$$
DYNAMIC LIGHT SCATTERING FROM THE ISOTROPIC PHASE OF A LIQUID CRYSTAL

The isotropic phase is the most symmetric phase in which there is not any ordering of molecular orientations or their center of masses. Dynamic light scattering by the isotropic phase is typically due to density fluctuations (translational motions) of the molecules. However, near the phase transition to the nematic liquid crystal phase, anisotropic molecules of the liquid crystal form local clusters possessing short-range orientational order characterized by a coherence length \( \xi(T) \) \( (\xi(T) \sim 100 \text{ Å}) \). Most of the light scattering in the isotropic phase near the \( I-N \) phase transition comes from fluctuations of such clusters arising and decaying in time. The presence of coherently ordered clusters can be described by an order parameter. The indistinguishability of the nematic states for the director \( \hat{n} \) and \( -\hat{n} \) (or \( \hat{m} \) and \( -\hat{m} \) in the case of biaxiality) leaves us a second rank tensor order parameter \( Q_{\alpha\beta} \): the average value of which must be zero in the isotropic phase and must be symmetric and traceless in order to yield zero when averaged over all directions. Rotational invariance in the isotropic phase requires that the anisotropy in all other physical quantities should be a scalar multiple of \( Q_{\alpha\beta} \). The dielectric constant tensor which is important in light scattering experiments may, therefore, be expressed as

\[
\varepsilon_{\alpha\beta} = \bar{\varepsilon}\delta_{\alpha\beta} + \frac{2}{3}\Delta\varepsilon_{\text{sat}}Q_{\alpha\beta} \tag{2.16}
\]
where \( \Delta \varepsilon_{sat} \) is the saturated anisotropy in \( \varepsilon_{ab} \) for a completely ordered uniaxial nematic and \( \bar{\varepsilon} \) is the value of the dielectric constant in the isotropic liquid.

From equation (2.10) it is clear that intensity of the scattered light is proportional to \( \langle \delta \varepsilon_{ij}^*(\vec{q}) \delta \varepsilon_{ij}^*(\vec{q}) \rangle \). To calculate \( \langle \delta \varepsilon_{ij}^*(\vec{q}) \delta \varepsilon_{ij}^*(\vec{q}) \rangle \) in the isotropic phase, we need to expand the free energy in terms of the nematic order parameter, \( Q_{ab} \). We may use the Landau-deGennes mean field model of the expansion of the free energy per unit volume near the nematic-isotropic transition [6] as a power series of the order parameter,

\[
F_{iso} = F_0(\rho, T) + \frac{A(T)}{2} Q_{ab} Q_{ba} + \frac{B}{3} Q_{ab} Q_{ba} Q_{aa} + \frac{C}{4} (Q_{ab} Q_{ba})^2 + \frac{L_1}{2} \partial_a Q_{\beta\gamma} \partial_a Q_{\beta\gamma} + \frac{L_2}{2} \partial_a Q_{\alpha\alpha} \partial_a Q_{\beta\beta} \tag{2.17}
\]

Here the coefficient \( A(T) \) has the form \( a(T - T^*) \) where \( a > 0 \), and \( T^* \) is the absolute limit of metastability of the isotropic phase. The temperature where the order parameter actually attains a nonzero equilibrium value (the actual isotropic-uniaxial nematic transition temperature) is given by \( T_c = T^* + \frac{2B^2}{9AC} \). The coefficients \( B \) and \( C \) are assumed temperature independent. Non-zero \( B \) requires the isotropic-uniaxial nematic phase transition to be of the first order. If \( B = 0 \), \( T_c = T^* \) and the transition would be of second order. \( L_1 \) and \( L_2 \) may be called the elastic coefficients in the isotropic phase and provide an energy scale for spatial variations (gradients) of the order parameter.

In the isotropic phase, the free energy associated with the fluctuations in \( Q_{ab} \) is, to the lowest order,
\[
\delta F_{iso} = \frac{1}{2} \int \frac{d^3r}{V} \left[ \frac{A(T)}{2} Q_{\alpha\beta} (\vec{r}) Q_{\beta\alpha} (\vec{r}) + \frac{L_1}{2} \partial_\alpha Q_{\beta\gamma} (\vec{r}) \partial_\alpha Q_{\gamma\beta} (\vec{r}) + \frac{L_2}{2} \partial_\alpha Q_{\alpha\gamma} (\vec{r}) \partial_\beta Q_{\beta\gamma} (\vec{r}) \right] 
\]  
(2.18)

Consider Fourier Transforms:

\[
\int \frac{d^3r e^{i(\vec{q}-\vec{q}')\cdot \vec{r}}}{V} = V \delta_{\vec{q}, \vec{q}'} ; \quad Q_{\alpha\beta} (\vec{r}) = \sum_\vec{q} Q_{\alpha\beta} (\vec{q}) e^{i\vec{q}\cdot \vec{r}} ; \quad Q_{\alpha\beta} (\vec{q}) = \sum_\vec{q} Q_{\alpha\beta} (\vec{q}) e^{-i\vec{q}\cdot \vec{r}}
\]  
(2.19)

Using equations (2.19) and \(Q_{zz} = 0\), i.e. \(Q_{xx} = -\left(Q_{zz} + Q_{yy}\right)\) and choosing fluctuations only along \(z\)-axis, equation (2.18) becomes

\[
\delta F_{iso} = \frac{V}{2} \sum_\vec{q} \left[ \frac{A(T)}{2} \left\{ Q_{xx}^2 (\vec{q}) + Q_{yy}^2 (\vec{q}) + Q_{zz}^2 (\vec{q}) + 2Q_{xy}^2 (\vec{q}) + 2Q_{zx}^2 (\vec{q}) + 2Q_{zy}^2 (\vec{q}) \right\} + \right. \\
\left. L_1 \left\{ q_1^2 Q_{xx}^2 (\vec{q}) + q_2^2 Q_{yy}^2 (\vec{q}) + 2q_1^2 Q_{zx}^2 (\vec{q}) + 2q_2^2 Q_{zy}^2 (\vec{q}) \right\} \right] 
\]  
(2.20)

Equation (2.20) simplifies to

\[
\delta F_{iso} = \frac{V}{2} \sum_\vec{q} \left[ \frac{3A}{2} \left( 1 + \xi_1^2 q^2 + \frac{2}{3} \xi_2^2 q^2 \right) Q_{xx}^2 (\vec{q}) + \frac{A}{2} \left( 1 + \xi_1^2 q^2 \right) \left( Q_{xx}^2 (\vec{q}) - Q_{yz}^2 (\vec{q}) \right) \right] + \right. \\
\left. 2A \left( 1 + \xi_1^2 q^2 \right) Q_{xy}^2 (\vec{q}) + 2A \left( 1 + \xi_1^2 q^2 + \frac{1}{2} \xi_2^2 q^2 \right) \left( Q_{zz}^2 (\vec{q}) - Q_{yz}^2 (\vec{q}) \right) \right] 
\]  
(2.21)

where \(\xi_1 = \sqrt{\frac{L_1}{A}}\) and \(\xi_2 = \sqrt{\frac{L_2}{A}}\) are defined as the correlation lengths corresponding to the spatial variation of the order parameter [7].

Applying the equipartition theorem to equation (2.21), we get the mean fluctuations in the square of the order parameter. For example

\[
\left\langle Q_{zz}^2 (\vec{q}) \right\rangle = \frac{2k_B T}{3AV \left( 1 + \xi_1^2 q^2 + \frac{2}{3} \xi_2^2 q^2 \right)}
\]  
(2.22)
Substituting values of $\langle Q_{a\beta}^+(\vec{q}) \rangle$ in equation (2.16), we can get $\langle \delta\epsilon_{a\beta}(\vec{q})^2 \rangle$. The general result obtained this way is very complicated. It can be simplified for specific light polarizations. If the incident light is polarized along $\hat{i}$ and scattered light is polarized along $\hat{f}$, then we get [7]

$$
\langle \delta\epsilon_{a\beta}(\vec{q})^2 \rangle = \left[ \left( \hat{i} \cdot \hat{f} \right)^2 - 3 \hat{i}_f f_f \cos^2 \frac{\theta_s}{2} \right]^{\frac{1}{2}} \frac{4(\Delta\epsilon_{\text{sat}})^2 k_B T}{54 VA \left( 1 + \xi_s^2 q_z^2 + \frac{2}{3} \xi_z^2 q_z^2 \right)} + \left[ \left( i_i f_i \right)^2 + \left( i_i f_i + i_h f_h \right) \sin^2 \frac{\theta_s}{2} \right]^{\frac{1}{2}} \frac{4(\Delta\epsilon_{\text{sat}})^2 k_B T}{18 VA \left( 1 + \xi_i^2 q_z^2 + \frac{1}{2} \xi_z^2 q_z^2 \right)} \right]
$$

where $\theta_s$ is the scattering angle in the sample. Equation (2.23) can be further simplified substantially for purely polarized or depolarized scattered light. The sample scattering angle can be converted into the angle in laboratory coordinate system $\theta_f$ using Snell’s law.
2.5 LIGHT SCATTERING BY A UNIAXIAL NEMATIC PHASE

2.5.1 ELASTIC FREE ENERGY AND DIRECTOR MODES OF A UNIAXIAL NEMATIC

The uniaxial nematic phase is characterized by a long range orientational order along an arbitrary common axis called the director \( \hat{n} \). Nematic liquid crystals flow like liquid with viscosity \( \sim 10^{-2} - 10^{-1} \) Poise. It is usually higher than the viscosity of water at 20 °C (10^{-2} Poise). Since the LC molecular dimension along the longer axis (20 Å – 30 Å) is very much smaller than the length scale (optical wavelength) probed in the light scattering experiment, a continuum approach may be used to interpret the measurements. Thus, \( \hat{n} \) is treated as a continuous quantity in space i.e. \( \hat{n} = \hat{n}(\vec{r}) \).

Because the minimum free energy of a nematic corresponds to spatially uniform \( \hat{n} \), the continuum model allows one to express it in terms of gradients in \( \hat{n} \) - i.e., as an elastic energy. The bulk elastic free energy associated with the distortion of the director is given by [6]

\[
f_N = \frac{1}{2} K_{11} \left( \vec{V} \cdot \hat{n} \right)^2 + \frac{1}{2} K_{22} \left( \hat{n} \cdot \vec{V} \times \hat{n} \right)^2 + \frac{1}{2} K_{33} \left( \hat{n} \times \vec{V} \times \hat{n} \right)^2 \tag{2.24}
\]

where \( K_{11}, K_{22}, \) and \( K_{33} \) are called splay, twist, and bend elastic constants respectively. They are associated with the specific director distortions in the bulk of the sample shown in Figure 2.2. Typical magnitudes of the elastic constants in thermotropic calamitics are of the order of \( 10^{-6} \) dynes (or \( 10^{-11} \) N) and in general \( K_{33} > K_{11} \geq K_{22} \). (For example, for
the compound PAA at 120°C, $K_{11} = 0.7 \times 10^{-6}$ dyne, $K_{22} = 0.43 \times 10^{-6}$ dyne and $K_{33} = 1.7 \times 10^{-6}$ dyne [6]).

For fluctuations of the director, we can write

$$\hat{n}(\vec{r}) = \hat{n}_0(\vec{r}) + \delta \hat{n}(\vec{r})$$
$$= \hat{z} + \delta n_x(\vec{r}) \hat{x} + \delta n_y(\vec{r}) \hat{y}$$

(2.25)

where $\hat{n}_0(\vec{r}) (= \hat{z})$ is the average direction of the director and $\delta \hat{n}(\vec{r})$ is the fluctuating part. The Fourier transformation of fluctuations is given by

$$\delta n_j(\vec{q}) = \sum_{\vec{q}} \delta n_j(\vec{q}) e^{i\vec{q} \cdot \vec{r}}, \quad j = x, y$$

(2.26)

In terms of Fourier components, the nematic distortion free energy becomes [6]

$$F_N = \frac{V}{2} \sum_{\vec{q}} \left[ K_{11} \left| \delta n_x(\vec{q}) q_x + \delta n_y(\vec{q}) q_y \right|^2 + K_{22} \left| \delta n_x(\vec{q}) q_y - \delta n_y(\vec{q}) q_x \right|^2 \right.$$  
$$+K_{33} q_z^2 \left( |\delta n_x(\vec{q})|^2 + |\delta n_y(\vec{q})|^2 \right) \left. \right]$$

(2.27)
where $V$ is the sample volume.

For a given $\vec{q}$, the free energy can be diagonalized using a linear transformation

$$\delta \hat{n} = \delta n_1 \hat{e}_1 + \delta n_2 \hat{e}_2$$  \hspace{1cm} (2.28)

where $\hat{e}_2 = \frac{\hat{n}_0 \times \vec{q}}{|\hat{n}_0 \times \vec{q}|}$ and $\hat{e}_1 = \frac{\hat{n}_0 \times \hat{e}_2}{|\hat{n}_0 \times \hat{e}_2|}$. When diagonalized, nematic free energy becomes

$$F_N = \frac{V}{2} \sum_\vec{q} \left[ (K_{11} q_{\perp}^2 + K_{33} q_{z}^2) \left| \delta n_1 (\vec{q}) \right|^2 + (K_{22} q_{\perp}^2 + K_{33} q_{z}^2) \left| \delta n_2 (\vec{q}) \right|^2 \right]$$  \hspace{1cm} (2.29)

where $q_{\perp} = \sqrt{q_x^2 + q_y^2}$ and $q_{\parallel} = q_z$.

The mean square amplitude of the thermally induced normal mode fluctuations can then be obtained using the equipartition theorem

$$\left\langle |\delta n_1 (\vec{q})|^2 \right\rangle = \frac{k_B T}{V} \frac{1}{K_{11} q_{\perp}^2 + K_{33} q_{z}^2}$$  \hspace{1cm} (2.30)

$$\left\langle |\delta n_2 (\vec{q})|^2 \right\rangle = \frac{k_B T}{V} \frac{1}{K_{22} q_{\perp}^2 + K_{33} q_{z}^2}$$  \hspace{1cm} (2.31)

where $k_B$ is Boltzmann’s constant. Mode one ($\delta n_1$) is the splay-bend mode and mode two ($\delta n_2$) is the twist-bend mode. As $\vec{q} \to 0$ the mean square amplitudes diverge. Since the restoring force for fluctuations from equilibrium must go to zero for infinite wavelength, these modes are Goldstone modes and are responsible for stray light scattering.

The parameters describing the dynamics of nematics are velocity field, $\vec{v}(\vec{r},t)$, director field, $\hat{n}(\vec{r},t)$, density $\rho(\vec{r},t)$, and the pressure, $P(\vec{r},t)$. The macroscopic theory for the dynamics of nematics was formulated originally by Ericksen, Leslie, and Parodi [8-11] and the microscopic description was studied by the Harvard group [12].
The dynamics of the director modes can be determined by the balance of inertial, elastic, and viscous forces. The elastic force acting on the mode $\delta n_{\alpha}(\vec{q},t)$ ($\alpha = 1, 2$) is defined by the molecular field

$$h_{\alpha}(\vec{q}) = -\frac{\partial F_N(\vec{q},t)}{\partial \delta n_{\alpha}(\vec{q},t)} = -(K_{aa}q^2 + K_{33}q_z^2)\delta n_{\alpha}(\vec{q},t)$$

(2.32)

The viscous force can be defined by the term

$$-\eta_{\alpha}(\vec{q})\frac{\partial \delta n_{\alpha}(\vec{q},t)}{\partial t}$$

(2.33)

where $\eta_{\alpha}(\vec{q})$ are effective viscosities – a combination of the five fundamental viscosities of a uniaxial nematic – which characterize a frictional resistance to orientational deformations.

The equation of motion for the director modes is obtained by balancing the elastic, viscous, and inertial forces acting on the director [13]. Neglecting the inertial contribution ($I(n_{\alpha}(\vec{q}))$), which corresponds to the motion of the center of mass of the molecules, as in a normal fluid

$$-\eta_{\alpha}(\vec{q})\frac{\partial \delta n_{\alpha}(\vec{q},t)}{\partial t} = \frac{\partial F_N(\vec{q},t)}{\partial \delta n_{\alpha}(\vec{q},t)}$$

(2.34)

This gives the solution for $\delta n_{\alpha}(\vec{q},t)$ as two overdamped modes

$$\delta n_{\alpha}(\vec{q},t) \propto e^{-\Gamma_{\alpha}(\vec{q})t}$$

(2.35)

where $\Gamma_{\alpha}(\vec{q}) = \frac{K_{22}q^2 + K_{33}q_z^2}{\eta_{\alpha}(\vec{q})}$. 
The characteristic relaxation rate corresponding to the velocity field fluctuation (inertial term) is \( \Gamma_v \sim D_v q^2 \) [14], where \( D_v = \frac{\eta}{\rho} \) (\( \rho \) is the density) characterizes the diffusion of vorticity \( \vec{\nabla} \times \vec{v} \). The ratio of these relaxation rates \( \mu \sim \frac{\Gamma_a}{\Gamma_v} \sim \frac{K \rho}{\eta^2} \sim 10^{-2} - 10^{-4} \) (using typical values of \( K \sim 10^{-6} \) dynes, \( \rho \sim 1 \) gcm\(^{-3}\), and \( \eta \sim 0.01 - 0.1 \) Poise). This separates the motion into the slow and fast modes.

The significance of the inertial term, which is neglected in the equation of motion, can be estimated [14]. This term is of the order of \( \rho a^2 \frac{\partial^2 \eta_a}{\partial t^2} \sim \rho a^2 \Gamma_a^{-2} \sim \frac{\rho a^2 K^2 q^4}{\eta^2} \), where \( a \) is the molecular dimension. Comparing inertial and elastic terms \( \frac{I(n_a(\vec{q}))}{h_a(\vec{q})} \sim \frac{K \rho}{\eta^2} (qa)^2 \sim \mu(qa)^2 \) \( (q \sim 10^4 \) cm\(^{-1}\), \( a \sim 10^{-7} \) cm, and \( \mu \sim 10^{-4} \)), the inertial term is always negligible.

Uniaxial liquid crystals have five independent viscosities: four shear viscosities \([15]\) \( \eta_a, \eta_b, \eta_c, \) and \( \alpha_i \); and one twist viscosity \( \gamma_i \) describing the rotations of the director with respect to the background fluid. Their relationship is given by [13]

\[
\eta_i(\vec{q}) = \gamma_i - \frac{1}{4} \left[ q_z^2 \gamma_i + (q_\perp^2 - q_z^2)(\eta_b - \eta_c) \right]^2 \frac{q_z^4 \eta_b + q_z^2 q_\perp^2 (\alpha_i + \eta_b + \eta_c) + q_z^4 \eta_c}{q_z^4 \eta_b + q_z^2 q_\perp^2 (\alpha_i + \eta_b + \eta_c) + q_z^4 \eta_c}
\]  

(2.36)

\[
\eta_z(\vec{q}) = \gamma_i - \frac{1}{4} q_z^2 (\gamma_i + \eta_c - \eta_b)^2 \frac{q_z^4 \eta_a - q_z^2 \eta_c}{q_z^4 \eta_a - q_z^2 \eta_c}
\]  

(2.37)
With a proper choice of $q (q_z = 0 \text{ or } q_\perp = 0)$, these equations can be simplified considerably.

2.5.2 OPTICAL SELECTION RULES FOR UNIAXIAL NEMATIC

The orientational state of the uniaxial nematic phase can be characterized mathematically by a tensor $Q_{\alpha\beta}$ called an order parameter which, in the case of uniaxial order, may be defined as

$$Q_{\alpha\beta}(\vec{r}) = \frac{3}{2} S(T) \left[ n_\alpha(\vec{r}) n_\beta(\vec{r}) - \frac{1}{3} \delta_{\alpha\beta} \right]$$  \hspace{0.5cm} (2.38)

where $\alpha, \beta = x, y, z$, $n_\alpha(\vec{r})$, $n_\beta(\vec{r})$ are the Cartesian components of the director $\hat{n}(\vec{r})$, $\delta_{\alpha\beta}$ is the Kronecker’s delta function, and

$$S(T) = \frac{\Delta \varepsilon^u(T)}{\Delta \varepsilon^u_{\text{sat}}}$$  \hspace{0.5cm} (2.39)

where $\Delta \varepsilon^u(T)$ is the temperature dependent dielectric anisotropy, $\Delta \varepsilon^u = \varepsilon_\parallel - \varepsilon_\perp$, of the uniaxial nematic, and $\Delta \varepsilon^u_{\text{sat}}$ is its saturated value (i.e., for molecular axes perfectly aligned along $\hat{n}$). $S(T)$ measures the macroscopic degree or magnitude uniaxial order.

From equation (2.16) we get

$$\varepsilon_{\alpha\beta} = \varepsilon_0 \delta_{\alpha\beta} + \Delta \varepsilon^u_{\text{sat}} S(T) \left[ n_\alpha(\vec{r}) n_\beta(\vec{r}) - \frac{1}{3} \delta_{\alpha\beta} \right]$$  \hspace{0.5cm} (2.40)
where $\bar{\varepsilon} = \frac{1}{3} (\varepsilon_{xx} + \varepsilon_{yy} + \varepsilon_{zz}) = \frac{1}{3} Tr \varepsilon_{a\beta}$, $\varepsilon_{zz} = \varepsilon_\parallel$, and $\varepsilon_{xx} = \varepsilon_{yy} = \varepsilon_\perp$ (for a uniaxial phase with average $\hat{n} \parallel \hat{z}$). We can write equation (2.40) more exactly as

$$
\varepsilon_{a\beta} = \varepsilon_\parallel \delta_{a\beta} + \left( \varepsilon_\parallel - \varepsilon_\perp \right) n_\alpha n_\beta = \varepsilon_\perp \delta_{a\beta} + \Delta \varepsilon^u n_\alpha n_\beta
$$

(2.41)

Fluctuations of the dielectric tensor are related to the director fluctuations by

$$
\delta \varepsilon_{a\beta} = \Delta \varepsilon^u \left( n_\alpha \delta n_\beta + n_\beta \delta n_\alpha \right)
$$

(2.42)

In light scattering experiment, polarized light along $\hat{i}$ is incident on the sample and the polarized light along $\hat{f}$ is collected at the detector (Figure 2.1). The component of the dielectric tensor fluctuations along the polarizer and analyzer is given by

$$
\delta \varepsilon_{ij} = \Delta \varepsilon^u \left[ \left( \hat{n}_o \cdot \hat{i} \right) \left( \delta \hat{n} \cdot \hat{f} \right) + \left( \hat{n}_o \cdot \hat{f} \right) \left( \delta \hat{n} \cdot \hat{i} \right) \right]
$$

(2.43)

where $\hat{n}_o$ is the average director.

Using equation (2.28), we calculate

$$
\delta \varepsilon_{ij} (q) = \Delta \varepsilon^u \left[ \delta n_1 (\hat{q}) \left\{ \left( \hat{n}_o \cdot \hat{i} \right) \left( \hat{e}_1 \cdot \hat{f} \right) \right\} + \delta n_2 (\hat{q}) \left\{ \left( \hat{n}_o \cdot \hat{i} \right) \left( \hat{e}_2 \cdot \hat{f} \right) \right\} \right]
$$

(2.44)

From equations (2.7) and (2.10), it is clear that the intensity of scattered light, $I$, which is proportional to differential cross-section, $\sigma$, is proportional to $\langle \delta \varepsilon_{ij}^2 (q) \rangle$. Using equations (2.30), (2.31), and (2.44), we get

$$
I \propto \sigma \propto \langle \delta \varepsilon_{ij}^2 (q) \rangle = \frac{k_BT (\Delta \varepsilon^u)^2}{V} \left[ \frac{G_1}{\lambda_1} + \frac{G_2}{\lambda_2} \right]
$$

(2.45)
where $\hat{n}_o = \hat{z}$, $\lambda_1 = K_1 q_z^2 + K_{33} q_z^2$, $\lambda_2 = K_{22} q_z^2 + K_{33} q_z^2$, $G_1 = \left\{ (\hat{i})_z (\hat{f})_1 + (\hat{f})_z (\hat{i})_1 \right\}^2$, $G_2 = \left\{ (\hat{i})_z (\hat{f})_2 + (\hat{f})_z (\hat{i})_2 \right\}^2$. Equation (2.45) may be used to select scattering geometries to single out a specific mode through proper choice of $\hat{i}$, $\hat{f}$, $\hat{n}_o$, and the incident and scattering angles. At the same time by making $q_z$ or $q_\perp$ equal to zero, we can get the scattering purely due to either splay, twist, or bend. In principle, by measuring absolute intensities (or intensities calibrated against accepted standards), equations (2.35), (2.36), and (2.37) provide the basis for measuring the viscosity coefficients and/or elastic constants of the nematic liquid crystals.

Equation (2.45) can also be used to deduce the information of temperature dependence of scattered intensity in the nematic phase. The factor $k_B T$ gives only a weak effect in the narrow range of the nematic phase. Therefore, the intensity is essentially proportional to $\frac{(\Delta e^u)^2}{K} (K_{11} \cong K_{22} \cong K_{33} \cong K)$. Both $\Delta e^u$ and $K$ tend to decrease rather strongly when $T \to T_c$ (the nematic-isotropic transition temperature) – specifically, according to mean field theory, $\Delta e^u \sim S$ and $K_i \sim S^2$ to leading order (equation (2.89) Section 2.6.5) such that the ratio $\frac{(\Delta e^u)^2}{K}$ is expected to be essentially temperature-independent. Indeed, experimentally, the temperature dependence is found to be very small [6, 16].
2.6 BIAXIAL NEMATIC PHASE

2.6.1 BIAXIAL ORDER PARAMETER

To describe biaxial order, one must use the complete form of the symmetric, traceless, second rank tensor order parameter $Q_{\alpha\beta}$, which may be expressed in terms of two global scalar order parameter magnitudes and the locally averaged molecular alignment directions (directors $\hat{\mathbf{n}}, \hat{\mathbf{m}}$) defined at each $\mathbf{r}$ [17]

$$Q_{\alpha\beta}(\mathbf{r}) \equiv \frac{3S(T)}{2} \left\{ n_{\alpha}(\mathbf{r}) n_{\beta}(\mathbf{r}) - \frac{\delta_{\alpha\beta}}{3} \right\} + \frac{P(T)}{2} \left\{ m_{\alpha}(\mathbf{r}) m_{\beta}(\mathbf{r}) - \epsilon_{\alpha\gamma\delta} m_{\gamma}(\mathbf{r}) n_{\delta}(\mathbf{r}) \right\}$$

(2.46)

where $\delta_{\alpha\beta}$ is the Kronecker’s delta function and $\epsilon_{\alpha\gamma\delta}$, the Levi-Civita tensor, is defined as

$$\epsilon_{\alpha\beta\gamma} = \begin{cases} 1 & \text{for even permutation of } \alpha, \beta, \text{ and } \gamma \\ -1 & \text{for odd permutation of } \alpha, \beta, \text{ and } \gamma \\ 0 & \text{if two of them are equal} \end{cases}$$

(2.47)

In equation (2.46) the macroscopic uniaxial order parameter $S$ is defined as

before, $S(T) = \frac{\Delta \varepsilon^u(T)}{\Delta \varepsilon_{sat}^u}$, and the macroscopic biaxial order parameter is introduced with the definition

$$P(T) = \frac{\Delta \varepsilon^b(T)}{\Delta \varepsilon_{sat}^b}$$

(2.48)
with $\Delta \varepsilon^b$ representing the dielectric anisotropy associated with the biaxial order and $\Delta \varepsilon^b_{\text{sat}}$ being its saturated value (i.e. corresponding to perfect alignment of the relevant molecular axis along $\hat{m}$). In the biaxial nematic, dielectric anisotropies are related to principal values of the (diagonal) dielectric tensor as

$$
\Delta \varepsilon^u = \varepsilon_{zz} - \left( \varepsilon_{xx} + \varepsilon_{yy} \right) = \varepsilon_3 - \left( \varepsilon_1 + \varepsilon_2 \right)
$$

(2.49)

$$
\Delta \varepsilon^b = \varepsilon_{yy} - \varepsilon_{xx} = \varepsilon_2 - \varepsilon_1
$$

If we assume a single domain in $\hat{n}$ and choose it along the $z$-axis i.e. $\hat{n} \equiv \hat{z}$, the biaxial director $\hat{m}$ then lies in the $xy$ plane. If the biaxial director makes an angle of $\phi = \phi(\vec{r})$ with the $x$-axis (Figure 2.3), $\hat{m} = \cos \phi \hat{x} + \sin \phi \hat{y}$. Then, substituting $\hat{n}$ and $\hat{m}$ in equation (2.46), we get (Appendix A.1)

$$
Q_{\alpha\beta}(\vec{r}) = \begin{pmatrix}
\frac{-S}{2} + \frac{P}{2} \cos 2\phi & \frac{P}{2} \sin 2\phi & 0 \\
\frac{P}{2} \sin 2\phi & \frac{-S}{2} - \frac{P}{2} \cos 2\phi & 0 \\
0 & 0 & S
\end{pmatrix}
$$

(2.50)

A diagonal form of equation (2.50) is obtained when $\phi = 0$ i.e. $\hat{m} \equiv \hat{x}$ (single biaxial domain).

### 2.6.2 LANDAU TYPE FREE ENERGY FOR BIAXIAL ORDER PARAMETER

We can form a Landau type of free energy [6, 18] in terms of the order parameter from equation (2.50). As we shall explain below, we need a free energy expansion
containing terms up to sixth order to stabilize a biaxial phase from this order parameter. The free energy then becomes

$$F = F_0 + \frac{A(T)}{2} \text{Tr}(\bar{Q}^2) + \frac{B}{3} \text{Tr}(\bar{Q}^3) + \frac{C}{4} \left[ \text{Tr}(\bar{Q}^2) \right]^2 + \frac{D}{5} \left[ \text{Tr}(\bar{Q}^2) \right]\left[ \text{Tr}(\bar{Q}^3) \right] + \frac{E}{6} \left[ \text{Tr}(\bar{Q}^2) \right]^3 + \frac{E'}{6} \left[ \text{Tr}(\bar{Q}^3) \right]^2 + \ldots$$

(2.51)

where \(A = A_0 (T - T^*)\), and \(A_0, B, C, D, E,\) and \(E'\) are assumed to be temperature-independent.

For any symmetric \(3\times3\) matrix \(\bar{Q}\), \(\text{Tr}(\bar{Q}^r)\) can be expressed as a polynomial in \(\text{Tr}(\bar{Q})\), \(\text{Tr}(\bar{Q}^2)\), and \(\text{Tr}(\bar{Q}^3)\) [18]. Tracelessness of \(\bar{Q}\) leaves the Landau expansion in terms of only two absolute rotational invariants \(\text{Tr}(\bar{Q}^2)\) and \(\text{Tr}(\bar{Q}^3)\). It is because, the free energy being a scalar, the expansion of \(F\) in powers of \(\bar{Q}\) can only contain terms that

Figure 2.3 Left: biaxial director along \(\hat{x}\) axis, right: arbitrarily aligned biaxial director making an angle \(\phi\) with \(\hat{x}\) axis.
are invariant combinations of the elements $Q_{\alpha\beta}$ of the order parameter tensor. Letting

$$\delta = \text{Tr}(\bar{Q}^2)\left(\alpha Q_{\alpha\beta} Q_{\beta\alpha}\right) \quad \text{and} \quad \Delta = \text{Tr}(\bar{Q}^3)\left(\alpha Q_{\alpha\beta} Q_{\beta\gamma} Q_{\gamma\alpha}\right),$$

the Landau-deGennes free energy for the biaxial nematic phase becomes

$$F_B = \frac{A(T)}{2} \delta + \frac{B}{3} \Delta + \frac{C}{4} \delta^2 + \frac{D}{5} \delta \Delta + \frac{E}{6} \Delta^2 + \frac{E'}{6} \delta^3$$

(2.52)

up to sixth order in $Q_{\alpha\beta}$.

From equation (2.50), we find

$$\delta = Q_{\alpha\beta} Q_{\beta\alpha} = \frac{1}{2} (3S^2 + P^2), \quad \text{and} \quad \Delta = Q_{\alpha\beta} Q_{\beta\gamma} Q_{\gamma\alpha} = \frac{3}{4} S (S^2 - P^2)$$

(2.53)

A useful relation between $\delta$ and $\Delta$ is $\delta^3 \geq 6\Delta^2$; the equality sign holds in the uniaxial case only ($P = 0$) \cite{6, 18}. As a result, the minimum free energy gives a uniaxial phase as long as no terms higher than linear in $\Delta$ are present; this is the reason that sixth order terms in $Q_{\alpha\beta}$ are needed in equation (2.51) to stabilize a biaxial phase. Substituting the value of $\delta$ and $\Delta$ from equation (2.53) in equation (2.52), we get the free energy in terms of the biaxial scalar order parameter $P$ in the form \cite{19}

$$F_B = \alpha(S) + \beta(S)P^2 + \gamma(S)P^4 + \zeta(S)P^6$$

(2.54)

where
\[
\alpha(S) = \frac{3A}{4} S^2 + \frac{B}{4} S^3 + \frac{9C}{16} S^4 + \frac{9D}{40} S^5 + \left(\frac{9E'}{16} + \frac{3E}{32}\right) S^6
\]
\[
\beta(S) = \frac{A}{4} - \frac{B}{4} S + \frac{3C}{8} S^2 - \frac{3D}{20} S^3 + \left(\frac{9E'}{16} - \frac{3E}{16}\right) S^4
\]
\[
\gamma(S) = \frac{C}{16} - \frac{3D}{40} S + \left(\frac{3E'}{16} - \frac{3E}{32}\right) S^2
\]
\[
\varsigma(S) = \frac{E'}{48}
\]

2.6.3 LANDAU THEORY OF PHASE TRANSITION

Landau theory provides the simplest and most powerful phenomenological model that encompasses both the uniaxial and biaxial nematic phases and yields important predictions for the temperature dependence of the order parameters near phase transitions. One can further simplify equation (2.54) to a minimal model which allows the biaxial nematic phase, and is easier to treat algebraically. As discussed by Gramsbergen \textit{et al.} [18], this can be done by neglecting the constants \(D\) and \(E\) in equation (2.51). In this case equation (2.54) reduces to

\[
F_B = \alpha(S) + \beta(S) P^2 + \gamma(S) P^4
\]

where

\[
\alpha(S) = \frac{3A}{4} S^2 + \frac{B}{4} S^3 + \frac{9C}{16} S^4 + \frac{9E'}{16} S^6,
\]

\[
\beta(S) = \frac{A}{4} - \frac{B}{4} S + \frac{3C}{8} S^2 + \frac{9E'}{16} S^4, \text{ and}
\]

\[
\gamma(S) = \frac{C}{16} - \frac{3D}{40} S + \left(\frac{3E'}{16} - \frac{3E}{32}\right) S^2.
\]
\[
\gamma(S) = \frac{C}{16} + \frac{3E'}{16}S^2
\] (2.58)

Minimization of equation (2.55) with respect to \( P \) gives

\[
P = 0 \text{ (uniaxial)} \quad \text{and} \quad P^2 = -\frac{\beta(S)}{2\gamma(S)} \quad \text{(biaxial)}
\] (2.59)

and the free energy becomes

\[
F_U(S) = \alpha(S) \quad \text{(uniaxial)} \quad \text{and} \quad F_B(S) = \alpha(S) - \frac{\beta^2(S)}{4\gamma(S)}
\] (2.60)

Since \( \gamma(S) > 0 \) (required for stability in equation (2.60)), the biaxial solution in equation (2.59) is only allowed when \( \beta(S) < 0 \) and, from equation (2.60), also requires \( F_B(S) < F_U(S) \). So the problem reduces to finding the minimum of the function

\[
f(S) = F_U(S) = \alpha(S) \quad \text{when} \quad \beta(S) \geq 0 \quad \text{(uniaxial)},
\]

\[
f(S) = F_B(S) = \alpha(S) - \frac{\beta^2(S)}{4\gamma(S)} \quad \text{when} \quad \beta(S) < 0 \quad \text{(biaxial)}
\] (2.61)

At the point \( \beta(S) = 0 \), \( f(S) \) and \( f'(S) \) are continuous and \( f''_U(S) > f''_B(S) \) (Figure 2.4 (left)).

The limit of stability of the uniaxial phase occurs at a temperature \( T_{ub}^* \) and a value of \( S = S_0 \) given by the conditions

\[
\beta(S_0) = 0, \quad \alpha'(S_0) = 0
\] (2.62)
Figure 2.4 Left: schematic drawing of the free energy vs. order parameter $S$ according to equation (2.61), near the point $S = S_0$ where $\beta(S)$ changes sign; middle: a second order $N_u-N_b$ phase transition; and right: at the vanishing of local minimum of the $N_u$ phase near a first-order $N_u-N_b$ phase transition.

The transition is second order if
\[
\frac{d^2}{dS^2} \left[ \left( \alpha - \frac{\beta^2}{2\gamma} \right) \right]_{S=S_0} \geq 0 \quad \text{(Figure 2.4 (middle))}
\]
and first order (Figure 2.4 (right)) (with $S_0$ representing the limit of metastability for the uniaxial phase) if
\[
\frac{d^2}{dS^2} \left[ \left( \alpha - \frac{\beta^2}{2\gamma} \right) \right]_{S=S_0} \leq 0.
\]
In the latter case, the actual transition occurs at a temperature $T_{ub}$ above $T_{ub}^*$. 

2.6.4 BIAXIAL NEMATIC DIRECTOR MODES

The development of the biaxial nematic order introduces a new hydrodynamic Goldstone mode corresponding to the biaxial director fluctuation. To find the nature of the director modes, we need to write an appropriate director distortion free energy for a
biaxial nematic. Using an approach developed by Saupe [20], the distortion free energy of the biaxial nematic liquid crystal can be written in terms of three unit vectors \( \hat{a}, \hat{b}, \hat{c} \) forming a right-handed system, where \( \hat{a} = \hat{m}, \hat{c} = \hat{n}, \) and \( \hat{b} = \hat{n} \times \hat{m}. \) The bulk orientational distortion free energy density of the biaxial nematic liquid crystal can then be written as

\[
f_{db} = \frac{1}{2} K_{aa} \left[ \left( \hat{a} \cdot \vec{V} \right) \hat{b} \cdot \hat{c} \right]^2 + \frac{1}{2} K_{bb} \left[ \left( \hat{b} \cdot \vec{V} \right) \hat{c} \cdot \hat{a} \right]^2 + \frac{1}{2} K_{cc} \left[ \left( \hat{c} \cdot \vec{V} \right) \hat{a} \cdot \hat{b} \right]^2 + \frac{1}{2} K_{ab} \left[ \left( \hat{a} \cdot \vec{V} \right) \hat{c} \cdot \hat{b} \right]^2 + \frac{1}{2} K_{bc} \left[ \left( \hat{b} \cdot \vec{V} \right) \hat{a} \cdot \hat{c} \right]^2 + \frac{1}{2} K_{ca} \left[ \left( \hat{c} \cdot \vec{V} \right) \hat{b} \cdot \hat{a} \right]^2 + \frac{1}{2} K_{ac} \left[ \left( \hat{a} \cdot \vec{V} \right) \hat{b} \cdot \hat{c} \right]^2 + \frac{1}{2} K_{ab} \left[ \left( \hat{a} \cdot \vec{V} \right) \hat{c} \cdot \hat{b} \right]^2 + \frac{1}{2} K_{bc} \left[ \left( \hat{b} \cdot \vec{V} \right) \hat{a} \cdot \hat{c} \right]^2 + \frac{1}{2} K_{ca} \left[ \left( \hat{c} \cdot \vec{V} \right) \hat{b} \cdot \hat{a} \right]^2 + \frac{1}{2} K_{ab} \left[ \left( \hat{a} \cdot \vec{V} \right) \hat{c} \cdot \hat{b} \right]^2 + C_{ab} \left[ \left( \hat{a} \cdot \vec{V} \right) \hat{b} \cdot \hat{c} \right] + C_{bc} \left[ \left( \hat{b} \cdot \vec{V} \right) \hat{c} \cdot \hat{a} \right] + C_{ca} \left[ \left( \hat{c} \cdot \vec{V} \right) \hat{a} \cdot \hat{b} \right]
\]

where \( K_{aa}, K_{bb}, \) and \( K_{cc} \) are elastic constants corresponding to the twist around the axes \( \hat{a}, \hat{b}, \) and \( \hat{c} \) respectively; \( K_{ab}, K_{ac} \) are the elastic constants corresponding to the curvature of \( \hat{a} \) (i.e. \( \hat{a} \cdot \vec{V} \)) towards \( \hat{b} \) and \( \hat{c} \) respectively; \( K_{bc}, K_{ba}, K_{ca}, \) and \( K_{cb} \) have the similar definition; and \( C_{ab}, C_{bc}, \) and \( C_{ca} \) are associated with the coupling of two bend-splay terms together. The biaxial elastic constants can be expressed in terms of the uniaxial elastic constants, \( K_{11}, K_{22}, K_{33} \); the uniaxial order parameter \( S \); and the biaxial order parameter \( P \) (Section 2.6.5) which is summarized in Table 2.1 (page 71).
The scattering of light in the biaxial nematic is due to the thermal fluctuations of the directors about their equilibrium values. In aligned samples, each unit vector can be decomposed into an equilibrium (uniform) part and a fluctuation part such that

\[
\hat{a}(\vec{r}) = \hat{a}_0 + \delta \hat{a}(\vec{r}), \quad \hat{b}(\vec{r}) = \hat{b}_0 + \delta \hat{b}(\vec{r}), \quad \text{and} \quad \hat{c}(\vec{r}) = \hat{c}_0 + \delta \hat{c}(\vec{r})
\]  

(2.64)

Considering \( \hat{c}_0 \) along \( \hat{z} \), \( \hat{a}_0 \) along \( \hat{x} \) and \( \hat{b}_0 \) along \( \hat{y} \)

\[
\hat{a}(\vec{r}) = \hat{x} + \delta a_y(\vec{r}) \hat{y} + \delta a_z(\vec{r}) \hat{z}
\]  

(2.65)

\[
\hat{b}(\vec{r}) = \delta b_x(\vec{r}) \hat{x} + \hat{y} + \delta b_y(\vec{r}) \hat{z}
\]  

(2.66)

\[
\hat{c}(\vec{r}) = \delta c_x(\vec{r}) \hat{x} + \delta c_y(\vec{r}) \hat{y} + \hat{z}
\]  

(2.67)

The unit vectors form an orthogonal system i.e.

\[
\hat{a} \cdot \hat{b} = 0 \Rightarrow \delta b_x = -\delta a_y
\]

\[
\hat{b} \cdot \hat{c} = 0 \Rightarrow \delta c_y = -\delta b_z
\]  

(2.68)

\[
\hat{c} \cdot \hat{a} = 0 \Rightarrow \delta c_z = -\delta a_x
\]

Using equation (2.68) for small fluctuations, the fluctuating part of free energy in equation (2.63) can be written as

\[
\delta f_{db} = \frac{1}{2} K_{aa} \left( \partial_x \delta a_x \right)^2 + \frac{1}{2} K_{bb} \left( \partial_y \delta a_y \right)^2 + \frac{1}{2} K_{cc} \left( \partial_z \delta a_z \right)^2
\]

\[
+ \frac{1}{2} K_{ab} \left( \partial_x \delta b_x \right)^2 + \frac{1}{2} K_{bc} \left( \partial_y \delta c_y \right)^2 + \frac{1}{2} K_{ca} \left( \partial_z \delta c_z \right)^2
\]

\[
+ \frac{1}{2} K_{ac} \left( \partial_x \delta a_z \right)^2 + \frac{1}{2} K_{ba} \left( \partial_y \delta b_z \right)^2 + \frac{1}{2} K_{cb} \left( \partial_z \delta b_y \right)^2
\]

\[
- 2C_{ab} \left( \partial_x \delta a_x \right) \left( \partial_y \delta b_y \right) - 2C_{bc} \left( \partial_y \delta c_y \right) \left( \partial_z \delta a_z \right) -
\]

\[
2C_{ca} \left( \partial_z \delta c_z \right) \left( \partial_x \delta b_x \right)
\]  

(2.69)

Equation (2.69) can be converted into momentum space using Fourier transformation of the fluctuations – e.g.,
\[
\delta a_z (\vec{r}) = \sum_q \delta a_z (\vec{q}) e^{i\vec{q}\cdot\vec{r}}, \text{ etc} \quad (2.70)
\]

In terms of these Fourier components, the total biaxial nematic distortion free energy becomes

\[
F_{db} = \frac{V}{2} \sum_q \left[ \delta a_z (\vec{q}) + K_{a\sigma} q_x^2 \delta a_z (\vec{q}) + K_{a\nu} q_z^2 \delta a_z (\vec{q}) + \cdots \right] - \cdots \quad (2.71)
\]

which can be written in matrix form as

\[
F_{db} = \frac{V}{2} \sum_q \begin{bmatrix} \delta a_z (\vec{q}) & \delta b_x (\vec{q}) & \delta c_y (\vec{q}) \end{bmatrix} \begin{bmatrix} M \end{bmatrix} \begin{bmatrix} \delta a_z (-\vec{q}) \\ \delta b_x (-\vec{q}) \\ \delta c_y (-\vec{q}) \end{bmatrix} \quad (2.72)
\]

where

\[
M = \begin{pmatrix}
K_{b\sigma} q_y^2 + K_{a\nu} q_z^2 + K_{a\nu} q_x^2 & -C_{b\sigma} q_x q_y & -C_{a\sigma} q_x q_y \\
-C_{b\sigma} q_x q_y & K_{c\nu} q_x^2 + K_{a\sigma} q_z^2 + K_{a\nu} q_y^2 & -C_{a\nu} q_x q_y \\
-C_{a\sigma} q_x q_y & -C_{a\nu} q_x q_y & K_{a\nu} q_x^2 + K_{b\nu} q_y^2 + K_{c\nu} q_z^2
\end{pmatrix}
\]

The eigenvalues, \( \lambda_i \), of this matrix can be calculated to find the normal director modes of the biaxial nematic phase. These modes are linear combinations of \( \delta a_z, \ delta b_x, \) and \( \delta c_y \) (or equivalent components of \( \hat{n}, \hat{m}, \) and \( \hat{n} \times \hat{m} \)) that diagonalize the matrix \( M \). Dynamical equations similar to equation (2.35) can be constructed in terms of these
normal modes and an appropriate set of phenomenological viscosities. These equations yield normal mode relaxation rates of the form

$$\Gamma_i(q) = \frac{\lambda_i(q)}{\eta_i(q)}$$

(2.73)

and corresponding mean square normal mode fluctuation amplitudes given, through the equipartition theorem, by

$$\langle |\psi_i(q)|^2 \rangle = \frac{k_B T}{\lambda_i(q)}$$

(2.74)

In general, the scattered intensity from the coupled fluctuations in a biaxial nematic will be given by scattering geometry-specific combinations of the $$\langle |\psi_i(q)|^2 \rangle$$.

The effective viscosities $$\eta_i$$ in equation (2.73) are complicated expressions containing the twelve independent viscosity coefficients for a biaxial nematic liquid crystal [20]. Nine of the latter are associated with simple shear flow for uniform alignment. For example viscosity $$\eta_{mn}$$ is defined when $$\hat{m} \parallel \vec{v}$$ and $$\hat{n} \parallel \nabla \vec{v}$$ [20], where $$\vec{v}$$ is a constant flow velocity. Seven other shear viscosities can be defined similarly and one is associated with the coupling between them. The remaining three viscosities are associated with the rotation of the alignment axes along $$\hat{a}$$, $$\hat{b}$$, and $$\hat{c}$$ in the absence of flow.

In practical cases, the matrix $$M$$ takes a more complicated form because it is not known how to align the biaxial director in a fixed direction. Suppose $$\hat{m}$$ makes an
arbitrary angle $\phi$ in the $xy$ plane with respect to $\hat{x}$ (Figure 2.3). This replaces the $q_x$ and $q_y$ components of the wavevector $(q_x, q_y, q_z)$ in the previous discussion as follows

$$q_x \rightarrow q_x \cos \phi + q_y \sin \phi$$
$$q_y \rightarrow -q_x \sin \phi + q_y \cos \phi$$

(2.75)

I will now turn to some special cases in which the eigenvalues have relatively simple forms.

### 2.6.4.1 Homogeneous Planar Alignment of the Uniaxial Director parallel to the Scattering Plane

Consider a homogeneous planar alignment with $\hat{n} (=\hat{z})$ in $xz$ plane, $\hat{m}$ along $\hat{x}$ and normal to the substrate plane so that $q_y = 0$ (Figure 2.5 (ii)). In this case, the eigenvalues of matrix $M$ are:

$$\lambda_1 = K_{xx} q_x^2 + K_{zz} q_z^2$$

$$\lambda_{2,3} = \frac{1}{2} \left[ (K_{xx} + K_{zz}) q_x^2 - (K_{xx} - K_{zz}) q_z^2 + \sqrt{\left( (K_{xx} - K_{zz}) q_x^2 + (K_{xx} - K_{zz}) q_z^2 \right)^2 + 4C_{zz} q_x^2 q_z^2} \right]$$

(2.77)

For the three Goldstone modes, $\lambda_1$ corresponds to the splay-bend distortions of $\hat{n}$, $\lambda_2$ and $\lambda_3$ correspond to the coupling of $\hat{m}$ fluctuations with twist-bend distortions of $\hat{n}$. If $\hat{m}$ is along $\hat{y}$ (i.e. $\phi = 90^\circ$), the eigenvalues are:

$$\lambda_1 = K_{yy} q_x^2 + K_{zz} q_z^2$$

(2.78)
\begin{align}
\lambda_{2,3} &= \frac{1}{2} \left[ (K_{bb} + K_{uu}) q_x^2 + (K_{aa} + K_{cc}) q_z^2 \pm \sqrt{\left( (K_{bb} - K_{uu}) q_x^2 + (K_{aa} - K_{cc}) q_z^2 \right)^2 + 4C_{bc}^2 q_x^2 q_z^2} \right] \tag{2.79}
\end{align}

These eigenvalues can be compared with well established uniaxial nematic liquid crystals when biaxial elastic constants are written in terms of $K_{11}$, $K_{22}$, $K_{33}$, $S$, and $P$ (Section 2.6.5 and Table 2.1 (page 71)). When $P = 0$, $\Delta = 0$, mode 1 and 2 in equations (2.76) and (2.77) reduce to the splay-bend and twist-bend modes of the director $\hat{n}$. The additional eigenvalue vanishes (i.e. $\lambda_3 = 0$); physically, the restoring force for this mode vanishes in the absence of biaxiality.

### 2.6.4.2 Homogeneous Planar Alignment with Uniaxial Director Perpendicular to the Scattering Plane

For a homogeneous planar alignment with the director $\hat{n}$ perpendicular to the scattering plane and the director $\hat{m}$ along $\hat{x}$ ($\phi = 0^\circ$), $q_z = 0$ (Figure 2.6 (i)). The eigenvalues for this case are given by

\begin{align}
\lambda_{1,2} &= \frac{1}{2} \left[ (K_{ac} + K_{aa}) q_x^2 + (K_{bc} + K_{bb}) q_y^2 \pm \sqrt{\left( (K_{ac} - K_{aa}) q_x^2 + (K_{bc} - K_{bb}) q_y^2 \right)^2 + 4C_{ac}^2 q_x^2 q_y^2} \right] \tag{2.80}
\end{align}

\begin{align}
\lambda_3 &= K_{aa} q_x^2 + K_{bb} q_y^2 \tag{2.81}
\end{align}

If $\hat{m}$ is along $\hat{y}$ ($\phi = 90^\circ$), $q_x$ and $q_y$ are interchanged in equations (2.80) and (2.81). The new director mode corresponding to eigenvalue $\lambda_3$ represents splay-bend
Table 2.1 Elastic constants of a biaxial nematic phase expressed in terms of uniaxial elastic constants, the biaxial order parameter $P$ and uniaxial order parameter $S$; here the parameter $\Delta = \frac{2P}{3S}$. 

<table>
<thead>
<tr>
<th></th>
<th>$K_{aa}$</th>
<th>$K_{bb}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$K_{22}\left(1+\Delta+\frac{\Delta^2}{4}\right)$</td>
<td>$K_{22}\left(1-\Delta+\frac{\Delta^2}{4}\right)$</td>
</tr>
<tr>
<td>$K_{cc}$</td>
<td>$\Delta^2 K_{22}$</td>
<td>$\Delta^2 K_{33}$</td>
</tr>
<tr>
<td>$K_{bc}$</td>
<td>$K_{11}\left(1+\Delta+\frac{\Delta^2}{4}\right)$</td>
<td>$K_{33}\left(1-\Delta+\frac{\Delta^2}{4}\right)$</td>
</tr>
<tr>
<td>$K_{ba}$</td>
<td>$\Delta^2 K_{11}$</td>
<td>$K_{33}\left(1+\Delta+\frac{\Delta^2}{4}\right)$</td>
</tr>
<tr>
<td>$K_{ac}$</td>
<td>$K_{11}\left(1-\Delta+\frac{\Delta^2}{4}\right)$</td>
<td>$C_{ab} = (K_{11} - K_{22})\left(1-\frac{\Delta^2}{4}\right)$</td>
</tr>
<tr>
<td>$C_{bc}$</td>
<td>$(K_{11} - K_{22})\left(-\Delta + \frac{\Delta^2}{2}\right)$</td>
<td>$C_{cu} = (K_{33} - K_{22})\left(\Delta + \frac{\Delta^2}{2}\right)$</td>
</tr>
</tbody>
</table>
fluctuations of the biaxial director \( \mathbf{m} \). It decouples from the other two modes \( \lambda_{1,2} \), which are associated with splay and twist fluctuations of the uniaxial director \( \mathbf{n} \).

2.6.4.3 Homeotropic Alignment with Uniaxial Director parallel to the Scattering Plane

For the homeotropic alignment with the director \( \mathbf{n} \) normal to the substrate plane and \( \mathbf{m} \) normal to the scattering plane (Figure 2.7 (ii)), \( q_x = 0 \). The eigenvalues in this case are given by equations (2.78) and (2.79) with \( q_x \Leftrightarrow q_y \) i.e.

\[
\lambda_1 = K_{bc} q_y^2 + K_{cb} q_z^2
\]

\[
\lambda_{2,3} = \frac{1}{2} \left[ (K_{bb} + K_{ba}) q_y^2 + (K_{ca} + K_{cc}) q_z^2 \pm \sqrt{\left( (K_{bb} - K_{ba}) q_y^2 + (K_{ca} - K_{cc}) q_z^2 \right)^2 + 4C_{bc}^2 q_y^2 q_z^2} \right]
\]

\( \lambda_1 \) corresponds to splay-bend fluctuation of the uniaxial director \( \mathbf{n} \), while \( \lambda_2 \) and \( \lambda_3 \) correspond to the coupling of the biaxial director \( \mathbf{m} \) with the twist-bend of the uniaxial director \( \mathbf{n} \) fluctuation. On the other hand for \( \phi = 90^\circ \) (Figure 2.7 (i)), the eigenvalues are given by equations (2.76) and (2.77) with \( q_x \Leftrightarrow q_y \) i.e.

\[
\lambda_1 = K_{ac} q_x^2 + K_{ca} q_z^2
\]

\[
\lambda_{2,3} = \frac{1}{2} \left[ (K_{aa} + K_{ab}) q_x^2 + (K_{cb} + K_{cc}) q_z^2 \pm \sqrt{\left( (K_{aa} - K_{ab}) q_x^2 + (K_{cb} - K_{cc}) q_z^2 \right)^2 + 4C_{ac}^2 q_x^2 q_z^2} \right]
\]
2.6.5 LANDAU-GINZBURG THEORY OF NEMATIC FREE ENERGY

To elucidate the scaling of nematic elastic constants, which describe spatial distortions of the director, in terms of the scalar order parameters, we consider an extension of the minimal Landau theory that includes spatial variation of the order parameter tensor [21, 22]. For a complete description, we need terms that are third order in $\tilde{Q}(\vec{r})$ tensor but quadratic in the derivative of $\tilde{Q}$. $S$ and $P$ are assumed to be constant in space, so the space variation of $\tilde{Q}$ is due to the spatial variation of the director field. Allowing for terms up to third order in $Q_{a\beta}(\vec{r})$, a complete distortion free energy of a nematic phase consists of five independent terms which are rotationally invariant i.e.

$$F_{el} = \frac{L_1}{2}(\partial_i Q_{jk})(\partial_j Q_{ik}) + \frac{L_2}{2}(\partial_i Q_{ik})(\partial_j Q_{jk}) + \frac{L_3}{2} Q_{a\beta}(\partial_a Q_{\mu\nu})(\partial_\beta Q_{\mu\nu}) + \frac{L_4}{2} Q_{a\beta}(\partial_\mu Q_{\alpha\nu})(\partial_\beta Q_{\nu\alpha}) + \frac{L_5}{2} Q_{a\beta}(\partial_\alpha Q_{\mu\nu})(\partial_\beta Q_{\nu\mu})$$

(2.86)

where the coefficients $L_1$ etc are constants. When the value of $Q_{a\beta}(\vec{r})$ from equation (2.46) is substituted into equation (2.86) and simplified, we get the elastic free energy in the form of equation (2.24) for a uniaxial nematic phase (with $P = 0$) and (2.63) for a biaxial nematic phase (with $P \neq 0$ and $\hat{a} = \hat{m}$, $\hat{c} \equiv \hat{n}$, and $\hat{b} \equiv \hat{n} \times \hat{m}$).

The simplest approximation uses only the first two (quadratic) terms in equation (2.86). Equation (2.86) then becomes

$$F_{el} = \frac{L_1}{2}(\partial_i Q_{jk})(\partial_j Q_{ik}) + \frac{L_2}{2}(\partial_i Q_{ik})(\partial_j Q_{jk})$$

(2.87)
Substituting $Q_{\alpha\beta}(\vec{r})$ from equation (2.46) with $P = 0$ into equation (2.87) and simplifying, we get

$$F_{\alpha} = \frac{9S^2}{4}(L_1 + L_2)(\vec{\nabla} \cdot \hat{n})^2 + \frac{9S^2}{4}L_1(\hat{n} \cdot (\vec{\nabla} \times \hat{n}))^2 + \frac{9S^2}{4}(L_1 + L_2)(\hat{n} \times (\vec{\nabla} \times \hat{n}))^2$$  

(2.88)

Comparing equations (2.24) and (2.88), we get

$$K_{11} = K_{33} = \frac{9S^2}{4}(2L_1 + L_2)$$

$$K_{22} = \frac{9S^2}{2}L_1$$

(2.89)

Though equation (2.89) does not distinguish between $K_{11}$ and $K_{33}$, it shows, to a lowest order, an important relation between uniaxial nematic elastic constants and the uniaxial scalar order parameter $S$, i.e. $K_{ii} \propto S^2$.

Complete simplification of equation (2.86) for the order parameter tensor $Q_{\alpha\beta}(\vec{r})$ from equation (2.46) gives the relations for the elastic constants of the uniaxial nematic liquid crystal ($K_{11}$, $K_{22}$, and $K_{33}$) and the biaxial nematic liquid crystal ($K_{\alpha\alpha}$ etc) in terms of constants $L_i$ etc and both orientational order parameters $S$ and $P$. We can then express biaxial elastic constants in terms of the uniaxial elastic constants, $K_{11}$, $K_{22}$, $K_{33}$; the uniaxial order parameter $S$; and the biaxial order parameter $P$. Prof. David Allender has derived the expressions for them, which are shown in Table 2.1 [24].
2.6.6 OPTICAL SELECTION RULES FOR BIAXIAL NEMATIC LIQUID CRYSTALS

As discussed in Section 2.6.1, the biaxial order parameter can be considered as the sum of a uniaxial part $Q^u_{\alpha\beta}(\vec{r})$ and the biaxial part $Q^b_{\alpha\beta}(\vec{r})$ i.e.

$$Q_{\alpha\beta}(\vec{r}) = Q^u_{\alpha\beta}(\vec{r}) + Q^b_{\alpha\beta}(\vec{r})$$

(2.90)

where

$$Q^u_{\alpha\beta}(\vec{r}) = \frac{3}{2} S(T) \left[ n_\alpha(\vec{r}) n_\alpha(\vec{r}) - \frac{1}{3} \delta_{\alpha\beta} \right]$$

$$Q^b_{\alpha\beta}(\vec{r}) = \frac{1}{2} P(T) \left[ m_\alpha(\vec{r}) m_\beta(\vec{r}) - \epsilon_{\alpha\gamma}\epsilon_{\beta\delta} m_\gamma(\vec{r}) n_\delta(\vec{r}) + \epsilon_{\alpha\delta}\epsilon_{\beta\gamma} m_\gamma(\vec{r}) n_\delta(\vec{r}) \right]$$

For $\hat{m}$ in the $xy$ plane making an angle $\phi$ with the $x$-axis (Appendix A.1),

$$Q_{\alpha\beta}^u = \begin{pmatrix} \frac{-S}{2} & 0 & 0 \\ 0 & \frac{-S}{2} & 0 \\ 0 & 0 & S \end{pmatrix}$$

(2.91)

$$Q_{\alpha\beta}^b = \begin{pmatrix} \frac{1}{2} P \cos 2\phi & \frac{1}{2} P \sin 2\phi & 0 \\ \frac{1}{2} P \sin 2\phi & -\frac{1}{2} P \cos 2\phi & 0 \\ 0 & 0 & 0 \end{pmatrix}$$

(2.92)

The dielectric tensor of the biaxial nematic can be written as

$$\varepsilon_{\alpha\beta} = \bar{\varepsilon} \delta_{\alpha\beta} + \frac{2}{3} \Delta \varepsilon^u_{\alpha\beta} Q^u_{\alpha\beta} + 2 \Delta \varepsilon^b_{\alpha\beta} Q^b_{\alpha\beta}$$

(2.93)
where \( \bar{\varepsilon} = \frac{\varepsilon_{xx} + \varepsilon_{yy} + \varepsilon_{zz}}{3} = \frac{\varepsilon_i + \varepsilon_j + \varepsilon_k}{3} \). Substituting equation (2.49), (2.91), and (2.92) in equation (2.93) and assuming for simplicity \( S = 1 \) (so that \( \Delta \varepsilon_{sat}^u = \Delta \varepsilon_{sat}^u \) from now on), we get

\[
\varepsilon_{ab}^{b} = \begin{pmatrix}
    \varepsilon_{\perp} + \Delta \varepsilon_{sat}^b P \cos 2\phi & \Delta \varepsilon_{sat}^b P \sin 2\phi & 0 \\
    -\Delta \varepsilon_{sat}^b P \sin 2\phi & \varepsilon_{\perp} - \Delta \varepsilon_{sat}^b P \cos 2\phi & 0 \\
    0 & 0 & \varepsilon_{||}
\end{pmatrix}
\] (2.94)

Equation (2.94) can be simplified by choosing \( \hat{n} \parallel \hat{z} \) and \( \hat{m} \parallel \hat{x} \) such that \( \phi = 0 \), so that

\[
\varepsilon_{ab}^{b} = \begin{pmatrix}
    \varepsilon_{\perp} + \Delta \varepsilon_{sat}^b P & 0 & 0 \\
    0 & \varepsilon_{\perp} - \Delta \varepsilon_{sat}^b P & 0 \\
    0 & 0 & \varepsilon_{||}
\end{pmatrix}
\] (2.95)

Dynamic light scattering is associated with the intensity of the light scattered due to the fluctuation of the dielectric constant tensor which is defined as \( \delta \varepsilon_{ab} \). Above a uniaxial – biaxial transition, one expects significant scattering from fluctuations in the uniaxial director (\( \hat{n} \)) and of the biaxial order parameter \( P \), while below the transition (in the biaxial phase) the scattering should be dominated by fluctuations in \( \hat{n} \) and \( \hat{m} \). The latter can be represented by infinitesimal rotations \( \delta \phi_x \), \( \delta \phi_y \), and \( \delta \phi_z \) about \( x \), \( y \), and \( z \) axes respectively. The associated rotation operations in matrix form can be defined as

\[
R_x(\delta \phi_x) = \begin{pmatrix}
    1 & 0 & 0 \\
    0 & 1 & \delta \phi_x \\
    0 & -\delta \phi_x & 1
\end{pmatrix},
R_y(\delta \phi_y) = \begin{pmatrix}
    1 & 0 & -\delta \phi_y \\
    0 & 1 & 0 \\
    \delta \phi_y & 0 & 1
\end{pmatrix},
R_z(\delta \phi_z) = \begin{pmatrix}
    1 & \delta \phi_z & 0 \\
    -\delta \phi_z & 1 & 0 \\
    0 & 0 & 1
\end{pmatrix}
\] (2.96)
Since these rotations are infinitesimal, they commute, and the order of rotation is not important [23].

On the other hand, fluctuations in the amplitude of the biaxiality can be accounted defining $P = P_0 + \delta P$, where $P_0 = P_0(T)$ is the nonfluctuating (average) component of $P$. If $P_0 = 0$, $\delta \phi_x$ and $\delta \phi_y$ represent the rotations of the uniaxial director and $\delta P$ represents biaxial order parameter fluctuations. The biaxial phase exists when $P_0 > 0$. In this case $\delta \phi_x$, $\delta \phi_y$, and $\delta \phi_z$ represent rotational fluctuations of the directors $\hat{n}$ and $\hat{m}$ and $\delta P$ represents the biaxial order parameter fluctuation.

The transformation of $\varepsilon_{\alpha\beta}$ under the infinitesimal rotations is given by

$$\left[R_x(\delta \phi_x) \cdot R_y(\delta \phi_y) \cdot R_z(\delta \phi_z)\right] \varepsilon_{\alpha\beta} \left[R_x(\delta \phi_x) \cdot R_y(\delta \phi_y) \cdot R_z(\delta \phi_z)\right]^{-1}$$

This gives (Appendix A.2)

$$\varepsilon_{\alpha\beta} = \begin{pmatrix}
e_1 + \Delta \varepsilon_{\text{sat}} (P_0 + \delta P) & -2\Delta \varepsilon_{\text{sat}} (P_0 + \delta P) \delta \phi_z & (\Delta \varepsilon_{\text{sat}} (P_0 + \delta P) - \Delta \varepsilon_{\text{sat}}) \delta \phi_y \\
-2\Delta \varepsilon_{\text{sat}} (P_0 + \delta P) \delta \phi_z & e_1 - \Delta \varepsilon_{\text{sat}} (P_0 + \delta P) & (\Delta \varepsilon_{\text{sat}} (P_0 + \delta P) + \Delta \varepsilon_{\text{sat}}) \delta \phi_z \\
(\Delta \varepsilon_{\text{sat}} (P_0 + \delta P) - \Delta \varepsilon_{\text{sat}}) \delta \phi_y & (\Delta \varepsilon_{\text{sat}} (P_0 + \delta P) + \Delta \varepsilon_{\text{sat}}) \delta \phi_z & \varepsilon_{11}
\end{pmatrix}$$

(2.97)

The fluctuating part of $\varepsilon_{\alpha\beta}$ to first order is

$$\delta \varepsilon_{\alpha\beta} = \begin{pmatrix}
\Delta \varepsilon_{\text{sat}} \delta P & -2\Delta \varepsilon_{\text{sat}} P_0 \delta \phi_z & (\Delta \varepsilon_{\text{sat}} P_0 - \Delta \varepsilon_{\text{sat}}) \delta \phi_y \\
-2\Delta \varepsilon_{\text{sat}} P_0 \delta \phi_z & -\Delta \varepsilon_{\text{sat}} \delta P & (\Delta \varepsilon_{\text{sat}} + \Delta \varepsilon_{\text{sat}} P_0) \delta \phi_z \\
(\Delta \varepsilon_{\text{sat}} P_0 - \Delta \varepsilon_{\text{sat}}) \delta \phi_y & (\Delta \varepsilon_{\text{sat}} + \Delta \varepsilon_{\text{sat}} P_0) \delta \phi_z & 0
\end{pmatrix}$$

(2.98)

(2.99)

The rotations $\delta \phi_x$, $\delta \phi_y$, and $\delta \phi_z$ can be replaced with the $\hat{n}$-director components $\delta n_x$, $\delta n_y$ and the $\hat{m}$-director components $\delta m_y$, $\delta m_z$ i.e.
\[ \delta \phi_x = -\delta n_y, \quad \delta \phi_y = \delta n_x = -\delta m_z, \quad \text{and} \quad \delta \phi_z = \delta m_y \]  

(2.100)

Plugging equations (2.100) into equation (2.99), we get

\[
\delta \varepsilon_{ab} = \begin{pmatrix}
\Delta \varepsilon_{sat}^b \delta P & -2\Delta \varepsilon_{sat}^b P_0 \delta m_y & \left(\Delta \varepsilon_{sat}^b P_0 - \Delta \varepsilon_{sat}^u\right) \delta n_x \\
-2\Delta \varepsilon_{sat}^b P_0 \delta m_y & -\Delta \varepsilon_{sat}^u \delta P & -\left(\Delta \varepsilon_{sat}^u + \Delta \varepsilon_{sat}^b P_0\right) \delta n_y \\
\left(\Delta \varepsilon_{sat}^b P_0 - \Delta \varepsilon_{sat}^u\right) \delta n_x & -\left(\Delta \varepsilon_{sat}^u + \Delta \varepsilon_{sat}^b P_0\right) \delta n_y & 0
\end{pmatrix}
\]  

(2.101)

For a particular light scattering geometry, equation (2.101) can be simplified substantially choosing specific polarizer, \( \hat{i} \), and analyzer, \( \hat{f} \), directions. The suitable possible combinations of incident and scattered polarization for our experiments are: \((V,V), (V,H), (H,V), \) and \((H,H)\), where the labels \( V \) and \( H \) stand for vertical and horizontal polarization, respectively, with respect to the scattering plane.

Choosing the principle axis coordinate system such that \( \hat{n} \parallel \hat{z} \) and \( \hat{m} \parallel \hat{x} \), \( \delta \varepsilon_{ab} \) given by equation (2.101) determines specific components of the fluctuating dielectric constant tensor for a particular scattering geometry (Appendix A.3). These are discussed in the next several subsections and then summarized in Table 2.2.

### 2.6.6.1 Geometry 1

Consider a biaxial nematic liquid crystal with \( \hat{n} \) in the substrate plane and parallel to the scattering plane and \( \hat{m} \) in the substrate plane and normal to the scattering plane (Figure 2.5 (i)). Then there are four possible cases, distinguished by incident-scattered polarization combinations:
(a) for $VH$- depolarized scattering:

\[ \hat{i} = \hat{x}, \quad \hat{f} = -\sin \theta_s \hat{y} + \cos \theta_s \hat{z} \]

\[ \delta \varepsilon_{vh} = \hat{f} \cdot \delta \varepsilon \cdot \hat{i} = -\left( \Delta \varepsilon_{sat}^u - \Delta \varepsilon_{sat}^b P_0 \right) \cos \theta_s \delta n_x + 2 \Delta \varepsilon_{sat}^b P_0 \sin \theta_s \delta m_y \]

(b) for $HV$- depolarized scattering:

\[ \hat{i} = \sin \theta_s \hat{y} + \cos \theta_s \hat{z}, \quad \hat{f} = \hat{x} \]

\[ \delta \varepsilon_{hv} = \hat{f} \cdot \delta \varepsilon \cdot \hat{i} = -\left( \Delta \varepsilon_{sat}^u - \Delta \varepsilon_{sat}^b P_0 \right) \cos \theta_s \delta n_x - 2 \Delta \varepsilon_{sat}^b P_0 \sin \theta_s \delta m_y \]

(c) for $VV$- polarized scattering:

\[ \hat{i} = \hat{x}, \quad \hat{f} = \hat{x} \]

\[ \delta \varepsilon_{vv} = \hat{f} \cdot \delta \varepsilon \cdot \hat{i} = \Delta \varepsilon_{sat}^b \delta P \]

(d) for $HH$- polarized scattering:

\[ \hat{i} = \sin \theta_s \hat{y} + \cos \theta_s \hat{z}, \quad \hat{f} = -\sin \theta_s \hat{y} + \cos \theta_s \hat{z} \]

\[ \delta \varepsilon_{hh} = \hat{f} \cdot \delta \varepsilon \cdot \hat{i} = \Delta \varepsilon_{sat}^b \sin \theta_s \sin \theta_s \delta P - \left( \Delta \varepsilon_{sat}^u + \Delta \varepsilon_{sat}^b P_0 \right) \sin \left( \theta_i - \theta_s \right) \delta n_y \]

Here $\theta_i$ ($\theta_s$) are the incident (scattering) angles, respectively, for laser light directed onto (and collected from) the sample at specific directions. (The angles are defined within the sample – i.e., after accounting for refraction at the boundary surfaces.)
Figure 2.5 Experimental geometries: (i) homogeneous cell with $\hat{n}$ in the scattering plane and $\hat{m}$ normal to the scattering plane, and (ii) $\hat{n}$ in the scattering plane, and $\hat{m}$ in the scattering plane and normal to the cell.
2.6.6.2 Geometry 2

Consider a planarly aligned biaxial nematic with \( \hat{n} \) in the substrate plane and parallel to the scattering plane and \( \hat{m} \) normal to the substrate plane and parallel to the scattering plane (Figure 2.5 (ii)). Then:

(a) for \( VH \)- depolarized scattering:
\[
\hat{i} = \hat{y}, \quad \hat{f} = \sin \theta \hat{x} + \cos \theta \hat{z}
\]
\[
\delta e_{vH} = \hat{f} \cdot \delta \hat{e} \cdot \hat{i} = - \left( \Delta e_{sat}^u + \Delta e_{sat}^b P_0 \right) \cos \theta n_x \delta m_y - 2 \Delta e_{sat}^b P_0 \sin \theta \delta m_y
\]

(b) for \( HV \)- depolarized scattering:
\[
\hat{i} = - \sin \theta \hat{x} + \cos \theta \hat{z}, \quad \hat{f} = \hat{y}
\]
\[
\delta e_{HV} = \hat{f} \cdot \delta \hat{e} \cdot \hat{i} = - \left( \Delta e_{sat}^u + \Delta e_{sat}^b P_0 \right) \cos \theta n_y + 2 \Delta e_{sat}^b P_0 \sin \theta \delta m_y
\]

(c) for \( HH \)- polarized scattering:
\[
\hat{i} = \hat{y}, \quad \hat{f} = \hat{y}
\]
\[
\delta e_{vV} = \hat{f} \cdot \delta \hat{e} \cdot \hat{i} = - \Delta e_{sat}^b \delta P
\]

(d) for \( VV \)- polarized scattering:
\[
\hat{i} = - \sin \theta \hat{x} + \cos \theta \hat{z}, \quad \hat{f} = \sin \theta \hat{x} + \cos \theta \hat{z}
\]
\[
\delta e_{HH} = \hat{f} \cdot \delta \hat{e} \cdot \hat{i} = - \Delta e_{sat}^b \sin \theta \sin \theta \delta P + \left( \Delta e_{sat}^u - \Delta e_{sat}^b P_0 \right) \sin \left( \theta_i - \theta_s \right) \delta n_x
\]
2.6.6.3 Geometry 3

Consider a planarly aligned biaxial nematic with \( \hat{n} \) in the substrate plane and normal to the scattering plane and \( \hat{m} \) in the substrate plane and parallel to the scattering plane (Figure 2.6 (i)). Then:

(a) for \( VH \)- depolarized scattering:

\[
\hat{i} = \hat{z}, \quad \hat{f} = \cos \theta \hat{x} + \sin \theta \hat{y}
\]

\[
\delta \epsilon_{VH} = \hat{f} \cdot \delta \hat{e} \cdot \hat{i} = - \left( \Delta \epsilon^a_{sat} + \Delta \epsilon^b_{sat} P_0 \right) \sin \theta \delta n_y - \left( \Delta \epsilon^a_{sat} - \Delta \epsilon^b_{sat} P_0 \right) \cos \theta \delta n_x
\]

(b) for \( HV \)- depolarized scattering:

\[
\hat{i} = \cos \theta \hat{x} - \sin \theta \hat{y}, \quad \hat{f} = \hat{z}
\]

\[
\delta \epsilon_{HV} = \hat{f} \cdot \delta \hat{e} \cdot \hat{i} = \left( \Delta \epsilon^a_{sat} + \Delta \epsilon^b_{sat} P_0 \right) \sin \theta \delta n_y - \left( \Delta \epsilon^a_{sat} - \Delta \epsilon^b_{sat} P_0 \right) \cos \theta \delta n_x
\]

(c) for \( VV \)- polarized scattering:

\[
\hat{i} = \hat{z}, \quad \hat{f} = \hat{z}
\]

\[
\delta \epsilon_{VV} = \hat{f} \cdot \delta \hat{e} \cdot \hat{i} = 0
\]

(d) for \( HH \)- polarized scattering:

\[
\hat{i} = \cos \theta \hat{x} - \sin \theta \hat{y}, \quad \hat{f} = \cos \theta \hat{x} + \sin \theta \hat{y}
\]

\[
\delta \epsilon_{HH} = \hat{f} \cdot \delta \hat{e} \cdot \hat{i} = \Delta \epsilon^b_{sat} \cos (\theta - \theta') \delta P + 2 \Delta \epsilon^b_{sat} P_0 \sin (\theta - \theta') \delta m_y
\]
Figure 2.6 Experimental geometries: (i) homogeneous cell with \( \hat{n} \) normal to the scattering plane and \( \hat{m} \) in the scattering plane and parallel to the substrate, and (ii) \( \hat{n} \) normal to the scattering plane, and \( \hat{m} \) in the scattering plane and normal to the cell.
2.6.6.4 Geometry 4

For a planarly aligned biaxial nematic with \( \hat{n} \) in the substrate plane and normal to the scattering plane and \( \hat{m} \) normal to the substrate plane and parallel to the scattering plane (Figure 2.6 (ii)):

(a) for \( VH \)- depolarized scattering:

\[
\hat{i} = \hat{z}, \quad \hat{f} = \sin \theta_s \hat{x} - \cos \theta_s \hat{y}
\]

\[
\delta e_{\text{VH}} = \hat{f} \cdot \delta e \cdot i = \left( \Delta \epsilon_{\text{sat}} + \Delta \epsilon_{\text{sat}}^b P_0 \right) \cos \theta_s \delta n_y - \left( \Delta \epsilon_{\text{sat}}^a - \Delta \epsilon_{\text{sat}}^b P_0 \right) \sin \theta_s \delta n_x
\]

(b) for \( HV \)- depolarized scattering:

\[
\hat{i} = -\sin \theta_i \hat{x} - \cos \theta_i \hat{y}, \quad \hat{f} = \hat{z}
\]

\[
\delta e_{\text{HV}} = \hat{f} \cdot \delta e \cdot i = \left( \Delta \epsilon_{\text{sat}}^a + \Delta \epsilon_{\text{sat}}^b P_0 \right) \cos \theta_i \delta n_x + \left( \Delta \epsilon_{\text{sat}}^a - \Delta \epsilon_{\text{sat}}^b P_0 \right) \sin \theta_i \delta n_x
\]

(c) for \( VV \)- polarized scattering:

\[
\hat{i} = \hat{z}, \quad \hat{f} = \hat{z}
\]

\[
\delta e_{\text{VV}} = \hat{f} \cdot \delta e \cdot i = 0
\]

(d) for \( HH \)- polarized scattering:

\[
\hat{i} = -\sin \theta_i \hat{x} - \cos \theta_i \hat{y}, \quad \hat{f} = \sin \theta_s \hat{x} - \cos \theta_s \hat{y}
\]

\[
\delta e_{\text{HH}} = \hat{f} \cdot \delta e \cdot i = -\Delta \epsilon_{\text{sat}}^b \cos (\theta_i - \theta_s) \delta P - 2 \Delta \epsilon_{\text{sat}}^b P_0 \sin (\theta_i - \theta_s) \delta m_y
\]
2.6.6.5 Geometry 5

For a homeotropically aligned biaxial nematic with \( \hat{n} \) normal to the substrate plane and parallel to the scattering plane and \( \hat{m} \) in the substrate plane and parallel to the scattering plane (Figure 2.7 (i)):

(a) for \( VH \)- depolarized scattering:
\[
\hat{i} = -\hat{y}, \quad \hat{f} = \cos \theta_s \hat{x} + \sin \theta_s \hat{z}
\]
\[
\delta \varepsilon_{VH} = \hat{f} \cdot \delta \varepsilon \cdot \hat{i} = \left( \Delta \varepsilon^u_{sat} + \Delta \varepsilon^b_{sat} P_0 \right) \sin \theta_s \delta n_x + 2 \Delta \varepsilon^b_{sat} P_0 \cos \theta_s \delta m_y
\]

(b) for \( HV \)- depolarized scattering:
\[
\hat{i} = \cos \theta_s \hat{x} - \sin \theta_s \hat{z}, \quad \hat{f} = -\hat{y}
\]
\[
\delta \varepsilon_{HV} = \hat{f} \cdot \delta \varepsilon \cdot \hat{i} = -\left( \Delta \varepsilon^u_{sat} + \Delta \varepsilon^b_{sat} P_0 \right) \sin \theta_s \delta n_x + 2 \Delta \varepsilon^b_{sat} P_0 \cos \theta_s \delta m_y
\]

(c) for \( VV \)- polarized scattering:
\[
\hat{i} = -\hat{y}, \quad \hat{f} = -\hat{y}
\]
\[
\delta \varepsilon_{VV} = \hat{f} \cdot \delta \varepsilon \cdot \hat{i} = -\Delta \varepsilon^b_{sat} \delta P
\]

(d) for \( HH \)- polarized scattering:
\[
\hat{i} = \cos \theta_s \hat{x} - \sin \theta_s \hat{z}, \quad \hat{f} = \cos \theta_s \hat{x} + \sin \theta_s \hat{z}
\]
\[
\delta \varepsilon_{HH} = \hat{f} \cdot \delta \varepsilon \cdot \hat{i} = \Delta \varepsilon^b_{sat} \cos \theta_s \cos \theta_s \delta P + \left( \Delta \varepsilon^u_{sat} - \Delta \varepsilon^b_{sat} P_0 \right) \sin \left( \theta_s - \theta_s \right) \delta n_x
\]
2.6.6.6 Geometry 6

Finally, consider a homeotropically aligned biaxial nematic with \(\hat{n}\) normal to the substrate plane and parallel to the scattering plane and \(\hat{m}\) in the substrate plane and normal to the scattering plane (Figure 2.7 (ii)). In this case:

(a) for \(VH\)- depolarized scattering:

\[
\hat{i} = \hat{x}, \quad \hat{f} = \cos \theta \hat{y} + \sin \theta \hat{z}
\]

\[
\delta \varepsilon_{VH} = \hat{f} \cdot \delta \varepsilon \cdot \hat{i} = -\left(\Delta \varepsilon^a_{sat} - \Delta \varepsilon^b_{sat} P_0\right) \sin \theta \delta n_x - 2\Delta \varepsilon^b_{sat} P_0 \cos \theta \delta m_y
\]

(b) for \(HV\)- depolarized scattering:

\[
\hat{i} = \cos \theta \hat{y} - \sin \theta \hat{z}, \quad \hat{f} = \hat{x}
\]

\[
\delta \varepsilon_{HV} = \hat{f} \cdot \delta \varepsilon \cdot \hat{i} = \left(\Delta \varepsilon^a_{sat} - \Delta \varepsilon^b_{sat} P_0\right) \sin \theta \delta n_x - 2\Delta \varepsilon^b_{sat} P_0 \cos \theta \delta m_y
\]

(c) for \(VV\)- polarized scattering:

\[
\hat{i} = \hat{x}, \quad \hat{f} = \hat{x}
\]

\[
\delta \varepsilon_{VV} = \hat{f} \cdot \delta \varepsilon \cdot \hat{i} = \Delta \varepsilon^b_{sat} \delta P
\]

(d) for \(HH\)- polarized scattering:

\[
\hat{i} = \cos \theta \hat{y} - \sin \theta \hat{z}, \quad \hat{f} = \cos \theta \hat{y} + \sin \theta \hat{z}
\]

\[
\delta \varepsilon_{HH} = \hat{f} \cdot \delta \varepsilon \cdot \hat{i} = -\Delta \varepsilon^b_{sat} \cos \theta \cos \theta \delta P + \left(\Delta \varepsilon^a_{sat} + \Delta \varepsilon^b_{sat} P_0\right) \sin \left(\theta - \theta_s\right) \delta n_y
\]
Figure 2.7 Experimental geometries: (i) homeotropic cell with both $\hat{n}$ and $\hat{m}$ in the scattering plane, and (ii) $\hat{n}$ in the scattering plane and $\hat{m}$ normal to the scattering plane.
Table 2.2 Selection rules for an aligned biaxial nematic phase.
2.6.7 BIAXIAL NEMATIC PHASE WITH ARBITRARILY ALIGNED BIAXIAL DIRECTOR

While preparing the sample cell, \( \hat{n} \) is aligned along a specified direction by appropriate surface treatment, but it is not known how to align \( \hat{m} \). Therefore, the biaxial director can point anywhere in the \( xy \) plane (taking \( \hat{n} = \hat{z} \)). Let the biaxial director make an arbitrary angle \( \phi \) in the \( xy \) plane with respect to \( \hat{x} \). In this case the fluctuating part of the dielectric tensor to the first order becomes (Appendix A.4)

\[
\begin{pmatrix}
\Delta \epsilon_{xx}^{b} \delta P \cos 2\phi + & \Delta \epsilon_{xx}^{b} \delta P \sin 2\phi - & (\Delta \epsilon_{xx}^{b} P_{0} \cos 2\phi - \\
2\Delta \epsilon_{xx}^{b} P_{0} \sin 2\phi \delta m_{\perp} & 2\Delta \epsilon_{xx}^{b} P_{0} \cos 2\phi \delta m_{\perp} & \Delta \epsilon_{xx}^{b} P_{0} \sin 2\phi \delta n_{y} + \\
-\Delta \epsilon_{xx}^{b} \delta P \sin 2\phi - & -\Delta \epsilon_{xx}^{b} \delta P \cos 2\phi & \Delta \epsilon_{xx}^{b} P_{0} \sin 2\phi \delta n_{x} - \\
2\Delta \epsilon_{xx}^{b} P_{0} \cos 2\phi \delta m_{\perp} & \Delta \epsilon_{xx}^{b} P_{0} \cos 2\phi & (\Delta \epsilon_{xx}^{b} P_{0} \cos 2\phi + \\
-\Delta \epsilon_{xx}^{b} P_{0} \sin 2\phi \delta n_{y} + & \Delta \epsilon_{xx}^{b} P_{0} \sin 2\phi \delta n_{x} - & \Delta \epsilon_{xx}^{b} P_{0} \cos 2\phi - \Delta \epsilon_{xx}^{b} P_{0} \cos 2\phi \delta m_{\perp} + \\
(\Delta \epsilon_{xx}^{b} P_{0} \cos 2\phi - \Delta \epsilon_{xx}^{b} P_{0} \cos 2\phi) \delta n_{x} & (\Delta \epsilon_{xx}^{b} P_{0} \cos 2\phi - \Delta \epsilon_{xx}^{b} P_{0} \cos 2\phi \delta n_{y} & 0
\end{pmatrix}
\]

Here we have used \( \delta \phi_{x} = -\delta n_{y}, \delta \phi_{y} = \delta n_{x}, \) and \( \delta \phi_{z} = \delta m_{y} \equiv \delta m_{\perp}. \) From this expression, I will focus on the selection rules (Appendix A.5) for only a few selected geometries which are particularly suitable to isolate the biaxial order parameter and director fluctuations. The results are summarized in Table 2.3.
2.6.7.1 Homeotropic H1 Geometry

Consider a homeotropic geometry with \( \hat{n} \) in the \( yz \) scattering plane. For the incident light polarized normal to the scattering plane and scattered light polarized parallel to the scattering plane (Figure 2.8 (i)):

\[
\hat{i} = \hat{x} \\
\hat{f} = \cos \theta_s \hat{y} + \sin \theta_s \hat{z}
\]  
(2.103)

\[
\delta\varepsilon_{vH} = \hat{f} \cdot \delta\varepsilon \cdot \hat{i} \\
= \left( \Delta\varepsilon_b^u P_0 \cos 2\phi - \Delta\varepsilon_u^u \right) \sin \theta_s \delta n_x - \Delta\varepsilon_b^u P_0 \sin 2\phi \sin \theta_s \delta n_y - 2\Delta\varepsilon_b^b P_0 \cos 2\phi \cos \theta_s \delta m_\perp + \Delta\varepsilon_b^b \sin 2\phi \cos \theta_s \delta P
\]  
(2.104)

2.6.7.2 Homeotropic Geometry (H2 Geometry)

Consider a homeotropic geometry with \( \hat{n} \) again in the \( yz \) scattering plane. For both the incident and scattered light polarized normal to the scattering plane (Figure 2.8 (ii)):

\[
\hat{i} = \hat{x}, \hat{f} = \hat{x}
\]  
(2.105)

\[
\delta\varepsilon_{vH} = \hat{f} \cdot \delta\varepsilon \cdot \hat{i} \\
= \Delta\varepsilon_b^b \delta P \cos 2\phi + 2\Delta\varepsilon_b^b P_0 \sin 2\phi \delta m_\perp
\]  
(2.106)
2.6.7.3 Planar Geometry (P1 Geometry)

Consider a planar geometry with \( \hat{n} \) along \( \hat{z} \) in the \( xz \) scattering plane. For the incident light polarized normal to the scattering plane and scattered light polarized in the scattering plane (Figure 2.9 (i)):

\[
\hat{i} = \hat{y} \\
\hat{f} = \sin \theta_x \hat{x} + \cos \theta_x \hat{z}
\]

\[
\delta \varepsilon_{VH} = \hat{f} \cdot (\delta \varepsilon \cdot \hat{i})
\]

\[
= \Delta \varepsilon_{sat}^b \sin 2\phi \sin \theta_x \delta \epsilon - 2 \Delta \varepsilon_{sat}^a P_0 \cos 2\phi \sin \theta_x \delta n_x + \]

\[
(\Delta \varepsilon_{sat}^b P_0 \sin 2\phi \cos \theta_x \delta n_x - (\Delta \varepsilon_{sat}^b P_0 \cos 2\phi - \Delta \varepsilon_{sat}^a) \cos \theta_x \delta n_y)
\]

2.6.7.4 Planar Geometry (P2 Geometry)

Finally, consider a planar geometry with \( \hat{n} = \hat{z} \) perpendicular to the \( xy \) scattering plane. For the incident light polarized normal to the scattering plane and scattering light polarized parallel to the scattering plane (Figure 2.9 (ii)):

\[
\hat{i} = \hat{z} \\
\hat{f} = \cos \theta_x \hat{x} + \sin \theta_x \hat{y}
\]

\[
\delta \varepsilon_{VH} = \hat{f} \cdot (\delta \varepsilon \cdot \hat{i})
\]

\[
= (\Delta \varepsilon_{sat}^b P_0 \cos (\theta_x - 2\phi) - \Delta \varepsilon_{sat}^a \cos \theta_x) \delta n_x -
\]

\[
(\Delta \varepsilon_{sat}^b P_0 \sin (\theta_x - 2\phi) + \Delta \varepsilon_{sat}^a \sin \theta_x) \delta n_y
\]
Figure 2.8 Experimental geometries: (i) homeotropic cell with $\hat{m}$ in the $xy$ plane, making an angle $\phi$ with respect to the $x$-axis for VH scattering and (ii) homeotropic cell with $\hat{m}$ in the $xy$ plane, making an angle $\phi$ with respect to the $x$-axis for VV scattering.
Figure 2.9 Experimental geometries: (i) homogeneous cell with \( \hat{n} \) in the scattering plane, \( \hat{m} \) making an angle \( \phi \) in the \( xy \) plane with respect to the \( x \)-axis for VH scattering, and (ii) homogeneous cell with \( \hat{n} \) normal to the scattering plane, \( \hat{m} \) making an angle \( \phi \) in the \( xy \) plane with respect to the \( x \)-axis for VH scattering.
### H1 Geometry

\[ \delta \epsilon_{vH} = (\Delta \epsilon_{sat}^b \cos 2\phi - \Delta \epsilon_{sat}^u \cos \theta_s \delta \mathbf{n}_x - \Delta \epsilon_{sat}^b \sin 2\phi \sin \theta_s \delta \mathbf{n}_y - 2\Delta \epsilon_{sat}^b P_0 \cos 2\phi \cos \theta_s \delta \mathbf{m}_\perp + \Delta \epsilon_{sat}^b \sin 2\phi \cos \theta_s \delta P \]
REFERENCES


CHAPTER 3

EXPERIMENTAL SET UP, MATERIALS, AND SAMPLE PREPARATION

3.1 EXPERIMENTAL SET UPS FOR LIGHT SCATTERING

Two dynamic light scattering setups with similar optical components but different lasers and correlators were used for the experiments performed for this dissertation. A schematic diagram of the experimental apparatus, common to both setups, is shown in Figure 3.1 and real experimental set up is shown in Figure 3.2. All the optics, except electronic hardware and computer, were assembled on vibration isolated optical tables in the Newport Corporation’s RS4000 Research Series. All optical components, including windows on the ovens housing the liquid crystal samples, were anti-reflection coated for the visible ($R \leq 0.5\%$).

The laser, which is linear-polarized (500:1), was first reflected through $90^\circ$ by a mirror and it was then passed through an iris. The iris is used to remove any background light mixing with the laser beam and to eliminate unwanted backscattering directed towards the laser beam due to multiple reflections from other optical components. The laser power was monitored, for most of the experiments, by splitting off (after the iris) a small portion, about 2%, of the incident beam and directing this portion into an amplified photodetector (Thorlabs Inc. model PDA55 or a Newport Model 1815-C). Measured
Figure 3.1 A schematic diagram of the experimental set up for light scattering experiments.
Figure 3.2 Our light scattering set up with the cylindrical oven and Helium-Neon laser. The cylindrical oven can be replaced with an Instec hot stage when required. Photomultiplier detectors are positioned in a light-tight box on the right corner of the table; electronic hardware and computer occupy a separate equipment rack. A schematic experimental geometry is superimposed on the main picture (center, left). The symbols are represented as: polarizer \( \hat{\imath} \), analyzer \( \hat{f} \), incident angle \( \theta_i \), scattering angle \( \theta_s \), inner circle goniometer position \( \theta \), outer circle goniometer position \( 2\theta \), incident wave vector \( \vec{k}_i \), scattering wave vector \( \vec{k}_f \), and q-vector \( \vec{q} = \vec{k}_f - \vec{k}_i \).
intensities of light scattered from our samples were then normalized for variations in incident laser power. The photodetector voltage was read on a computer interfaced digital multimeter (*Keithley* model 199).

After sampling for power normalization, the main laser beam was elevated to an optical rail at the height of the samples by two 90° reflections. All the mirrors were dielectriccoated mirrors manufactured by *New Focus* (model 9809), and have more than 99% reflectivity over the 400-700 nm visible range. The laser beam was then passed through a *Newport Corp* spatial filter in order to remove any spatial noise and produce a pure Gaussian (TEM$_{00}$) mode. The spatial filter consists of microscopic objective and pinhole aperture. The pinhole is positioned at the focal point of the objective. The laser beam was then collimated to a diameter of 3 – 5 mm, and passed through a second iris and through a half wave plate, and finally through the incident polarizer. By rotating the half wave plate, which rotates the laser beam polarization prior to the incident polarizer, the intensity incident on the sample could be changed. This is important when there is excessive light scattering by the sample (especially in the nematic phase for smaller scattering angles (small $q$-vector) or near the first order phase transition, such as isotropic to nematic phase transition), which could damage the sensitive photomultiplier used to detect the scattering, or when high powers could cause heating or damage in the sample itself. The incident polarizer was a *Glan-Laser* prism polarizer, a birefringent polarization element consisting of two air-spaced calcite prisms. The polarizer axis was oriented either perpendicular (vertical or V) or horizontal (H) to the scattering plane. Finally, the
laser beam was focused onto the sample by a lens of focal length 20 cm. A third, “clean-up” iris was placed after this lens and as close to the sample oven as possible.

The sample oven was mounted on the inner circle (θ angle) of a Huber model 410 two-circle goniometer. The oven could be independently translated in three orthogonal directions and rotated by small angle around an axis perpendicular to the sample substrates and parallel to the incident laser beam (at normal incidence). This arrangement enables three dimensional adjustments to the sample and makes it possible to find optimal spots on the sample (e.g., defect-free regions of the sample) for illumination. Careful adjustments were made to ensure homodyne scattering (i.e., \(g_1(\tau) \geq 0.9\)). Scattered light from the samples was collected via an optical assembly mounted on the 2θ arm of the goniometer; the optical axis of this assembly lies in the horizontal plane containing the incident beam direction (\(\vec{k}_i\)). The two circles could be rotated manually or using stepping motors and gear reducers with a resolution of 400 steps/degree. The motors were controlled by an Advanced Control Systems model MCU-2 motion controller, serially interfaced to a PC computer. The goniometer angles θ and 2θ correspond to incident and scattered angles, \(\theta_i\) and \(\theta_s\), in the lab, according to \(\theta_i = \theta\) and \(\theta_s = 2\theta - \theta\). (Here 2θ is a symbol for an independent angular degree of freedom, not literally “twice” the θ setting.)

The detector arm assembly consisted of a pinhole aperture, imaging lens, a Glan-Thompson prism polarizer used as an analyzer, and an optical fiber mounted on an XY translator. The analyzer was mounted into a Newport SR50 compact motorized rotation
stage which was controlled by a Newport universal motion controller model ESP300 interfaced to the PC computer. The light scattered from the sample was first collected through a 400 μm diameter pinhole – the first element on the scattering arm – at a distance of approximately 50 cm from the illuminated volume of the sample. This gives a theoretical q-resolution of \( \sim 80 \text{ cm}^{-1} \) for an incident wavelength of 600 nm.

An important parameter of interest in a dynamic light scattering experiment is the coherence area over which the scattered light is spatially coherent. According to equation (2.13) of Chapter 2, the coherence area is \( A_{\text{coh}} \approx \frac{\lambda^2}{\Omega} \), where \( \Omega \) is the solid angle of the illuminated sample volume subtended at the detector. Using the known size of the latter, defined by the focused waist of the laser and the fixed sample thickness, and the known distance from the sample to the detection aperture, we estimate that typically 3 coherence areas are collected in our experiments.

An imaging lens was placed after the collection aperture and analyzer. The purpose of the lens was to form a real image of the scattering volume on the face of a 200 μm core optical fiber, thus ensuring that all light transmitted to the photodetector originated from the illuminated volume of the sample, and any stray light scattered from points outside this volume was rejected. The tip of the fiber could be translated horizontally or vertically by two micrometers incorporated to the stage holding the fiber, so that the detected signal could be peaked. The scattered light carried by the fiber was then routed to a beam splitter. The beam splitter divided the optical signal into two signals of approximately equal intensity, which were admitted onto the active areas of two independent photomultiplier tubes. The purpose of splitting the signal was to perform
cross-correlation measurements of the two independent photomultipliers, eliminating effects of single-tube afterpulsing and dead time, which is important for correlation measurements with delay time < 1 μsec. In fact, such performance was rarely required for our studies, but, as it was available, we made use of it.

The photomultipliers used in our studies of nematic tetrapodes were *Electron Tubes* model P30CWAD5F-56; each consists of a photomultiplier tube with a bialkali photocathode and a photoelectron gain section, a high voltage circuit, a low voltage power supply, and a high speed *amplifier/discriminator*. All sensitive components are shielded from external electromagnetic fields by a compact cylindrical mu-metal case. The quantum efficiency of the tubes, used at 633 nm, is ~10%. The outputs of the amplifier-discriminators were sent to a digital correlator described in the next section (*Flexible Instruments* model Flex2K-12Dx2 [1]). Alternatively, in our study of lyotropic chromonics, we used a light scattering set-up that included two *Hamamatsu* model HC120-08 [2] single photon counting photomultiplier modules, which have a quantum efficiency of ~16 % at the wavelength of 532 nm used. The signals from these photomultipliers were processed by *amplifier/discriminators* designed and constructed by Dr Alan Baldwin at Kent State. The PM tubes in both sets of experiments were operated at high voltages recommended by the manufacturers for optimum photon counting performance.
3.2 DETAILS OF KEY EQUIPMENT USED IN LIGHT SCATTERING STUDIES

3.2.1 LASERS

A Helium Neon laser, *Spectra Physics model 127* and a diode-pumped solid state laser, *Coherent model Verdi V8*, were used for our different experiments – the former primarily for biaxiality studies in liquid crystal tetrapodes and the latter for the lyotropic chromonic nematic. The Helium Neon laser has a fixed output power of 35 mW at a wavelength of 632.8 nm and emits a vertically-polarized TEM\(_{00}\) (single, Gaussian mode) beam of 1.25 mm \(1/e^2\) diameter and 0.6 mrad divergence. The Verdi laser also produces a vertically-polarized TEM\(_{00}\) mode output at a wavelength of 532 nm; although it has a maximum power of 8 watts, we typically used a 1 watt setting. The Verdi output beam diameter of 1.2 mm [3].

Typical incident laser powers (before focusing) on the samples were 1 – 20 mW. No evidence of laser heating of our samples was observed. We carefully checked for this by adjusting sample temperature (with the laser off) to points just below the N-I transition (on heating), where scattering properties are highly sensitive to small perturbations in temperature. We then illuminated the samples at the lowest feasible laser power and ramped up power while monitoring the scattered intensity correlation function. Significant effects of laser heating were only seen at powers 3 to 10 times higher than those used in our experiments.
3.2.2 OVENS AND TEMPERATURE CONTROL

Two different temperature controllers, a custom-made temperature controller and an *INSTEC model STC* 200 [4], were used to control temperature for two different ovens: a *cylindrical aluminum oven* with optical access for large incident/scattering angles (0° – 160°) and an *Instec model HCS400 Hot Stage* (0° – 40° optical access for scattering angle; 0° – 15° for incident angle). The cylindrical oven was heated by *Minco* thermofoil resistive heaters mounted directly to the cylindrical aluminum surfaces of the oven interior: the cylindrical aluminum surface was separated from the room environment by a small sealed air space, an outer aluminum shell, and a thick layer of high temperature foam insulation. The temperature for cylindrical oven was controlled using a custom-made temperature controller designed by Prof. J. D. Litster of M.I.T. It is based on a *Wheatstone bridge* circuit. The bridge circuit balanced the resistance of a control thermistor placed in the oven near the heater elements to a resistance set on the controller’s front panel. The controller’s output was fed to a *Kepco* power supply which provided up to 50 V to the heaters with a current limit of 2 A. Required temperatures could be set by sweeping the effective bridge resistance with an external $\pm 10$ V supplied by a computer-controlled 16-bit digital to analog converter. This combination of oven and controller provided a measured temperature stability of $\pm 1$ mK over approximately 1 hr, a precision that proved crucial to study pretransitional critical behavior over a very narrow temperature range ($\sim 0.3$ °C) in some of our samples. The sample temperature was measured using an ultra-precision *Thermometrics* thermistor.
model SP60AB134JA5 which was in direct contact with the sample cell. The thermistor was calibrated by the manufacturer according to the Steinhart-Hart equation [5, 6]

\[
\frac{1}{T} = a_0 + a_1 \ln(R) + a_2 \ln(R)^2 + a_3 \ln(R)^3
\]  

(3.1)

where \( T \) is temperature in degrees Kelvin and \( R \) is resistance in kiloohms. The thermistor resistance was measured by a Keithley model 199 or 2000 DMM (using a constant current source of 1 \( \mu \)A), which was computer interfaced.

For experiments on chromonics, we used the INSTEC hot stage and temperature controller. It has a temperature resolution of 0.1 °C (calibration accuracy of ±0.1 °C) and a typical 1 hr stability of 0.01°C. The INSTEC was computer controlled via serial interface.

3.2.3 DIGITAL CORRELATORS

We used two different correlators: a commercial Flexible Instruments model Flex2K-12Dx2 [1] (used in our studies of tetrapodes) and an ultrafast pico-second correlator designed and built by Dr Alan Baldwin at Kent State (used with the LC chromonic samples). For the Flex instrument, the minimum sampling time is 12.5 ns, with a 289 channel layout distributed logarithmically over time decades from 12.5 nsec out to 3220 s. In cross correlation mode, the Flex computes the correlation functions for both channel A \( \times \) channel B and channel B \( \times \) channel A with 2\times289 logarithmically spaced data points. The Flex is computer-interfaced via USB.
The *pico-second correlator* features a minimum sampling time of either 62.5 or 125 picosec. It was specially designed to study very fast dynamics such as the layer undulation dynamics of free standing smectic liquid crystal films [7, 8], and the high speed section was not needed for our studies. The full channel layout on the pico-correlator is 204800 62.5 picosec or 102800 125 picosec channels in the fast section, supplemented by 128 logarithmically spaced channels in each of the decades 1, 10, 100 μsec; 1, 10, 100 msec; and 1, 10, 100 sec. The pico-correlator is controlled by a PC and custom software written by Dr. Baldwin.

### 3.2.4 LABVIEW CONTROL SOFTWARE AND DATA ANALYSIS

Both of our light scattering set-ups were operated under *National Instruments Labview* experimental control and data acquisition software. In practice, due to the relative novelty of the LC systems studied, we performed relatively short 6 – 12 hr experiments using a combination of manual and Labview control. For example, a wavevector (\( \vec{q} \)) scan at fixed temperature, or temperature scan at fixed \( \vec{q} \), would be performed, with each acquired correlation function monitored manually to catch interesting or unusual developments. The software could then be paused, various experiment parameter files changed as appropriate, and then software control resumed. This procedure generally required the experimenter’s attention every 1 – 2 hr.

All of our correlation data were analyzed by nonlinear least squares fitting to the form,
where \(0 \leq A_i \leq 1\). Here for \(S_i = 1\), one has a superposition of simple exponential decays expected for overdamped modes (order parameter or director) that may contribute to the dynamical scattering. The case of \(S_i \neq 1\) (and \(0 \leq S_i < 1\)) corresponds to a “stretched” exponential, a form that can arise when there is a narrow range of relaxation rates about a well-defined mean value – for example, if (in a colloidal system) there is a distribution of particle sizes about a mean, or, for a hydrodynamic mode, if a range of \(\bar{q}\) values about a central value is admitted onto the detector (limited \(q\)-resolution). Stretching may also arise in the case of small variations (or mosaicity) in director alignment in liquid crystals (resulting in an uncertain mixture of normal modes). Stretched exponentials typically improve the fitting of correlation data at longer times compared to simple exponentials applied to the same set of data. Thus, they can also be used to model data where there is an unknown (or uncontrollable) degree of static scattered light mixing with dynamic scattering; this almost inevitably occurs when the signal from fluctuations is inherently weak. In this case, the correlation function is slightly stretched toward longer times because the decay \(e^{-\Gamma r}\) mixes with the component \(e^{-2\Gamma r}\). One can see this easily by adding a static amplitude to the sum in equation (3.2), and then expanding the square.

In our case, the stretched exponential was typically used to confirm the presence of two modes in the fitting – e.g., we would first note the inadequacy of a single simple exponential (two parameters \(A\) and \(\Gamma\)), then check the quality of a stretched exponential fit (3 parameters), before settling on a second exponential (4 parameters). Additional
guidance was, of course, obtained from the actual experimental conditions and from theory. Theory might, for instance, support observation of a nonhydrodynamic mode in addition to a hydrodynamic director mode, in a uniaxial nematic, since one can expect fluctuations of the biaxial order parameter to contribute. Moreover, if the scattering vector is tightly determined by the acceptance aperture and the quality of sample (director) alignment, one would expect simple exponential decays \( S_i \cong 1 \). As a general rule, we noticed improved fits from stretching only when there was evidence of a combination of both static light contamination (typically encountered when the dynamic signal was inherently weak) and inhomogeneities in alignment could be suspected (such as near phase transitions). Even in those cases, one additional parameter (i.e., \( S_i \equiv S \)) and found results close to simple exponential decays \( S \geq 0.8 \). More details of the data analysis are provided for individual cases in Chapters 4 and 5.

The data analysis and fitting were performed with commercial software; we used two different packages, Origin 8.0 (OriginLabs) and C-PLOT (Certified Scientific). The latter (which is Linux-based) lacks a GUI, but, since the functions used for fitting are written by the user into a C-program template, is extremely powerful and versatile – allowing, for example, the direct incorporation of Numerical Recipes code for numerical calculation of special functions, integrals, etc.


## 3.3 LIQUID CRYSTAL SAMPLES AND ALIGNMENT

Two different types of liquid crystalline samples were studied in this dissertation. One type consists of Germanium tetrapodes (Figure 3.3) in which we probed for order parameter fluctuations and the associated Goldstone mode of the biaxial nematic phase previously reported to these LCs [9, 10]. We also studied viscoelastic properties of uniaxial lyotropic chromonic nematic liquid crystals formed by aqueous solution of disodium cromoglycate, DSCG (also called cromolyn). Details about these materials, their phase behavior, and preparation of aligned samples between fixed optical substrates are discussed in the following subsections.

### 3.3.1 SAMPLES AND THEIR PHASE BEHAVIORS

#### 3.3.1.1 TETRAPODES

Two different tetrapodic LCs, 3- and 4-membered aromatic phenyl mesogens tethered to a Germanium (Ge) core (Figure 3.3), were used to study dynamics associated with reported biaxial nematic ordering [11, 12]. These tetrapodes were synthesized by Prof. G. H. Mehl at the University of Hull, Hull, UK and supplied to us by our colleagues at Kent State, Prof. Satyendra Kumar and Dr. Shinwoong Kang. They feature four identical mesogenic groups laterally attached through flexible siloxane chains to a Ge-core [9, 10, 13]. Mesogens in the Ge 3-ring and 4-ring tetrapodes contain three and four
benzene rings, respectively. The 3-ring tetrapode has an isotropic \( (I) \) to uniaxial nematic \( (N_u) \) phase transition temperature \( T_{IN} \) of 46.5 °C and a reported \( N_u \) to biaxial nematic \( (N_b) \) transition temperature \( T_{UB} \) of 22.5 °C. For the 4-ring tetrapode, \( T_{IN} \) is 135.5 °C and \( T_{UB} \) is reportedly 135.0 °C; a \( SmC \) phase occurs at 60 °C on cooling. X-ray diffraction studies [14] have confirmed that these tetrapodes exhibit a quasiflat platelet morphology in the nematic phases, with the mesogens being tilted on average in the plane of the platelets [13]. The uniaxial director is parallel to the average long axis of the mesogenic groups of the tetrapodes. It is believed that the hindrance of molecular rotations due to the mesogenic-core linkages, or interdigitation of mesogens connected to different cores, favors a biaxial nematic ordering [9, 15]. A schematic diagram of the proposed average tetrapode configuration in the \( N_b \) phase is shown in Figure 1.3.

### 3.3.1.2 CROMOLYN

The cromolyn molecule is composed of two rigid heterocycles connected by a flexible bridge. Its structural formula and three dimensional structure are shown in Figure 3.4. The flexible bridge allows the molecule to assume many energetically similar conformations. One of the possible conformations of a free and isolated cromolyn molecule is shown in Figure 3.4 (ii) [16, 17]. Two sodium atoms are positioned at the opposite ends of the molecule. Cromolyn molecules are, in general, are disk-shaped and are soluble in water due to the presence of ionic (such as \(-\text{COO}^- \text{Na}^+\)) or hydrophilic
Figure 3.3 Upper left: molecular structure of the 3-ring Ge-tetrapode, upper right: molecular structure of the 4-ring Ge-tetrapode, and lower: schematic representation of tetrapodes forming platelet or “plank-like” morphology. Germanium core (red circle) is connected to the benzene rings (blue rods) with siloxane linkages (pink). Proposed structure of tetrapodes in $N_u$ phase ($\langle \phi \rangle \sim 0$) (left) and in $N_b$ phase ($\langle \phi \rangle > 0$) (right) (courtesy of Prof. S. Kumar’s group).
(such as –OH) groups at the periphery of their disk-like conformation. In aqueous solutions these mesogens self-organize, with face-to-face arrangements of aromatic cores, into cylindrical aggregates with the cores being basically perpendicular to the axis of the cylinder [18, 19]. For certain concentrations, the aggregates develop different liquid crystal phases.

Depending upon the concentration, cromolyn in water can form a uniaxial nematic (chromonematic) phase (labeled \( N \) in the phase diagram in Figure 3.5 (i)) and a columnar, \( M \), phase [20-22]. Both the phases are formed by the rod-like aggregates of the stacked cromolyn molecules (Figure 1.10). At room temperature (23 °C) and for concentrations by weight \( c \) less than 10 wt%, there are no LC phases. For concentrations of 10-12 wt%, coexistence of \( N_u \) and \( I \) phases is observed at near ambient temperatures. For \( 12 < c < 17 \) wt% the \( N_u \) phase is observed. For \( 17 < c < 21 \) wt% a biphasic region of \( N \) and \( M \) phases is observed. The \( M \) phase is observed for \( 21 < c < 35 \) wt%. Figure 3.5 (i) presents the detailed phase diagram reproduced from DSC studies by Lee et al. [23].

For this study we used a 14 wt% solution of cromolyn in water which exhibited a uniaxial nematic phase over the temperature range ~ 20-27 °C. The molecular stacking distance within the aggregates is about 0.34 nm. Over the uniaxial \( N \) phase, the scalar order parameter, \( S \), is determined by deuterium NMR spectroscopy to lie in the range of 0.76 \pm 0.08 to 0.97 \pm 0.1 [19].
Figure 3.4 (i): molecular structural formula of DSCG, (ii) its three dimensional structure; left: top view and right: side view [17, 24].
Figure 3.5 (i) phase diagram of DSCG/H₂O as determined by DSC [23], (ii) an experimental geometry for a homogeneous cell with the director $\hat{n}$ on the scattering plane.
3.3.2 SAMPLE PREPARATION, ALIGNMENT, AND TEXTURES

3.3.2.1 TETRAPODES

Standard electro-optic cells (EHC Inc, Japan) treated for homogeneous planar alignment of the mesogenic groups, as well as custom-assembled substrates prepared for homeotropic LC alignment, were used in our measurements. The typical gap between substrates (sample thickness) was fixed by 10 – 20 μm spacers. In the homogeneous cell, the average long axis of the mesogens (defining the uniaxial director $\hat{n}$) remain parallel to the surface of the glass substrate; this is achieved by rubbing a thin layer of spin-coated polyimide on the glass surface along a specific direction with a velvet cloth. For homeotropic alignment the inner surfaces of the substrates were coated with an unrubbed polyimide (provided by Samsung Electronics Corporation, Korea), which induced alignment of the director $\hat{n}$ along the normal to the substrates. The tetrapode compounds were loaded by a capillary action at a temperature just above $T_{IN}$. High quality alignment of the uniaxial director $\hat{n}$ was subsequently confirmed by observing polarized optical textures in the uniaxial nematic phase. For a homogeneous alignment, sinusoidal variation of transmitted light intensity by rotating the sample under crossed polarizers confirms that the uniaxial director is aligned uniformly and parallel to the polyimide rub-direction. For a homeotropic sample, a complete extinction of transmitted light through
samples in the $N_u$ phase, rotated between crossed polarizers, indicates that the optic axis is aligned normal to the substrate. The optical texture of the homeotropically aligned sample of 4-ring tetrapode at different temperatures is shown in Figure 3.6. The uniform dark texture observed while looking through crossed polarizers indicated a very good homeotropic alignment. The 3-ring compound exhibited a similar texture. At lower temperatures, consistent with the reported uniaxial-biaxial transition [9, 10], a Schlieren texture appears in the homeotropic samples, suggesting development of in-plane correlated domains of the biaxial director $\hat{n}$. By itself, however, such an observation is not conclusive, as a surface anchoring transition (without a change in phase symmetry or introduction of symmetry-restoring Goldstone mode) could account for the textural change. Just prior to and after light scattering measurements, the sample alignment was thoroughly checked and confirmed by in situ polarizing microscopy and by measuring the depolarized forward transmitted intensity of laser light.

3.3.2.2 CROMOLYN-BASED CHROMONIC LIQUID CRYSTAL

Planar (homogeneous) cells of 14 wt% cromolyn in deionized water (18 MΩ.cm resistance) and thickness 16 μm were assembled at Liquid Crystal Institute in Prof. Oleg Lavrentovich’s lab by Dr Yuriy A. Nastishin. Very good planar alignment was achieved. Polarizing microscope textures for a combination of different orientation of polarizer, analyzer, and the director are shown in Figure 3.7. Details of the procedure for obtaining high quality homogeneously-aligned samples are as follows.
Figure 3.6 Optical textures looking through cross polarizer and analyzer for a homeotropically aligned cell of 4-ring tetrapode: (i) in the $N_a$ phase at 133.3 °C, and (ii) at 132.9 °C. At lower temperature bright texture with some defect lines may be due to the development of the biaxial director.
Figure 3.7 Polarizing microscope textures of DSCG in two flat cells formed by (i) untreated glass surface; (ii), (iii) glassed plates with buffed polyimide SE-7511, as an aligning agent. (ii) and (iii) differ in the orientation of the average director with respect to the polarizer (P) and analyzer (A) directions; note the weak director distortions caused by the cylindrical spacers marked by arrows in part (iii) [16].
Cromolyn, purchased from Spectrum Inc, was first mixed with water in a glass vial. It was stirred on a vibrator for 30 min, then heated to a temperature about 10 °C above the isotropic phase transition and stirred for another 15 min. It was then centrifuged for 20 min at 3500 rpm and heated to the isotropic phase of about 10 °C above \( T_{NI} \) and was filtered with 0.2 \( \mu \)m filter. To align cromolyn in the \( N_u \) phase, spin-coated and buffed films of polyimide SE-7511 obtained from Nissan Chemical Industries Limited was used [16]. Glass substrates were washed in an ultrasonic bath of Alconox detergent and water for 10 min at 60 °C. They were then removed and dried. The polyimide SE-7511 Sunever, grade 7511L, and the solvent Sunever, both from Nissan Chemicals, were mixed by volume in the proportion of 1:1. The solution was coated onto the glass substrates by a spincoater rotating at 1500 rpm. The coating was dried at 100 °C for 2 min and then baked at 180 °C for 1 hr. The polyimide-coated substrates were rubbed using an aluminum block covered with felt. Cells were assembled from pair of substrates with antiparallel-rubbed opposing sides. The pretilt angle (angle between nematic director and substrate plane) was less then 1°.

The cell gap was measured by optical interference before the sample was filled. The cells were heated to about 10 °C above the nematic to isotropic transition and filled by capillary flow assisted by negative pressure applied to one of the two open sides of the cell; it was then sealed by a UV epoxy. The direction of flow and pressure gradient were kept parallel to the buffing direction of the polyimide layers.
3.4 ADDITIONAL EXPERIMENTAL PROCEDURES

The quantities measured in light scattering experiments are the dynamic correlation function $g^{(2)}(\tau)$ and the average intensity $\bar{I}$. The correlator computes the normalized time correlation function as,

$$g^{(2)}(\tau) = \frac{\langle I(0)I(\tau) \rangle}{\bar{I}^2} + 1$$  \hspace{1cm} (3.3)

Updated correlation data and the average scattered intensity were transferred from the correlator to the host computer every second via a USB interface or through customized I-O hardware. Before beginning a measurement, we minimized the stray light and maximized signal to background by careful adjustments of sample position in the laser beam. At the same time, the detection fiber’s position was carefully adjusted to maximize count rate.

After loading a sample in the oven, the experiment would be started with the computer reading the instructions from a previously created formatted text file that contained a series of steps for a complete experiment. These steps would be different combinations of the following procedures: changing temperature or angles; waiting for temperature equilibration; changing polarizer and analyzer orientations; running the correlator for specified time; recording and saving the correlated data, temperature, and laser power readings in specific files; etc.

During the experiments, the alignment of the sample was checked periodically by a polarizing microscope using a manual set up. This was done during programmed pauses
(e.g., while temperature was equilibrating). The sample was rotated on the $\theta$ stage of the goniometer into a position between a fiber optic white light source and the objective of a long distance microscope. The sample texture was then carefully observed through crossed polarizers and photographed for the experimental record.

3.5 ILLUSTRATIVE CALCULATION OF THE SCATTERING VECTOR ($\vec{q}$) FOR A TYPICAL EXPERIMENTAL GEOMETRY

Different experimental scattering geometries, suitable for particular purposes, were used throughout the experiments. Here I will illustrate the procedures for calculating the scattering wave vector ($\vec{q}$) in a simple representative geometry in terms of angles measured in the lab (lab angles) for a uniaxial nematic phase.

Consider a homogeneously-aligned LC with the director $\hat{n}$ in the scattering plane (Figure 3.5 (ii)). Consider light with incident angle $\theta_i$, polarization normal to the scattering plane ($\hat{n}_y = \hat{x}$), and incident wave vector

$$\vec{k}_i = \frac{2\pi}{\lambda} n_x (\cos \theta_i \hat{x} + \sin \theta_i \hat{z})$$

on the sample. Suppose the detected scattered light, at scattering angle $\theta_s$, propagates with wavevector

$$\vec{k}_s = \frac{2\pi}{\lambda} n_x (\theta_s \cos \theta_s \hat{x} - \sin \theta_s \hat{z})$$

and polarization $\hat{f} = \sin \theta_s \hat{x} + \cos \theta_s \hat{z}$. Here the angles $\theta_i$ and $\theta_s$ are measured in the sample. The angles in the sample can be converted into lab angles using Snell’s law of refraction between two linear homogeneous dielectric media with different refractive indices (liquid crystal and air).
For the geometry considered (Figure 3.5 (ii)), on the incident side, we have \( n_\perp \sin \theta_i = \sin \theta_{slab} \) and for the scattering side \( n_e (\theta_s) \sin \theta_s = \sin \theta_{slab} \). Lab angles are identified with subscripts \( \text{lab} \), and \( n_\parallel \) and \( n_\perp \) are the refractive indices along and perpendicular to the aligned nematic director, respectively, and \( n_e \) is the refractive index for an extraordinary-polarized ray propagating in a uniaxial LC. Unless specified with the subscript \( \text{lab} \), all the angles mentioned in mathematical expressions in this dissertation are the angles in the sample. \( n_e (\theta_s) \) can be converted into \( n_\parallel \) and \( n_\perp \) using

\[
\frac{1}{{\left( {n_e (\theta_s)} \right)^2}} = \frac{{\cos^2 (\theta_s)}}{{n_\parallel^2}} + \frac{{\sin^2 (\theta_s)}}{{n_\perp^2}}
\]  

(3.4)

The scattering vector is defined as

\[
\vec{q} \equiv \vec{k}_f - \vec{k}_i = q_x \hat{x} + q_z \hat{z}
\]

(3.5)

for the geometry considered, where \( q_x = \frac{2\pi}{\lambda} \left\{ n_e (\theta_s) \cos (\theta_s) - n_\perp \cos (\theta_i) \right\} \) and \( q_z = -\frac{2\pi}{\lambda} \left\{ n_e (\theta_s) \sin (\theta_s) + n_\perp \sin (\theta_i) \right\} \). After converting the sample angles into lab angles using Snell’s law and equation (3.4), the components of the scattering vector for this geometry become

\[
q_s \equiv q_\perp = \frac{2\pi}{\lambda} \left\{ \frac{n_\parallel}{n_\perp} \sqrt{\left( n_\perp^2 - \sin^2 \theta_{slab} \right)} - \sqrt{\left( n_\parallel^2 - \sin^2 \theta_{slab} \right)} \right\} \quad \text{and}
\]

\[
q_z \equiv q_\parallel = -\frac{2\pi}{\lambda} \left( \sin \theta_{slab} + \sin \theta_{slab} \right)
\]
Analysis similar to the foregoing will be used in subsequent Chapters to obtain appropriate expression for $\bar{q}$ and the optical factors relating the scattering cross-section

$$\left( |\hat{i} \cdot \delta \bar{e} \cdot \hat{f} |^2 \right).$$
REFERENCES


CHAPTER 4
LIGHT SCATTERING STUDY OF BIAXIAL NEMATIC ORDERING IN LIQUID CRYSTALLINE TETRAPODES: RESULTS AND DISCUSSION

As reviewed in Chapter 1 Section 1.1.1, recent experimental studies from different techniques – including infrared (IR) absorbance spectroscopy, dichroism (anisotropic optical absorption), and Deuterium NMR – performed by different research groups, have strongly supported the existence of the $N_b$ phase in Si- and Ge-core tetrapodic mesogens [1-4]. Theoretical studies, including computer simulations, have also suggested the presence of the $N_b$ phase in such molecules [5-8]. Merkel et al. [4] have calculated the complete phase diagram for tetrapodes using mean field model of Sonnet et al. [5]; their results, combined with the experiments [1, 2, 9], which indicates first-order transition from $N_a$-$N_b$ phase in one of the 4-ring compounds and second-order $N_a$-$N_b$ transition in the 3-ring analogs. Motivated by those exciting observations, we performed dynamic light scattering study on 3- and 4-ring Ge-tetrapodes. Our objective is to identify the key dynamical fluctuations – nonhydrodynamic biaxial order parameter and hydrodynamic Goldstone modes – that, by providing a critical signature of symmetry change, could confirm a uniaxial-biaxial transition.
By using a specific, optimized scattering geometries, we are able to detect the critical slowing down or softening of order parameter fluctuations while approaching the $N_u$-$N_b$ transition reported in the earlier IR and NMR studies, and to confirm scattering due to the additional director mode expected in the lower temperature phase. In both tetrapodes, we made a careful effort to distinguish biaxial from uniaxial order parameter fluctuations by separately investigating the critical behavior and characterizing the time scale of the former at the isotropic – uniaxial nematic transition.

4.1 EXPERIMENTAL SETUP AND PROCEDURE

The details about the experimental set up were discussed in Chapter 3. The sample cells loaded with the tetrapodes (10 μm thickness) were illuminated with the Helium-Neon laser of wavelength 632.8 nm at a typical power of a few milliwatts. Most of the experiments were conducted with the cylindrical oven described in Chapter 3. Continuous temperature scans, focusing on the transition regions reported from the prior studies on tetrapodes, were performed on both 4- and 3-ring samples. For most of the cases, “dark uniaxial” geometries – geometries in which the uniaxial director scattering cross section is selectively minimized (as described in Section 4.2 below) – were used to optimize the opportunity to observe fluctuations associated with biaxiality. The low scattering intensities in this geometry required us to perform ~1 hr long acquisitions of each correlation function; thus, all experiments were repeated at least once to confirm
sample stability (e.g., no drift in transition temperatures). Consistent results were always obtained.

4.2 EXPERIMENTAL SCATTERING GEOMETRIES

The specific geometries, from among the general summary in Chapter 2, employed in our study of the tetrapodes are discussed briefly in the following subsections.

4.2.1 PIVH GEOMETRY

A more conventional scattering geometry employed a homogeneous planar cell geometry with the director $\hat{n}$ along $\hat{z}$ and perpendicular to the scattering plane defined by the incident light direction normal to the sample cell ($\theta_{\text{lab}} = \theta_i = 0^\circ$) and the scattered light direction making an angle $\theta_s$ with respect to the cell normal (Figure 4.1 (i)). (The angle in the sample corresponds to a lab angle $\theta_{\text{slab}} = 10^\circ$.). We also consider incident (scattered) polarization perpendicular, $V$ (parallel, $H$) to the scattering plane – i.e., $VH$ scattering.

In the $N_u$ phase, the scattering vector is given by

$$\vec{q} = q_x \hat{x} + q_y \hat{y} = \frac{2\pi}{\lambda} \left( \left( n_\perp \cos \theta_s - n_\parallel \right) \hat{y} - n_\perp \sin \theta_s \hat{x} \right)$$

(4.1)
Figure 4.1 (i) **Geometry P1VH:** Homogeneous planar alignment with the director $\hat{n}$ perpendicular to the scattering plane, depolarized ($VH$) scattering; (ii) **Geometry P2VH:** Homogeneous planar alignment with the director $\hat{n}$ in the scattering plane; $VH$ scattering.
where \( q_\perp = \sqrt{q_x^2 + q_y^2} \) and \( q_z = 0 \) since \( \vec{q} \cdot \hat{n} = \vec{q} \cdot \hat{z} = 0 \). The geometric factors for scattering coming from the contraction of the uniaxial dielectric fluctuation tensor with the polarizations are \( G_1 \propto (n_{||} \cos \theta_s - n_\perp)^2 \) (director mode 1) and \( G_2 \propto \sin^2 \theta_s \) (director mode 2) – see equation (2.45) in Chapter 2. The corresponding director fluctuations for \( q_z = 0 \) correspond to pure splay and pure twist distortions.

In an Nb phase, for an arbitrarily aligned biaxial director (Figure 2.9 (ii) with \( \theta_i = 0 \)), we found in Chapter 2 (equation 2.110, assuming \( S_0 = 1 \))

\[
\delta \varepsilon_{vH} = \left( \Delta \varepsilon_{vH}^b \right) P_0 \left( \cos(\theta_s - 2\phi) - \Delta \varepsilon_{vH}^s \cos \theta_s \right) \delta n_x - \\
\left( \Delta \varepsilon_{vH}^b \right) P_0 \left( \sin(\theta_s - 2\phi) + \Delta \varepsilon_{vH}^w \sin \theta_s \right) \delta n_y \tag{4.2}
\]

This equation indicates that, for the P1VH geometry, the uniaxial director fluctuations corresponding to splay and twist also dominate the light scattering in a biaxial nematic phase (The detailed form of the eigenvalues of the biaxial elastic free energy for this geometry are given by equations (2.80) and (2.81)).

### 4.2.2 P2VH GEOMETRY

Consider the same depolarized (VH) scattering geometry as above, except with the director \( \hat{n} \) now parallel to the scattering plane (Figure 4.1 (ii)). In the \( N_u \) phase, the scattering vector is given by

\[
\vec{q} = q_x \hat{x} + q_z \hat{z} = \frac{2\pi}{\lambda} \left( \left( n_e (\theta_s) \cos \theta_s - n_\perp \right) \hat{x} - n_e (\theta_s) \sin \theta_s \hat{z} \right) \tag{4.3}
\]
The geometric factors for the scattering give \( G_1 = 0 \) and \( G_2 \propto \cos^2 \theta_s \). We thus expect a contribution from director mode 2 (twist-bend mode) only.

In the \( N_b \) phase, for arbitrarily aligned biaxial director (Figure 2.9 (i) with \( \theta_{\text{lab}} = \theta_i = 0 \)), equation (2.108) gives

\[
\delta \varepsilon_{\gamma H} = \Delta \varepsilon_{\text{sat}}^b \sin 2\phi \sin \theta_s \delta P - 2 \Delta \varepsilon_{\text{sat}}^b P_0 \cos 2\phi \sin \theta_s \delta m_\perp + \\
\Delta \varepsilon_{\text{sat}}^b P_0 \sin 2\phi \cos \theta_s \delta n_x - (\Delta \varepsilon_{\text{sat}}^b P_0 \cos 2\phi - \Delta \varepsilon_{\text{sat}}^u) \cos \theta_s \delta n_y
\] (4.4)

In the \( N_b \) phase, we anticipate \( \Delta \varepsilon_{\text{sat}}^u >> \Delta \varepsilon_{\text{sat}}^b P_0 \); this is consistent with the available evidence from polarizing microscopy and conoscopy on tetrapodes [2, 4, 10]. Equation (4.4) then indicates that scattering is again dominated by twist-bend fluctuations \( \delta \hat{n} \). The detailed eigenvalues of the biaxial elastic free energy in the P2VH geometry are given by equations (2.77) for \( \phi = 0^\circ \) and (2.79) for \( \phi = 90^\circ \).

### 4.2.3 GEOMETRY HIVH

We now turn to a geometry we used to minimize \( \hat{n} \) director scattering in the \( N_u \) phase in order to isolate biaxial order fluctuations. Consider a depolarized (VH) scattering from a homeotropically aligned uniaxial nematic sample, Figure 4.2 (i), where the incident light makes an angle \( \theta_i \) (corresponding to \( \theta_{\text{lab}} = 10^\circ \)) to the cell normal (and to the average \( \hat{n} \)), and the scattered light is collected along \( \hat{n} \parallel \hat{z} \) (\( \theta_s = \theta_{\text{lab}} = 0 \)). In the \( N_u \) phase, the scattering vector is given by
Figure 4.2 (i) Geometry H1VH: Homeotropic alignment with the director $\hat{n}$ in the scattering plane, depolarized (VH) scattering, with the scattered light collected along the director $\hat{n}$; (ii) Geometry H2VH: homeotropic alignment with the director $\hat{n}$ in the scattering plane, VH scattering, and normally incident light with scattered light collected at angle $\theta_s$ with respect to $\hat{n}$.
This is a “dark uniaxial” geometry, since one calculates from equation (2.45) that the geometric scattering factors for the \( \hat{n} \) normal modes, \( G_1 = G_2 = 0 \), so the scattered intensity due to the director \( \hat{n} \) fluctuations vanishes in principle. Therefore, in the uniaxial phase, one is left theoretically only with scattering from (nonhydrodynamic) order parameter fluctuations; near a uniaxial-biaxial transition, these should be dominated by biaxial order fluctuations (i.e., by \( \delta P \)). One finds from equation (2.104) (for \( \theta = 0^\circ \)):

\[
\delta \varepsilon_{\nu H} = \Delta \varepsilon_{\text{sat}}^b P_0 \sin 2\phi \delta P
\]  

(4.6)

Practically, however, perfectly uniform alignment of \( \hat{n} \) is never achieved; some inhomogeneity or mosaicity exists. Since the hydrodynamic \( \hat{n} \) director modes are intrinsically very strongly scattering, one may expect some leakage or “contamination” from these modes in spite of efforts to obtain a “dark uniaxial” geometry. Indeed, the \( \hat{n} \) leakage may still contribute rather substantially compared to contributions from \( \delta P \), since \( \Delta \varepsilon_{\text{sat}}^a \) is likely significantly larger than \( \Delta \varepsilon_{\text{sat}}^b P_0 \).

In the \( N_b \) phase, for arbitrarily aligned biaxial director (Figure 2.8 (i) with \( \theta = 0^\circ \)), the “dark uniaxial” geometry gives (equation (2.104))

\[
\delta \varepsilon_{\nu H} = 2\Delta \varepsilon_{\text{sat}}^b P_0 \cos 2\phi \delta m_\perp + \Delta \varepsilon_{\text{sat}}^b P_0 \sin 2\phi \delta P
\]  

(4.7)
Eigenvalues corresponding to the elastic free energy for this geometry are given by equations (2.83) for $\phi = 0^\circ$ and (2.85) for $\phi = 90^\circ$; these correspond to the coupling of splay and twist fluctuations of $\hat{m}$ with the twist-bend mode of $\hat{n}$.

### 4.2.4 GEOMETRY H2VH

Now we consider a VH depolarized geometry with $\hat{n}$ aligned homeotropically, and with normally incident light ($\theta_i = \theta_{sab} = 0^\circ$) and a scattering angle (in the sample) $\theta_s$ (corresponding to lab angle $\theta_{sab} = 75^\circ$) (Figure 4.2 (ii)). In the $N_u$ phase

$$\bar{q} = \bar{k}_f - \bar{k}_i = \frac{2\pi}{\lambda} \left( \left( n_e(\theta_s) \cos \theta_s - n_\perp \right) \hat{z} - n_e(\theta_s) \sin \theta_s \hat{y} \right)$$

The geometric scattering factors are $G_1 = 0$ and $G_2 \propto \sin^2 \theta_s$. We thus expect a single mode corresponding to twist-bend deformation of the director $\hat{n}$.

In the $N_b$ phase for arbitrarily aligned biaxial director (Figure 2.8 (i) with $\theta_i = 0^\circ$), equation (2.102) gives

$$\delta \epsilon_{vh} = \left( \Delta \epsilon_{sat}^b P_0 \cos 2\phi - \Delta \epsilon_{sat}^u \right) \sin \theta_s \delta n_x - \Delta \epsilon_{sat}^b P_0 \sin 2\phi \sin \theta_s \delta n_y - 2\Delta \epsilon_{sat}^b P_0 \cos 2\phi \cos \theta_s \delta m_\perp + \Delta \epsilon_{sat}^b \sin 2\phi \cos \theta_s \delta P$$

Eigenvalues corresponding to the elastic free energy for this geometry for $\Delta \epsilon_{sat}^u \gg \Delta \epsilon_{sat}^b P_0$ are given by equations (2.83) for $\phi = 0^\circ$ and (2.85) for $\phi = 90^\circ$; which correspond to the twist-bend fluctuations of $\hat{n}$.
4.2.5 GEOMETRY H3VV

We also utilized several polarized scattering geometries. Consider a VV geometry with average \( \hat{n} \parallel \hat{z} \) aligned homotropically, Figure 4.3 (i), and corresponding to lab angles \( \theta_{slab} = \theta_{slab} = 25^\circ \). In the \( N_u \) phase, the scattering vector is given by

\[
\bar{q} = -\frac{2\pi n_\perp}{\lambda} \left( \sin \theta_s + \sin \theta_s \right) \hat{y}
\]  

(4.10)

In this geometry \( \hat{n} \) fluctuations are also theoretically “dark” (i.e. \( G_1 = G_2 = 0 \)). However, in the \( N_b \) phase

\[
\delta \epsilon_{VV} = \Delta \epsilon_{sat} \delta P \cos 2\phi + 2\Delta \epsilon_{sat} P_0 \sin 2\phi \delta m_\perp
\]  

(4.11)

The eigenvalues of the normal modes contributing to \( \delta m_\perp \) for this geometry can be obtained from equations (2.83) for \( \phi = 0^\circ \) and (2.85) for \( \phi = 90^\circ \) with \( q_z = 0 \). One gets \( \lambda = (K_{11} + K_{33}) \Delta^2 q_\perp^2 \) for either case, where \( q_\perp^2 = q_x^2 + q_y^2 \). The important advantage of this geometry is that \( \delta m_\perp \) corresponds to a pure eigenmode, the Goldstone mode of a biaxial nematic. This can be seen by the fact that \( \lambda \) depends only on \( \Delta = \frac{2P}{3} \) (assuming \( S_0 = 1 \)), a parameter that vanishes in the absence of biaxiality.
Figure 4.3 (i) **Geometry H3VV**: Homeotropic alignment with the director $\hat{n}$ in the scattering plane, polarized (VV) scattering, and equal incident and scattering angles; (ii) **Geometry H4VV**: homeotropic alignment with the director $\hat{n}$ in the scattering plane, polarized (VV) scattering, and normally incident light with scattering collected at angle $\theta_s$. 
4.2.6 GEOMETRY H4VV

Finally, we used a polarized (VV) geometry with homeotropic alignment, Figure 4.3 (ii), and with normally incident light, $\theta_i = \theta_{lab} = 0$, and scattered light collected at angle $\theta_s$ (corresponding to $\theta_{lab} = 70^\circ$). In the $N_u$ phase, the scattering vector is given by

$$\bar{q} = \frac{2\pi n}{\lambda} \left( -\sin \theta_s \hat{y} + (\cos \theta_s - 1) \hat{z} \right) \quad (4.12)$$

This is similar to the Geometry H3VV, since equation (2.45) again gives $G_i = G_z = 0$, and the dielectric constant fluctuation in the $N_b$ phase is also given by equation (4.11). Eigenvalues for this geometry can be obtained from equations (2.83) for $\phi = 0^\circ$ and (2.85) for $\phi = 90^\circ$. However, in this case since $q_z \neq 0$, one finds the $\hat{m}$ fluctuations are coupled with the $\hat{n}$ fluctuations, and therefore we do not single out an eigenmode associated purely with biaxiality.
4.3 PREDICTIONS FROM LANDAU-DEGENNES THEORY OF PHASE TRANSITION

4.3.1 ISOTROPIC-UNIAXIAL NEMATIC PHASE TRANSITION

The Landau-deGennes free energy for the $N_b$ phase in terms of uniaxial order parameter $S$ and biaxial order parameter $P$ was given by equation (2.54). In the $I$ phase, near the transition to a nematic phase, the uniaxial and biaxial order parameters are purely fluctuating quantities, $S = \delta S$ and $P = \delta P$. Up to second order in these fluctuations, the fluctuating part of the free energy of the $I$ phase can be written as

$$\delta F_I = \frac{A}{4} (3\delta S^2 + \delta P^2)$$  \hspace{1cm} (4.13)

where $A = A_0(T - T^*)$, $A_0$ is a positive constant, and $T^*$ is the supercooling limit of the isotropic phase.

Assuming $\Delta \varepsilon^a_{sat} \gg \Delta \varepsilon^b_{sat} P_0$, the discussion in Chapter 2 predicts that light scattering in the $I$ phase is mainly due to $\delta S$. The relaxation rate of the fluctuation $\delta S$ can be described by Landau-Khalatnikov dynamical equation [11]

$$-\eta_s \frac{\partial}{\partial t} \delta S = \frac{\partial \delta F_L}{\partial \delta S}$$ \hspace{1cm} (4.14)

where $\eta_s$ is a weakly temperature dependent viscosity which accounts for dissipation of nematic order fluctuations in the $I$ phase. This gives a simple exponential decay of order parameter fluctuations with relaxation rate
\[ \Gamma_s = \frac{3A_0}{2\eta_s} (T - T^*) \]  \hfill (4.15)

Thus, one expects a linear decrease in \( \Gamma_s \) on approaching the \( I \) to \( N_u \) transition from above, corresponding to a critical slowing down of order parameter fluctuations. Since the transition is first-order in general (see discussion in Section 2.4), this slowing down will be “cut off” at the actual transition, \( T_c = T^* + \frac{2B^2}{9AC} \), and the minimum observable \( \Gamma_s \) should be \( \Gamma_s \approx \frac{A_0}{\eta_s} (T_c - T^*) \). The fluctuations \( \delta S \) are nonhydrodynamic, exhibiting no dependence on the fluctuation wavevector \( \bar{q} \) to leading order.

The amplitude of the fluctuations \( \delta S \) is a strongly increasing function of \( T \) for \( T \to T^* \):

\[ \langle |\delta S|^2 \rangle = \frac{2k_B T}{3A_0(T - T^*)} \]  \hfill (4.16)

### 4.3.2 UNIAXIAL-BIAXIAL NEMATIC PHASE TRANSITION

In the \( N_u \) phase, the uniaxial nematic order parameter \( S = S_0(T) \) can be obtained by minimizing the free energy for \( P = 0 \), i.e. \( \alpha(S) = 0 \) in equation (2.54). Then, taking \( P = \delta P \) (i.e., biaxial order in the uniaxial phase is purely a fluctuation), the fluctuating free energy up to the second order is

\[ \delta F_U = \beta(S_0) \delta P^2 \]  \hfill (4.17)
The phenomenological Landau-Khalatnikov equation [11] for dynamics of $\delta P$ is

$$-\eta_p \frac{\partial}{\partial t} \delta P = \frac{\partial \delta F_\beta}{\partial \delta P}$$

(4.18)

where $\eta_p$ is the viscosity associated with dissipation of biaxial order parameter fluctuations in the $N_u$ phase. This gives a simple exponential decay of the fluctuations $\delta P$

$$\Gamma_p = \frac{2\beta(S_o)}{\eta_p}$$

(4.19)

Since as pointed out in Section 2.6.3 of Chapter 2, $\beta(S_o) \to 0$ at the temperature $T_{ub}^*$ describing the limit of stability of the uniaxial phase, we expect a critical slowing-down of fluctuations of the biaxial parameter as $T \to T_{ub}^*$. Thus, for $T$ near $T_{ub}^*$,

$$\beta(S_o) \approx \left(\frac{\partial \beta}{\partial T}\right)_{T_{ub}^*}(T - T_{ub}^*), \quad \text{and}$$

$$\Gamma_p \approx \frac{2}{\eta_p} \left(\frac{\partial \beta}{\partial T}\right)_{T_{ub}^*}(T - T_{ub}^*)$$

(4.20)

Of course, a second-order $N_u-N_b$ transition may be pre-empted by a first-order transition at a temperature $T_{ub} > T_{ub}^*$; the details are described in Chapter 2, Section 2.6.3.

In the $N_b$ phase, the equilibrium value of the biaxial order parameter $P_0$ is nonzero, and can be obtained from

$$\left(\frac{\partial F}{\partial S}\right)_S = 0 \quad \text{and} \quad \left(\frac{\partial F}{\partial P}\right)_S = 0.$$  

Approaching (from below) a first order transition at $T = T_{ub}$ (where $P_0 \to 0$), we can expand $P^2$ to lowest order in $T_{ub} - T$ as

$$P^2 \approx P_{ub}^2 + P_{ub}^2(T_{ub} - T)$$

(4.21)
For a second order transition

\[ P^2 \approx P_{ub}^2 (T_{ub} - T) \]  

These results will be useful in analyzing our data for the temperature dependence of the intensity scattered from director fluctuations in the putative Nb phase.

### 4.4 DATA AND RESULTS

The data in this section apply exclusively to isotropic and nematic phases of the tetrapodes. In the 3-ring compound, the nematic range extends below room temperature (the limit of the ovens used, which were not provided with subambient cooling), while the 4-ring is nematic down to ~60 °C, with the reported Nr-Nb transition at 132.9 °C. The X-ray scattering data shown in Figure 4.4 for the 4-ring tetrapode (courtesy of Prof. S. Kumar’s group at Kent State) clearly reveal the smectic phase developing only at ~56 °C; thus there is no smectic order anywhere near the region of interest (i.e., 131 – 136 °C) for our light scattering experiments.

#### 4.4.1 GERMANIUM 4-RING TETRAPODE

The most important subsections below are those which describe results from the “dark uniaxial” geometries (labeled H1VH, H2VH, H3VV, or H4VV). However, we
Figure 4.4  Small angle X-ray scattering data for Ge 4-ring tetrapode at different temperatures. In upper panel a sharp peak at low scattering angle corresponds to a layered structure at 56 °C corresponding to smectic phase (layer spacing 28 Å). Lower panel represents data for the isotropic phase (146 °C), $N_u$ phase (133 °C), and $N_b$ phase (70 °C) (provided by Dr. Hyung-Guen Yoon).
begin with results for two “less interesting” scattering geometries (geometries where fluctuations associated with biaxial order are swamped by the uniaxial director scattering). These geometries do provide benchmarks for the time scale of the director modes in a new type of nematic LC.

**Planar P1VH scattering geometry**

Figure 4.5 (upper panel) displays a typical light scattering correlation function recorded in the $N_a$ phase of the 4-ring tetrapode in the P1VH geometry. In this geometry (with $q_z = 0$ and $\theta_{slab} = 10^\circ$), we expect pure splay and pure twist fluctuations of $\hat{n}$ to contribute with approximately equal geometric scattering factors ($G_1 \approx G_2$). However, we find that the relaxation rates of these modes are too close to enable a meaningful double exponential fit. Hence the fit (red line) in Figure 4.5 (upper panel) corresponds to a slightly stretched exponential decay, and the data in Figure 4.6 (lower panel) represent an average of the splay and twist relaxation rates. The latter, as well as the average scattered intensity, are plotted in the Figure 4.6 as functions of temperature through the temperature ($T_{ub}$) of the putative transition (which corresponds to the textural change observed in Figure 3.6).

There are two useful conclusions to draw from Figure 4.6. First the average splay-twist to viscosity ratio, $\frac{\Gamma}{q_\perp^2} = \frac{K}{\eta} = 7.7 \times 10^{-8}$ cm$^2$ s$^{-1}$, is $\sim 100$ times lower than for typical small molecule calamitic nematics such as the cyanobiphenyls. Since we observed that
Figure 4.5 Upper panel: correlation function taken in the $N_u$ phase for the P1VH geometry. Lower panel: correlation function taken in the $N_u$ phase for the P2VH geometry. The red lines for both the panels are single exponential fits to the experimental data (Open circles). $q \sim 17300\,\text{cm}^{-1}$.
Figure 4.6  Upper panel: average scattered intensity collected for P1VH and P2VH geometries. Lower panel: Relaxation rates for P1VH and P2VH geometries corresponding to single exponential fit to the measured correlation functions.
the scattered intensity is comparable (for similarly prepared cells containing the tetrapode an 8CB, and for the same scattering set-up and laser power), the elastic constants $K_{11}$ and $K_{22}$ are of roughly comparable magnitudes, so that the reduction in $\Gamma$ for the tetrapodes must be due to substantially increased effective splay and twist orientational viscosities. This is consistent with a scenario in which the mesogenic groups are highly interdigitated with their neighbors attached to different tetrapodes, thereby enhancing rotational friction.

The second point is that the constancy of the scattered intensity ($I_{sc}$) from $\hat{n}$ fluctuations through the proposed $N_u$-$N_b$ transition at $T_{ub}$ is consistent with the Landau-de Gennes mean field theory. According to equation (2.45) and the discussion in section 2.5.2, $I_{sc} \propto \frac{(\Delta \epsilon_n^u)^2}{K_n}$. Since Landau-deGennes theory predicts $\Delta \epsilon^u_n \sim S$ and $K_n \sim S^2$ (Section 2.6.5), and since the uniaxial order parameter $S$ should be only weakly temperature dependent at a transition to a biaxial phase, we expect $I_{sc}$ to remain approximately constant for $T$ approaching $T_{ub}$. Below $T_{ub}$, in a biaxial phase, $I_{sc} \propto (\delta \epsilon_{vH})^2$ with $\delta \epsilon_{vH}$ given in equation (4.2) in terms of relevant orientational fluctuations. In this case, for $\Delta \epsilon_{sat}^u \gg \Delta \epsilon_{sat}^b P_0$, we find that $\delta \epsilon_{vH}$ is essentially the same as in the $N_u$ phase. Then the only signature of biaxiality would come through the impact of biaxial ordering on the uniaxial elastic constants. From equation (2.77) and Table 2.1 of Chapter 2, in a $N_b$ phase, the relevant elastic constants for the normal modes associated with splay and twist of $\hat{n}$ are $K_{ac} = K_{11} \left(1 - \Delta + \Delta^2 / 4\right)$, $K_{hc} = K_{11} \left(1 + \Delta + \Delta^2 / 4\right)$,
\[ K_{bb} = K_{22} \left( 1 - \Delta + \Delta^2 / 4 \right), \text{ and } K_{aa} = K_{22} \left( 1 + \Delta + \Delta^2 / 4 \right). \]
Assuming arbitrary alignment of the biaxial director \( \hat{m} \), light scattering experiments would detect average elasticities in the normal modes, namely \((K_{ac} + K_{bc})/2\) and \((K_{aa} + K_{bb})/2\). The modification to the uniaxial values due to biaxiality is then of order \( \Delta^2 / 4 = P^2 / 9S^2 \), which, considering \( P^2 \ll S^2 \) near \( T_{ab} \), should be much less than unity. Therefore, we expect the scattered intensity for the P1VH geometry to be almost constant throughout \( N_u-N_b \) phase transition, as observed in the data in Figure 4.6.

**Planar P2VH scattering geometry**

Figure 4.5 (lower panel) shows a typical correlation function taken in the \( N_u \) phase for a planar cell in the P2VH geometry. For this geometry in the \( N_u \) phase, we expect a single mode corresponding to twist-bend deformation of the director \( \hat{n} \). The measured correlation functions are fitted well with a single exponential function. Figure 4.6 (lower panel) presents the temperature dependence of the relaxation rate \( \Gamma \) extracted from the fit in the vicinity of the putative \( N_u-N_b \) transition. In the \( N_u \) phase, \( I(\omega) \propto \frac{(\Delta \varepsilon_{\text{un}})^2}{K_{22}q_z^2 + K_{33}q_z^2} \), and since \( q_z^2 \approx q_s^2 \) in our P2VH geometry, \( \Gamma = \frac{K_{22}q_s^2 + K_{33}q_z^2}{\eta_2} \approx \left( \frac{K_{22} + K_{33}}{\eta_2} \right) q_z^2 \) (where \( \eta_2 \) is the viscosity of the twist-bend mode); our experiment gives \( \frac{\Gamma}{q_z^2} = 1.5 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1} \). This value is \( \sim 2 \) times larger than found above for the combination of splay and twist, and is consistent with \( K_{33} \) being the largest uniaxial elastic constant (a result typical of small
molecule calamitic LCs). However, as noted above, the elasticity to viscosity ratio in the tetrapode is much smaller than in ordinary calamitics, reflecting a much higher orientational viscosity.

The scattered intensity is again observed (Figure 4.6 (upper panel)) to be approximately constant through the temperature where the $N_u$-$N_b$ transition is reported, and again this is not surprising, as uniaxial scattering is expected to dominate the P2VH geometry (see equation (4.4) for $\Delta \varepsilon_{sat}^u \gg \Delta \varepsilon_{sat}^h P_0$) and the biaxiality-related contributions to the relevant uniaxial elasticities ($K_{22}$ and $K_{33}$) should be quite small near $T_{ub}$. The argument for the latter is the same as in the previous discussion of the P1VH geometry, except the elastic constants $K_{ac}$ and $K_{bc}$ are replaced by $K_{ca}$ and $K_{cb}$ (see Table 2.1 of Chapter 2), and $K_{11}$ is replaced by $K_{33}$.

As anticipated, the experiments performed on homogeneously aligned samples in the aforementioned geometries provide no indication of light scattering due to either the biaxial order parameter or the biaxial director fluctuations. To detect these, we need to explore scattering in the “dark uniaxial” geometries, discussed Sections 2.6.7 and 4.2.

**Homeotropic H1VH scattering geometry**

Figure 4.7 illustrates correlation functions taken in the H1VH geometry with incident angle $\theta_{slab} = 10^\circ$ and scattering angle $\theta_s = \theta_{slab} = 0$ for different temperatures in the $N_u$ phase. Red lines correspond to fitting to a double exponential decay, while blue
Figure 4.7 Correlation functions taken in the $N_a$ phase of the Ge 4-ring tetrapode at 133.15, 133.06, 132.99, 132.96, 132.94, and 132.92 °C respectively from left to right for the H1VH geometry. Red lines correspond to the double exponential fit to the experimental data (black lines). Blue dotted lines correspond to the single exponential fit. It is clear from the figure that single exponential in not adequate to fit the experimental data.
dashed lines correspond to a single exponential fit, which is clearly insufficient to describe the data. In this “dark uniaxial” scattering geometry, assuming perfect homeotropic alignment, only one mode in the $N_u$ phase – fluctuations of the biaxial order parameter (equation (4.6)) – is expected. To understand the two observed modes, we performed a $q$-scan – specifically, we changed the incident angle from $5^\circ$ to $15^\circ$ while keeping scattering angle always zero (and thus maintaining conditions for the “dark uniaxial” geometry). Figure 4.8 displays correlation functions taken for different $q$-vectors at $133.0 \, ^\circ C$ in the $N_u$ phase. All the correlation functions are fitted by a double exponential function. The dispersion of the relaxation rates is plotted in Figure 4.9. The faster mode is nonhydrodynamic – i.e., $q$-independent – while the slower mode is clearly hydrodynamic and is linear with $q^2$. The faster mode in this geometry is about 100 times faster than the slower mode, and the slower mode has a relaxation rate of the same order as the uniaxial director modes observed in homogenous cell geometries for similar magnitudes of the $q$-vector (as discussed in the previous sections). The nonhydrodynamic nature of the faster mode suggests that it should be assigned to biaxial order parameter fluctuations ($\delta P$), which are expected to be nonhydrodynamic according to equation (4.19). However, could this mode on the other hand simply be associated with uniaxial order parameter fluctuations ($\delta S$) in the $N_u$ phase?

To test this possibility, we performed light scattering in the isotropic phase, where orientational order parameter fluctuations should be the sole source of depolarized scattering. Figure 4.10 shows representative correlation functions taken in the isotropic
Figure 4.8 Correlation functions taken in the $N_u$ phase for the H1VH geometry at 133.0 °C for incident angles of 7, 9, and 13° respectively from left to right.
Figure 4.9 Dispersion of relaxation rates observed in the \( N_a \) phase of the G4 4-ring tetrapode. The faster relaxation rate \( \Gamma_p \) is nonhydrodynamic and can be assigned to the biaxial order parameter relaxation. The slower mode is hydrodynamic and can be assigned to the leakage of the uniaxial director fluctuations.
Figure 4.10 Correlation functions taken in the isotropic phase for a scattering vector $q = 17300 \text{ cm}^{-1}$ at 133.20, 134.60, 134.10, and 133.70 $\text{°C}$ respectively from left to right. Red lines correspond to the single exponential fit to the experimental data (black lines).
phase near the transition to the uniaxial nematic phase. All the correlation functions are
fitted well to a single exponential; a scan in $q$ at fixed temperature in the isotropic phase
also shows them to be nonhydrodynamic. The relaxation rate corresponding to these
correlation functions shows a linear slowing down with temperature dependence (Figure
4.11 (upper panel)), which agrees with the prediction of equation (4.15) for the
pretransitional behavior of fluctuations $\delta S$ in the uniaxial order parameter – namely,
\[
\Gamma_s = \frac{3A_0}{2\eta_s} (T - T^*) .
\]
The linear fit to the data in Figure 4.11 (upper panel) gives the value
of $\frac{3A_0}{2\eta_s} = 5.9 \times 10^4 \text{ s}^{-1} \text{C}^{-1}$ and $T^* = T_{IN} - 0.63 \text{ °C}$, where $T_{IN}$ is the actual transition
temperature determined by the appearance of scattering due to nematic director
fluctuations. These results confirm a weakly first-order isotropic-nematic phase
transition, and also show that the order parameter relaxation rate just above $T_{IN}$ is about
an order of magnitude faster than the nonhydrodynamic mode detected below the
transition (Figure 4.11 (lower panel)). The large difference implies that it is highly
unlikely that the nonhydrodynamic fluctuations detected in the isotropic phase are the
same mode as the much slower nonhydrodynamic fluctuations observed in the nematic
phase – in other words, the two cases arise from different orientational order parameters.

A further, more decisive test for the identity of the nonhydrodynamic mode
detected in the nematic phase is to examine its temperature dependence on cooling.
Figure 4.11 (lower panel) presents the relaxation rate of this mode as a function of
temperature on cooling toward the reported $N_u-N_h$ transition (i.e., the temperature
Figure 4.11  Upper Panel: critical slowing down of uniaxial order parameter relaxation $\Gamma_s$ with temperature from $I$-$N_u$ phase. Lower Panel: critical slowing down of the biaxial order parameter relaxation $\Gamma_p$ with temperature through $N_u$-$N_b$ phase.
corresponding to the textural change in Figure 3.6). We clearly observe that the relaxation rate slows down linearly with temperature; the mode disappears at 132.90 °C, which is consistent with the reported $N_u-N_b$ transition at $T = T_{ub}$ and also with the behavior predicted by the Landau-deGennes model. Recall from Section 4.3.2 that this model implies a slowing down of biaxial order parameter fluctuations ($\delta P$) of the form

$$\Gamma_p \approx \frac{2}{\eta_p} \left( \frac{\partial \beta}{\partial T} \right)_{T_{ub}} (T - T_{ub}^*)$$

(equation (4.20)). A linear fit to the data in Figure 4.11 (lower panel) confirms this prediction and gives the slope of $\Gamma_p$ vs $T$ as $1.5 \times 10^4$ s$^{-1}$°C$^{-1}$ and the stability limit of the uniaxial phase as $T_{ub}^{\ast} = T_{ub} - 0.35$ °C. The slowing down of the nonhydrodynamic mode on cooling through a range of temperature below the isotropic-nematic transition strongly supports the mode’s identification with biaxial order parameter fluctuations and with the existence of a first-order $N_u-N_b$ phase transition in the 4-ring tetrapod. This transition also occurs at the same temperature relative to the isotropic phase, $T_{ub} = T_{IN} - 0.5$ °C, as determined by other researchers using different techniques [2, 9]. Finally, we note that the slopes of the pretransitional temperature dependences for $\Gamma_p$ vs $T$ ($N_u$ phase) and $\Gamma_S$ vs $T$ ($I$ phase) differ by a factor $\sim 4$, further establishing (particularly within the Landau-deGennes theory) distinct identities for these modes.

The slower, hydrodynamic mode in Figure 4.9 (or 4.12) (lower panel), observed for temperatures above $T_{ub}$ and which contributes significantly in the “dark uniaxial” geometry, can be attributed to “leakage” of uniaxial ($\hat{n}$) director fluctuations due to small
Figure 4.12 Upper Panel: temperature dependence of average intensity while cooling from the $N_u$ phase towards the $N_b$ phase for the H1VH geometry. Lower Panel: temperature dependence of relaxation rate corresponding to the leakage of the director $\hat{n}$ fluctuation in the $N_u$ phase and the directors $\hat{n}$ and $\hat{m}$ fluctuation in the $N_b$ phase.
imperfections or slight mosaicity in the homeotropic alignment of \( \hat{n} \) that we observed with careful scrutiny of the samples in the polarizing microscope. At the small scattering vector \( q = 17300 \text{ cm}^{-1} \) where our temperature scans were performed and near to \( T_{ub} \), the amplitude of this mode is typically comparable to the amplitude of the much faster nonhydrodynamic mode (6:1). We base our identification of the slower mode on three facts: (1) the mode is hydrodynamic (i.e., \( \Gamma \propto q^2 \)) as are director fluctuations; (2) the ratio of its relaxation rate to \( q^2 \), which we find from the slope of the linear fit in Figure 4.9 (lower panel) to be \( 7.9 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1} \), agrees well with the value \( 7.7 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1} \) found for combined splay / twist fluctuations of \( \hat{n} \) in the P1VH geometry (see above), and these are also the fluctuations that dominate the uniaxial elastic free energy in the limit \( q_z^2 \gg q_x^2 \) that applies in the H1VH geometry considered here; and (3) the scattered intensity of the hydrodynamic mode is \( \sim 100 \) times lower than in the planar geometries, which is consistent with a substantial suppression (but not complete elimination) of \( \hat{n} \) scattering achieved in the “dark uniaxial” geometry. As revealed in Figure 4.12 (lower panel), the relaxation rate of the “leakage” director fluctuations remains constant above \( T_{ub} \), but then decreases in the immediate vicinity of \( T_{ub} \).

Below \( T_{ub} \), the nonhydrodynamic biaxial order parameter mode was not detected; however, the scattering due to the slower (director) fluctuations increased steadily. Figure 4.13 displays a representative correlation function taken below \( T_{ub} \). In the present “dark uniaxial” geometry, the \( \hat{n} \) director fluctuations should remain relatively weak (not significantly change in amplitude with temperature). This suggests that the Goldstone
Figure 4.13 Correlation function taken at 132.80 °C in the $N_b$ phase. Red line corresponds to a single exponential fit to the experimental data (open circles).
mode of the biaxial phase, corresponding to splay-bend fluctuations of $\mathbf{m}$, which is not dark (since $\mathbf{m} \perp \mathbf{n}$), should dominate the director scattering below $T_{ub}$. The suggestion is confirmed by (1) the observation of an essentially pure exponential correlation function below $T_{ub}$, with relaxation rate comparable to (but somewhat lower than) that characteristic of the $\mathbf{n}$ fluctuations (see Figure 4.12, lower panel), and (2) the significant increase in associated dynamically scattered intensity which we present in Figure 4.12 (upper panel). From this figure, we see that in the $N_u$ phase, the scattered intensity is quite weak and almost constant with temperature, but, in the vicinity of and below $T_{ub}$, begins and continues to increase roughly linearly with decreasing $T$. Such a behavior cannot be associated with developments of the uniaxial order (e.g., with substantial changing of $\Delta \varepsilon_{sat}^{\prime}$); no indications of this were seen on crossing $T_{ub}$ in the two planar geometries which primarily probe $\mathbf{n}$ fluctuations (see Figure 4.6, upper panel). On the other hand, the development of biaxial order and, specifically, increasing $\Delta \varepsilon_{sat}^{\prime} P_a$, offers a compelling explanation. Below $T_{ub}$, the intensity scattered from the biaxial director should depend on the magnitude of $P$ as $(\Delta \varepsilon_{s}^{b})^2 \propto P^2$. Thus, according to equation (4.21), the intensity to lowest order should be linear with $T$. The linear fit to the experimental data in Figure 4.12 (upper panel) verifies this prediction. (A more complete argument of this point, which takes into account the dependence of the scattered intensity on the elastic constants as well as on $\Delta \varepsilon$, will be described below.)

The results of light scattering from the H1VH geometry very substantially support the detection of the biaxial order parameter mode in the $N_u$ phase: We have detected a
nonhydrodynamic mode that exhibits the critical temperature dependence expected for biaxial order parameter fluctuations within the standard Landau-deGennes theory, while cooling in an optically uniaxial nematic phase. A uniaxial surface anchoring transition, which could alter director alignment in the bulk but would produce no change in symmetry of the nematic, cannot explain the existence of an additional mode with characteristics totally distinct from director fluctuations. Another possibility, of course, is a surface biaxial phase that coexists with a uniaxial bulk. However, it would seem rather unlikely that our homeotropic surface treatment would selectively produce biaxial order only in a surface layer, while other experiments using different techniques and surface treatments indicated a bulk biaxial phase [2, 9]. Moreover, as we shall see below, the existence of microscopic surface biaxial layers covering a uniaxial bulk is totally incompatible with the results of our light scattering experiments that probed for \( \hat{m} \) fluctuations below \( T_{ub} \).

Let us then turn to the problem of exposing the presence of biaxial director fluctuations (or the Goldstone mode of the biaxial nematic) in the lower temperature nematic phase – i.e., for \( T < T_{ub} \) (where the transition temperature \( T_{ub} \) is identified as described above). The most obvious approach would be to demonstrate three distinct director eigenmodes below \( T_{ub} \). However, such a task is complicated by the fact that the two directors \( \hat{n} \) and \( \hat{m} \) are coupled in the biaxial elastic free energy, equation (2.63). This means that standard scattering geometries designed to unveil pure \( \hat{m} \) fluctuations will in general sample all three normal modes (each representing a linear superposition of \( \hat{n} \) and \( \hat{m} \)) that diagonalize the matrix \( M \) in equation (2.72). In other words, the
experiment would simply project out the \( \hat{m} \) component of each of the normal modes. We have already observed that, in scattering even from a uniaxial nematic, it can be difficult to separate the two contributing normal modes of the \( \hat{n} \) director through analysis of the intensity time correlation function; the relaxation rates of the modes can simply be too close in magnitude to resolve reliably through fitting to multiple exponential decays.

A more practical alternative is to study the temperature dependence of the intensity of scattered light \( (I_{sc}) \) below \( T_{ub} \), and to try to isolate selectively contributions from uniaxial and biaxial director fluctuations. In general, for director modes, one has \( I_{sc} \propto (\Delta \varepsilon)^2 / K \); thus, \( I_{sc} \) is influenced primarily by two material parameters – the dielectric anisotropy, representing either \( \Delta \varepsilon^u \) or \( \Delta \varepsilon^b \) (or both), and the appropriate Franck elastic constant(s), \( K \). Within Landau-deGennes theory, the dependence of \( \Delta \varepsilon^u \) and \( \Delta \varepsilon^b \) on the uniaxial and biaxial scalar order parameters is \( \Delta \varepsilon^u \propto S \), \( \Delta \varepsilon^b \propto P \), but the dependence of \( K \) is more complex because, as discussed in Section 2.6.5 and Table 2.1, expressions for the elastic constants in the biaxial phase generally contain both uniaxial and biaxial contributions – i.e., the expressions for the \( K \)s involve combinations of \( S^2 \) and \( P^2 \). Depending upon the scattering geometry selected and thus on the nature of \( \Delta \varepsilon \) and the particular \( K \)s picked out, one can find the following scaling relations (or combinations thereof) for \( I_{sc} \): \( I_{sc} \sim \frac{(\Delta \varepsilon)^2}{K} \sim \frac{S^2}{S^2} \), \( \frac{P^2}{S^2} \), or \( \frac{P^2}{P^2} \). Two of these should have essentially no temperature dependence for \( T < T_{ub} \), while the third \( (P^2/S^2) \) will dramatically decrease as \( T \rightarrow T_{ub} \) from below. Therefore, if one uses the light scattering selection rules and the biaxial elastic theory to choose geometries expected to match
these three individual cases, and the appropriate behavior of $I_{sc}$ vs $T$ is confirmed, then one can effectively, if indirectly, demonstrate the presence and expected contribution of the biaxial director (and associated Goldstone mode) below $T_{ub}$.

We have already presented and discussed experimental results for $I_{sc}$ vs $T$ for the H1VH geometry (see Figure 4.12, top panel). In this “dark uniaxial” geometry, the light scattering selection rules for a biaxial phase (see equation (2.74) in Chapter 2) give

$$I_{sc} \propto \left( \Delta \varepsilon^b \right)^2 / \lambda_{2,3},$$

where $\lambda_{2,3}$ are eigenvalues given in equations (2.83) and (2.85).

Assuming random orientation of $\hat{m}$ (in the plane perpendicular to $\hat{n}$), neglecting corrections to the uniaxial elastic coefficients of order $\Delta = 2P/3S$ (or higher) near $T_{ub}$, and using $q_\perp^2 \gg q_z^2$ (which applies in the H1VH geometry), we find

$$I_{sc} \sim \frac{\left( \Delta \varepsilon^b \right)^2}{K_{22} q_\perp^2 + K_{33} q_z^2} \sim \frac{\left( \Delta \varepsilon^b \right)^2}{K_{22}} \sim \frac{P^2}{S^2}$$

for eigenvalue $\lambda_2$. Additionally, if we neglect the coupling terms in equations (2.83) and (2.85) (i.e., the terms containing the coefficients $C$), we get

$$I_{sc} \sim \frac{\left( \Delta \varepsilon^b \right)^2}{(K_{11} + K_{33}) \Delta q_\perp^2 / 2 + K_{22} \Delta^2 q_z^2} \sim \frac{\left( \Delta \varepsilon^b \right)^2}{(K_{11} + K_{33}) \Delta^2} \sim \frac{P^2}{S^2 (P^2 / S^2)} \sim \frac{P^2}{P^2}$$

for eigenvalue $\lambda_3$. Since $S^2$ should vary only weakly with $T$ in the biaxial phase, the main temperature dependence of $I_{sc}$ below $T_{ub}$ should be given by the factor $P^2$ in the numerator of the scattering associated with $\lambda_2$. Near $T_{ub}$, this should scale linearly with $T$ (see equation (4.21)). This behavior was confirmed in our previous discussion of results for the H1VH geometry and by the solid line fit in Figure 4.12 (top panel). Of course $I_{sc}$ does not drop to zero at $T_{ub}$, since above $T_{ub}$ order parameter fluctuations and “leakage”
of uniaxial director fluctuations contribute finite scattering. What about the contribution to $I_{sc}$ of the eigenvalue $\lambda_3$ (which gives $I_{sc} \sim P^2/P^2$)? This should be constant in $T$ and equal to its value at $T_{ub}$, which could be rather low for a weakly first order transition. We note that the data for $I_{sc}$ in Figure 4.12 do indeed reveal a finite offset at $T_{ub}$, relative to the background value reached at temperatures above $T_{ub}$.

Figure 4.12 (top panel) also reveals that the magnitude of $I_{sc}$ at a temperature $0.3^\circ$C below $T_{ub}$ is >400 times its magnitude $0.3^\circ$C above $T_{ub}$ (where the scattering is due to “leakage” of $\hat{n}$ fluctuations and to $P$ fluctuations). It is extremely unlikely that such an enormous increase would be due solely to scattering from $\hat{m}$ fluctuations confined to surface biaxial layers; this result thus indicates a transition throughout the bulk.

**Homeotropic H2VH scattering geometry**

We next turn to results for the homeotropic H2VH geometry with $\theta_{slab} = 0^\circ$ and $\theta_{slab} = 75^\circ$ (see Section 4.2.4 and Figure 4.2 (ii) above). This is not a “dark uniaxial” geometry, and thus we expect a different behavior for the temperature dependence of $I_{sc}$ through the transition at $T_{ub}$ than observed for the H1VH geometry. Figure 4.14 presents sample correlation functions taken in both the $N_u$ (left plot in the figure) and $N_b$ (right plot) phases. Both correlation functions are fitted well with a single exponential function. In the $N_u$ phase, we expect the twist-bend director mode (see Section 4.2.4) with
Figure 4.14 Correlation functions taken in the $N_a$ (left) and the $N_b$ (right) phase in the H2VH geometry at a lab scattering angle $75^\circ$. Red line corresponds to a single exponential fit for both the correlation functions.
relaxation rate \( \Gamma = \frac{K_{22}q_z^2 + K_{33}q_z^2}{\eta_z(q)} \), where \( \eta_z \) is the \( q \)-dependent orientational viscosity for this mode. In the \( N_b \) phase, since \( \delta e_{\text{vH}} \) is dominated by the term containing \( \Delta e_{\text{sat}} \) corresponding to twist-bend of the uniaxial director fluctuation \( \delta n_x \) (see equation (4.9)), the relaxation rate is expected similar to that in the \( N_u \) phase, as observed. Moreover, in the \( N_b \) phase, assuming random orientation of \( \hat{m} \) and \( \Delta^2 \ll 1 \) in Table 2.1, the relevant eigenvalues, \( \lambda_{2,3} \) given by equations (2.83) and (2.85) in Section (2.6.4.3), both reduce to \( K_{22}q_\perp^2 + K_{33}q_z^2 \). Thus, the scattered intensity has the predicted dependence

\[
I_{sc} \sim \frac{(\Delta e_{\text{sat}}^u)^2}{K_{22}q_\perp^2 + K_{33}q_z^2} \sim \frac{S^2}{S'^2}.
\]

We then expect \( I_{sc} \) to be approximately independent of temperature below \( T_{ub} \), and the corresponding experimental data presented in Figure 4.15 confirm this expectation.

*Homeotropic H3VV scattering geometry*

Now let us consider a second “dark uniaxial” geometry to illustrate results for our third predicted scaling relation for \( I_{sc} \) in a biaxial phase – namely, \( I_{sc} \sim \frac{P^2}{P'^2} \). This polarized homeotropic geometry, labeled H3VV, has \( \theta_{\text{dab}} = \theta_{\text{slab}} = 25^\circ \) (see Section 4.2.5 and Figure 4.3 (i)), and both polarizer and analyzer normal to the scattering plane. Figure 4.16 shows representative correlation functions taken for this geometry. Equation (4.11) implies that in the \( N_b \) phase, only scattering due to biaxial director fluctuations should be
Figure 4.15  Temperature dependence of average intensity while cooling from the $N_u$ phase towards the $N_b$ phase for the H2VH geometry.
Figure 4.16 Correlation functions taken for the H3VV geometry with incident and scattering angles equal to 25°. Red line corresponds to single exponential fit in the $N_b$ phase (right). Unfitted correlation function corresponds to that observed in the $N_u$ phase. Observed intensity in the $N_u$ phase is very small.
observed. In this geometry, \( q_z = 0 \), and the coupling terms \( C_{kk} q_y^2 q_z^2 \) and \( C_{ca} q_y^2 q_z^2 \) in equations (2.83) and (2.85) for the eigenvalues \( \lambda_2 \) and \( \lambda_3 \) vanish; thus the \( \hat{m} \) fluctuations correspond purely to the Goldstone mode (\( \lambda_3 \)) of the biaxial phase. Assuming random orientation of \( \hat{m} \), the eigenvalue \( \lambda_3 \) is given by

\[
\frac{\Delta}{2} \left( K_{11} + K_{33} \right) q_\perp^2
\]

(Section 4.2.5) and therefore the scattered intensity scales as

\[
I_{sc} \sim \frac{(\Delta \epsilon^b)^2}{(K_{11} + K_{33}) \Delta^2} \sim \frac{P^2}{S^2 (P^2 / S^2)} \sim \frac{P^2}{P^2}
\]

which should be approximately constant in temperature below \( T_{ub} \). Our corresponding experimental data taken in the \( N_b \) phase (presented in Figure 4.17) agree with this prediction.

It is interesting to note that in the uniaxial phase (\( T > T_{ub} \)), where the scattering from fluctuations due to the biaxial Goldstone mode should drop to zero, the drop observed is not abrupt but occurs over \( \sim 0.1 - 0.2 \) °C. This could be due to two effects: either scattering from residual, surface layers of biaxial order (which melt continuously over a narrow range above \( T_{ub} \)), or the contribution of the biaxial order parameter mode which scatters more near \( T_{ub} \) (where fluctuations in biaxial order are softest).

**Homeotropic H4VV scattering geometry**

Finally, we examine results from the homeotropic H4VV geometry with \( \theta_{lab} = 0^\circ \) and \( \theta_{lab} = 70^\circ \) (Section 4.2.6 and Figure 4.3 (ii)). Figure 4.18 presents typical correlation functions taken for this case. Since both the polarizer and analyzer are
Figure 4.17 Average scattered intensity recorded in a homeotropic cell for the H3VV geometry for an incident and scattering angles of 25°.
Figure 4.18 Correlation functions taken for the H4VV geometry with incident angle $0^\circ$ and scattering angle $70^\circ$. Red lines correspond to single exponential fit in the $N_b$ phase (right). Left correlation function corresponds that observed in the $N_u$ phase.
perpendicular to the director $\hat{n}$, this is a dark uniaxial geometry i.e., the geometrical scattering factors $G_1 = G_2 = 0$ for $\hat{n}$ fluctuations in the uniaxial phase (Section 4.2.6). Indeed, the scattered intensity in the $N_u$ phase is very small and can be attributed to the leakage of the uniaxial director fluctuations. Equation (4.11) shows that below $T_{ub}$, the scattering in this geometry should be dominated by fluctuations of the biaxial director $\hat{m}$. The situation is analogous to our discussion for the H1VH geometry above: the contributing eigenvalues are again $\lambda_{2,3}$ (given by equations (2.83) and (2.85) for different extremes of $\hat{m}$ orientation), except, in the present case $q_z$ and $q_\perp$ are comparable. Thus $I_{sc}$ will have components that scale as $P^2 / S^2$ and $P^2 / P^2$, the former exhibiting the dominant and linear temperature dependence below $T_{ub}$, as documented in the data in Figure 4.19. The fact that $q_z$ and $q_\perp$ are comparable and fairly large should strengthen the couplings $C_{2c}q_z^2q_z^2$ and $C_{a2}q_z^2q_z^2$, relative to the situation in the H1VH geometry, so we expect the constant “background” arising from the biaxial Goldstone mode (which contributes $I_{sc} \sim P^2 / P^2$ ) to be suppressed, since this mode will be more strongly mixed with the uniaxial director. This is reflected in the fact that the intensity at $T_{ub}$ is only $\sim1.3$ times the level above $T_{ub}$ in Figure 4.19 (H4VV geometry) compared to $\sim7$ times the level in Figure 4.12 (top) (H1VH geometry).

To recapitulate, the measured temperature dependence of the scattered intensity in the lower temperature nematic phase for four distinct scattering geometries confirms the predictions of the light scattering and elastic theory for a biaxial nematic phase.
Figure 4.19  Average scattered intensity recorded for the H4VV at an incident angle of 0° and a scattering angle of 70°.
4.4.2 GERMANIUM 3-RING TETRAPODE

Motivated by our experiments on the 4-ring tetrapode, and by prior results suggesting a second-order \(N_u-N_b\) transition in the 3-ring counterpart, we performed light scattering measurements on the 3-ring Ge-tetrapode in the \(I\) and \(N_u\) phases for a homeotropically-aligned sample. In the 3-ring compound, the \(I-N_u\) transition occurs at 46.5 °C, and the \(N_u\) phase persists over a very wide temperature range (~23.5 °C) and to much lower temperatures than for the 4-ring tetrapode. The biaxial texture (analogous to that in Figure 3.6) appears only at ~22 °C. Figure 4.20 displays representative correlation functions taken for different temperatures in the \(N_u\) phase of the 3-ring tetrapode in the H1VH scattering geometry at an incident angle \(\theta_{\text{lab}} = 10^\circ\) and scattering angle \(\theta_s = 0^\circ\). Similarly to the analysis in Figure 4.7 for the 4-ring material, the correlation functions are fitted well a double exponential decay (shown as the red line). On the other hand, the dashed blue line in Figure 4.20 corresponds to a single exponential fit; it is clearly inadequate. The faster mode of the two detected is about two orders of magnitude faster than the slower mode. To establish the identity of the two modes, as in the case of the 4-ring studies, we performed a \(q\)-scan by changing incident angle from 5° to 17° while keeping the scattering angle fixed at 0°, thereby maintaining the “dark uniaxial” geometry. Figure 4.21 shows some of the correlation functions taken for this \(q\)-scan, all
Figure 4.20 Correlation functions taken in the $N_u$ phase of the Ge 3-ring tetrapode at 38.02, 35.02, 32.01, 29.01, and 23.97 °C respectively from left to right for the H1VH geometry. Red lines correspond to the double exponential fit to the experimental data (black lines). Blue dash line corresponds to the single exponential fit (35.02 °C). It is clear from the figure that single exponential in not adequate to fit the experimental data.
Figure 4.21 Correlation functions (black lines) taken at incident angles of 5, 10 and 16.5° respectively from left to right in the $N_u$ phase of Ge 3-ring for the H1VH geometry. All the correlation functions are fitted well with double exponentional function (red lines).
of which are fitted to a double exponential decay. The dispersion of the relaxation rates obtained from these fits is plotted in Figure 4.22. The faster mode is nonhydrodynamic ($q$-independent) while the slower mode is hydrodynamic (relaxation rate linear with $q^2$).

The situation is qualitatively identical to our results on the 4-ring tetrapode discussed in the previous section for the H1VH geometry, and, as in the that case, the faster mode in Figure 4.20 can be assigned to the biaxial order parameter fluctuation (relaxation rate $\Gamma_p$) and the slower, hydrodynamic mode can be assigned to the “leakage” of uniaxial director ($\hat{n}$) fluctuations. Comparing typical values of $\Gamma_p$ and the $\hat{n}$ director fluctuation rate in the 3-ring tetrapode with those in the 4-ring, we observe that the former ($\Gamma_p$) are $\sim 30$ times lower and $\sim 50$ times lower ($\hat{n}$ relaxation rate) than in the latter; in fact, for the $\hat{n}$ fluctuations, the value of $\Gamma / q^2$ (slope of the linear fit) in Figure 4.22 is $1.6 \times 10^{-9} \text{ cm}^2 \text{s}^{-1}$, or 50 times lower than the comparable value for the 4-ring compound. Although this may partly reflect the $\sim 100^\circ$C lower temperature of the measurements in the 3-ring tetrapode, it is interesting to speculate that orientational viscosities may be inherently higher for the compound with smaller mesogenic groups; perhaps there is more efficient interdigitation between neighboring tetrapode molecules in this case.

To compare $\Gamma_p$ with the uniaxial order parameter fluctuation relaxation rate $\Gamma_s$ in the $I$ phase of the 3-ring tetrapode, we performed a temperature scan through the $I$ to $N_u$ phase transition. Figure 4.23 represents shows correlation functions taken in the $I$ phase approaching the transition to the $N_u$ phase. The correlation functions are fitted to a single exponential decay, corresponding to a single mode identified with fluctuations of
Figure 4.22 Dispersion of relaxation rates observed in the $N_u$ phase. The faster relaxation rate $\Gamma_P$ is nonhydrodynamic and can be assigned to the biaxial order parameter relaxation. The slower mode is hydrodynamic and can be assigned to the leakage of the uniaxial director fluctuations.
Figure 4.23  Correlation functions taken in the / phase for a scattering vector 17300 cm\(^{-1}\) at 46.80, 46.60, 46.40, and 46.27 °C respectively from left to right. Red lines correspond to the single exponential fit to the experimental data (black lines).
the uniaxial order parameter. The temperature dependence of data for the relaxation rate of this mode, $\Gamma_s$, is shown in Figure 4.24. The solid line is a linear fit to the prediction of the Landau-deGennes theory – i.e. $\Gamma_s = \frac{3A_0}{2\eta_S} (T - T^*)$ (equation (4.15)). The fit gives

$$\frac{3A_0}{2\eta_S} = 5800 \text{ s}^{-1} \text{C}^{-1} \text{ and } T^* = T_{I_N} - 0.22 \text{ °C},$$

corresponding to a very weak first order $I$-$N_u$ phase transition. (In fact, the value of $T_{I_N} - T^*$ is approximately one fifth that for a typical small molecule calamitic thermotropic.) As will be seen shortly, the temperature dependence of $\Gamma_P$ in the $N_u$ phase is much weaker than $\Gamma_S$ in the isotropic phase, indicating that $\Gamma_P$ is distinct from uniaxial order parameter fluctuations.

To search for the signature and order of a $N_u$-$N_b$ transition, we cooled the 3-ring sample at fixed $q = 17300 \text{ cm}^{-1}$ in the H1VH geometry. Figure 4.25 displays the temperature dependence of the relaxation rate $\Gamma_P$. We observe that $\Gamma_P$ slows down linearly with the temperature and appears to vanish continuously at a temperature $T_{ub}$ corresponding to 23.0 °C. As in the case of the 4-ring tetrapode, we see that the nonhydrodynamic fluctuations observed in the $N_u$ phase soften linearly with $T$, in accordance with the prediction of Landau-deGennes theory for a $N_u$ to $N_b$ transition. However, in the present (3-ring) case, the softening (or critical slowing down) is not cut off by a first-order transition, but instead is consistent with a continuous (second-order) transition. Indeed, a linear fit to the data for $\Gamma_P$ versus $T$, Figure 4.25 (upper panel), confirms that the biaxial order parameter fluctuations soften all the way to $T = T_{ub} = T_{ub}^*$,
Figure 4.24  Uniaxial order parameter relaxation $\Gamma_s$ slowing down from the $I$ phase towards the $N_u$ phase. $\Gamma_s$ slows down linearly with temperature with a weakly first order isotropic to uniaxial nematic phase transition.
Figure 4.25  Upper Panel: critical slowing down of biaxial order parameter relaxation $\Gamma_p$ with temperature from $I-N_u$ phase. Lower Panel: temperature behavior of the director relaxation $\Gamma$ with temperature through $N_u-N_b$ phase.
signifying a second order $N_u$-$N_b$ transition, and gives a slope of $14 \text{ s}^{-1} \circ\text{C}^{-1}$ (~400 times lower than the slope describing the critical slowing down of uniaxial order fluctuations, $\Gamma_S$ vs $T$, in the isotropic phase while approaching the $N_u$ phase). Figure 4.25 also displays (bottom panel) the temperature dependence of the relaxation rate corresponding to the leakage of $\hat{n}$ director fluctuations in the $N_u$ phase; we see that these fluctuations slow down on approaching $T_{ub}$, indicating an increase in viscosity for director fluctuations.

We should reiterate that the biaxial order parameter mode, as well as the $\hat{n}$ director fluctuations, detected in the $N_u$ phase of the 3-ring tetrapode, are much slower than those in the 4-ring. In particular, the slope of $\Gamma_P$ vs $T$ is ~500 times lower in the 3-ring than the 4-ring compound – a remarkable difference that suggests a significant intrinsic difference in the microscopic configuration of the two nematics. In fact, the dynamics of the 3-ring nematic are so slow as to suggest almost a glassy nematic phase, or perhaps the proximity in composition or temperature to a glassy phase. The simplest explanation for this difference is strongly activated orientational viscosities – i.e., viscosities with a typical Arrhenius temperature dependence, $\eta \propto \exp(E_a/k_BT)$ ($T = $ absolute temperature), and an unusually high activation energy $E_a$ (which for typical small molecule calamitics is ~3300 J (for 5CB)[12, 13]).

Since our oven was not equipped to cool below ambient room temperature (~22°C), we were unable to study the dynamics of the biaxial nematic phase of the 3-ring tetrapode.
4.5 SUMMARY

We conclude this chapter with a brief summary of results. Both 4- and 3-ring tetrapodes reveal weakly scattering nonhydrodynamic modes accompanying the standard hydrodynamic director modes in the uniaxial nematic phase. The nonhydrodynamic nature and critical slowing down of these modes at temperatures consistent with the transition to a biaxial nematic phase reported from other experimental techniques (and with corresponding to textural changes in homeotropic samples such as that shown in Figure 3.6) strongly support their association with biaxial order fluctuations. The observed critical behavior indicates a first-order uniaxial-biaxial transition in the 4-ring tetrapode, and a second-order transition in the 3-ring tetrapode. Overall, the dynamics of both director and order parameter fluctuation modes in the (lower temperature) 3-ring are much slower than in the (higher temperature) 4-ring, suggesting strongly activated orientational viscosities in the tetrapodes. Finally, we used selected scattering geometries to study the temperature dependence of the intensity scattered by coupled director modes in the lower temperature (biaxial) phase, and confirmed that the pretransitional temperature dependence of $I_{sc}$ was consistent with biaxial order (or, specifically, with the predicted scaling of the dielectric anisotropies and elastic constants with order parameters $S$ and $P$ near a uniaxial-biaxial transition).

To close, we consider the question of how the biaxial phase of tetrapodes might be visualized structurally. Recent X-ray diffraction results from Prof. S. Kumar’s group at Kent State shed considerable light on this issue. In the 4-ring tetrapode, they find an
evolution in temperature in the average angle or “tilt” that the pendant mesogens make with their average long axis orientation in the tetrapode – as shown schematically in Figure 3.3 (above). (The average mesogens long axis is indicated as the uniaxial director \( \hat{n} \).) Referring to this figure, XRD indicates that the angle \( \phi \) is approximately \( 30^\circ \) in the phase corresponding to the \( N_b \) region, while it is much smaller in the uniaxial phase. Moreover, XRD in the lower temperature, smectic phase reveals that the tilting of the mesogens in the tetrapode is approximately coplanar. It is then easy to imagine a higher degree of hindrance in the rotation of the tetrapodes around \( \hat{n} \) in the presence of tilt compared to no tilt, and that this hindrance would promoting a biaxial phase (with \( \hat{m} \) perpendicular to \( \hat{n} \)). In this picture, the average tilting of the mesogenic groups in a tetrapode would correspond to the (microscopic) biaxial order parameter, and would be the origin of the nonhydrodynamic order parameter mode we detected in our light scattering.
REFERENCES


As pointed out in Chapter 1, studies of lyotropic chromonic liquid crystals (LCLCs) have focused chiefly on understanding their phase diagram, the structure of the chromonic aggregates and the aggregation mechanism, and on possible applications. However, their viscoelastic coefficients, which are potentially very important physical parameters for applications, have not been characterized quantitatively. The only systematic light scattering experiments carried out to date were performed on the isotropic phase [1, 2] of cromolyn in water for concentrations ranging from 1-14 wt%. These studies found: a strong contribution of concentration fluctuations of cromolyn aggregates to the scattered light intensity (in addition to the expected nematic order parameter mode); a deviation of the inverse scattered intensity from the linear pretransitional temperature dependence [2] typically observed in thermotropic liquid crystals [3]; and a time dependent evolution of aggregates length [1] for cromolyn concentrations above 8 wt%.

Recent development of techniques to align LCLCs, especially for cromolyn [4, 5] in nematic phase, now provide opportunities to separate and characterize viscoelastic
coefficients in well-defined light scattering geometries. We have performed such studies and used both the static and dynamic results to measure the elastic constants and orientational viscosities in the nematic phase formed by a 14 wt% cromolyn in water nematic LCLC.

5.1 EXPERIMENTAL SETUP AND SCATTERING GEOMETRIES

The preparations of the LCLC sample, its homogeneous alignment in a 16 μm thick layer, and the general experimental setup for the light scattering study are explained in detail in Chapter 3. Experiments were performed in two standard geometries: splay+twist and predominantly bend geometries.

5.1.1 SPLAY-TWIST GEOMETRY

Consider a depolarized (VH) nematic scattering geometry with the director \( \hat{n} (= \hat{z}) \) perpendicular to the scattering plane \((xy)\) and the laser light normally incident (Figure 5.1 (i)). In this case, the scattering \( q \)-vector is given by
\[
\tilde{q} \equiv \tilde{k}_f - \tilde{k}_i = \frac{2\pi n}{\lambda} \left\{ (\cos \theta_{st} - 1) \hat{y} - \sin \theta_{st} \hat{x} \right\},
\]
where \( \theta_{st} \) (subscript \( st \) for “splay+twist”') is the scattering angle in the sample, and \( n \) is the average (isotropic) refractive index of the LCLC sample. Here we ignore the refractive index anisotropy of the LCLC which is quite small, \( \Delta n = n_\parallel - n_\perp \approx 0.02 \) in the nematic phase [6]. We then have:
Figure 5.1 Light scattering geometries employed to study the nematic phase of cromolyn: (i) splay-twist geometry where the light scattering due to splay and twist deformation of the nematic director can be probed and (ii) bend geometry in which light scattering due to the bend deformation of the nematic director can be probed.
\[ q = |\vec{q}| = q_\perp = \sqrt{q_x^2 + q_y^2} = \frac{4\pi n}{\lambda} \sin \frac{\theta_\perp}{2} \]  

(5.1)

The optical factors for scattering from the normal modes 1 (splay-bend) and 2 (twist-bend) of a uniaxial nematic in this geometry are given by (see equation (2.45) for details)

\[ G_1 = \cos^2 \frac{\theta_\perp}{2} \]  

(5.2)

\[ G_2 = \sin^2 \frac{\theta_\perp}{2} \]  

(5.3)

Since \( q_z = 0 \) (i.e., the average \( \hat{n} \) is perpendicular to the scattering plane), we expect scattering from pure splay and twist components of the normal modes; their relaxation rates are given by (equation (2.35))

\[ \Gamma_1(\vec{q}) = \frac{K_{11}q_\perp^2}{\eta_1(q_\perp)} \]  

(5.4)

and

\[ \Gamma_2(\vec{q}) = \frac{K_{22}q_\perp^2}{\eta_2(q_\perp)} \]  

(5.5)

where \( \eta_1(q_\perp) \) (or \( \eta_{\text{splay}} \)) and \( \eta_2(q_\perp) \) (or \( \eta_{\text{twist}} \)) are given by equations (2.36) and (2.37), respectively. In terms of more fundamental Miesowicz viscosities of nematic [3], the effective viscosities are

\[ \eta_{\text{splay}} = \gamma_1 - \frac{(\gamma_1 + \eta_b - \eta_c)^2}{4\eta_b}, \eta_{\text{twist}} = \gamma_1, \text{ and } \eta_{\text{bend}} \text{ is } \eta_{\text{splay}} \text{ when } \eta_b \text{ and } \eta_c \text{ are exchanged.} \]
The amplitudes of these modes can be determined from equation (2.45) combined with equation (5.3) above. For the splay mode one has

\[ A_1 \propto \frac{\cos^2 \theta_\alpha / 2}{K_{11} q_{\perp}^2} \]  

(5.6)

and for the twist mode,

\[ A_2 \propto \frac{\sin^2 \theta_\alpha / 2}{K_{22} q_{\perp}^2} \]  

(5.7)

### 5.1.2 BEND GEOMETRY

Figure 5.1 (ii) shows a depolarized (VH) scattering geometry with the director \( \hat{n} = \hat{z} \) in the scattering plane and normal to the incident light direction, so that the scattering vector may be written \( \vec{q} = q_x \hat{x} + q_z \hat{z} \), where

\[ q_z = \frac{2\pi n}{\lambda} \sin \theta_b \]  

(5.8)

and

\[ q_x \equiv q_{\perp} = \frac{2\pi n}{\lambda} (1 - \cos \theta_b) \]  

(5.9)

Here \( \theta_b \) (subscript \( b \) stands for “bend”) is the scattering angle in the sample, \( n \) is the average (isotropic) refractive index, and we again neglect the anisotropy \( \Delta n \). The geometrical factors for this geometry are given by

\[ G_1 = 0 \quad \text{and} \quad G_2 = \cos^2 \theta_b \]  

(5.10)

Thus, only mode 2 (twist-bend) is detected. Its relaxation rate is
where $\eta_z(\bar{q})$ is given in equation (2.37). The amplitude of the bend mode can be determined from equation (2.45) as

$$A_3 \propto \frac{\cos^2 \theta_\parallel}{K_{22}q_{\perp}^2 + K_{33}q_{||}^2}$$

(5.12)

Assuming for the moment $K_{22} \approx K_{33}$ and birefringence $\Delta n = 0.02$ [6], the ratio of $K_{33}q_z^2$ to $K_{22}q_{\perp}^2$ ranges from 0.01-0.15 for the scattering lab angle range of 15°-65° used in our experiments. In fact, as shown below in the next section, $K_{33} \approx (25-40)K_{22}$ over the nematic temperature range studied. Hence the contribution of $K_{22}q_{\perp}^2$ to the amplitude and relaxation rate of the mode $[A_3, \Gamma_3]$ is utterly negligible over the whole angular range studied. In this case, equations (5.11) and (5.12) reduce to essentially pure bend fluctuations,

$$\Gamma_3(\bar{q}) \approx \frac{K_{33}q_z^2}{\eta_z(q_{||} = 0)}$$

(5.13)

and

$$A_3 \propto \frac{\cos^2 \theta_\parallel}{K_{33}q_z^2}$$

(5.14)

Here we have also used the fact $q_z^2 \gg q_{\perp}^2$ to simplify the expression for the orientational viscosity, $\eta_z(\bar{q}) \approx \eta_z(q_{||} = 0) = \eta_{bend}$.
5.2 DATA AND RESULTS ON THE NEMATIC PHASE OF 14 WT% CROMOLYN IN WATER

For the two studied geometries (splay+twist and bend), homodyne cross-correlation of the scattered light intensity were recorded as a function of time delay. Figure 5.2 shows some of the intensity correlation functions taken at different lab scattering angles in the nematic phase of our 14 wt% cromolyn LCLC sample at a fixed temperature of 21 °C in the splay+twist geometry. The correlation functions are fitted to double exponential decays (with four parameters, two amplitudes and two relaxation rates). The relaxation rates of the observed modes differ by about an order of magnitude. For conventional nematic LCs, such as calamitic (small molecule, rodlike) systems, viscosities associated with the splay $\eta_{\text{splay}}$ and twist $\eta_{\text{twist}}$ are expected to be comparable and $K_{11} \sim 2K_{22}$. Hence, faster relaxation rate $\Gamma_1$ is preliminarily assigned to the splay fluctuations and the slower relaxation rate $\Gamma_2$ is assigned to the twist fluctuations. A more definitive assignment can be based on the measured amplitudes obtained from the fits to the correlation functions. The amplitude ratio $A_2 / A_1$ (the ratio of equation (5.7) to equation (5.6)) of twist to splay is $\frac{K_{11}}{K_{22}} \tan^2 \frac{\theta_{\text{scat}}}{2}$. From our fits, $A_2 / A_1$ is found to be very small for lower scattering angles; e.g., $A_2 : A_1 = 1 : 9$ at the smallest lab scattering angle of 4°. Hence, the stronger mode in the lower scattering angles can be assigned to the splay deformation, and the weaker mode corresponds to the twist deformation. Figure 5.3 shows the dispersion, studied varying scattering angle from 4° to 65°, of relaxation
Figure 5.2 Correlation functions taken in the splay-twist geometry for scattering angles of 62°, 22°, 14°, and 10° from left to right respectively at temperature $T = 21$ °C. Red lines correspond to the double exponential fitting and black lines correspond to the experimental data.
Figure 5.3  Dispersion of the relaxation rates $\Gamma_1$ and $\Gamma_2$ in splay-twist geometry.
rates $\Gamma_1$ and $\Gamma_2$. As expected, they are linear with $q^2$. The slope of $\Gamma_1$ vs $q^2$ gives $K_{11}/\eta_{\text{play}} = 8.9 \times 10^{-9}$ cm$^2$s$^{-1}$ and the slope of $\Gamma_2$ vs $q^2$ gives $K_{22}/\eta_{\text{twist}} = 7 \times 10^{-10}$ cm$^2$s$^{-1}$.

Figure 5.4 shows representative correlation functions measured for different scattering angles in the predominantly bend geometry. Here we expect a single overdamped mode (predominantly bend component of twist-bend). Interestingly, however, we find, especially at lower angles, that fits to a single exponential decay fail to describe the data. This is highlighted in Figure 5.5, which displays, as open circles, data for a scattering angle of 8° ($q = 1.64 \times 10^4$ cm$^{-1}$). The blue line corresponds to the best single exponential fit to the data; it evidently does not match the slower portion of the decay. On the other hand, as shown in Figure 5.4, double exponential fits (red lines) to the correlation data (black lines) provide an excellent description over the full range of scattering angles studies.

The existence of an additional relaxation mode in the bend geometry is also confirmed by an alternative analysis using the so-called “regularization method” [7] to perform an inversion of the correlation data. In this method, one posits a correlation function characterized by a distribution of relaxation rates,

$$g_2(\tau) = \left[ \int_0^\infty A(\Gamma) \exp(-\Gamma \tau) d\Gamma \right]^2 + 1.$$  

For a pure single exponential decay (relaxation rate $\Gamma_0$), one has $A(\Gamma) = A_0 \delta(\Gamma - \Gamma_0)$. In practice, finite $q$-resolution and sample mosaicity imply a distribution of finite width. In the case of a double exponential, one can expect two separate peaks of different heights and widths. Commercial software such as $\textit{DYNALS}$ [8], based on an algorithm first developed by Provencher [7] and used by us,
inverts the data for $g_2(\tau)$ to obtain the distribution of relaxation rates $A(\Gamma)$ or relaxation times $A(1/\Gamma)$. A typical result of DYNALS of analysis for our correlation data in the bend geometry is shown in the inset to Figure 5.5; the small peak neighboring the larger peak clearly indicates the presence of an additional mode. A similar behavior was found for all the correlation functions taken in the bend geometry, both in $q$-scans and temperature scans and also for different sets of repeated data.

Our different analyses, ordinary exponential fitting and the regularization method, thus both reveal two modes with distinct relaxation rates, $\Gamma_3$ and $\Gamma_4$, and corresponding amplitudes, $A_3$ and $A_4$. We find that the faster mode ($\Gamma_3$) has the larger amplitude – typically, $A_3 \geq 7A_4$. Since for our depolarized scattering geometry we expect the director fluctuations to be most intense, we preliminarily assign the mode $[A_3, \Gamma_3]$ to director bend (as noted above, the bend component of mode 2 totally dominates twist for the scattering angles studied). The additional mode is therefore a new, unidentified fluctuation contributing in the bend geometry. To confirm our identification of the mode $[A_3, \Gamma_3]$, we performed additional optical measurements in collaboration with Dr. Yuriy Nastishin and Dr. Oleg Lavrentovich in the latter’s laboratory at the Liquid Crystal Institute. We will discuss these shortly. For now, we note that both modes, detected in the bend geometry, are hydrodynamic (linear with $q^2$), as demonstrated in Figure 5.6; the slope of $\Gamma_3$ vs $q^2$ gives $K_{33}/\eta_{\text{bend}} = 2.0 \times 10^{-5}$ cm$^2$s$^{-1}$. 
Figure 5.4 Correlation functions recorded in the bend geometry for scattering angles of 56°, 41°, 26°, 14°, 8° and 4° respectively from left to right at temperature $T = 21$ °C. Red lines correspond to the fit to the double exponential function.
Figure 5.5 Correlation function taken at a scattering angle of $8^\circ \ (q = 1.64 \times 10^4 \text{cm}^{-1})$ in the bend geometry: red line corresponds to a double exponential fit to the experimental data (black circle) and blue line corresponds to the fit to a single exponential function. Blue line is missing data points specially at long time scales. Inset corresponds to the analysis using regularization method which indicates two distinct relaxation modes.
Figure 5.6 Dispersion of the relaxation rates of the bend ($\Gamma_3$) mode and an additional ($\Gamma_4$) mode in the bend geometry.
The ratio of the elastic constants \((K_{11} : K_{22} : K_{33})\) can be obtained from the ratio of the normalized amplitudes of fits to the correlation functions. From equations (5.6) and (5.7), we get

\[
\frac{A_2}{A_1} = \frac{K_{11}}{K_{22}} \tan^2 \frac{\theta_{st}}{2}
\]

(5.15)

Figure 5.7 shows data for \(A_2 / A_1\) plotted with respect to \(\tan^2 \frac{\theta_{st}}{2}\) for our cromolyn sample at a temperature of 21°C in the nematic phase. The slope of the straight line fit gives \(\frac{K_{11}}{K_{22}} = 22\). Next, from equations (5.7) and (5.14), we obtain

\[
\frac{A_2}{A_3} = \frac{K_{33}}{4K_{22}} \tan^2 \theta_b
\]

(5.16)

Figure 5.8 shows the data for \(A_2 / A_3\) versus \(\tan^2 \theta_b\) at \(T = 21°C\). The slope of the straight line fit gives \(\frac{K_{33}}{K_{22}} = 43\). Finally, from equations (5.6) and (5.14), we calculate

\[
\frac{A_1}{A_3} = \frac{K_{33}}{4K_{11}} \tan^2 \frac{\theta_{st}}{2}
\]

(5.17)

Figure 5.9 shows our data for \(A_1 / A_3\) plotted as a function of \(\tan^2 \theta_b / \tan^2 \frac{\theta_{st}}{2}\) at 21°C. The slope of the straight line fit gives \(\frac{K_{33}}{K_{11}} = 1.8\). These ratios satisfy the inequality \(K_{33} > K_{11} > K_{22}\) which applies rather generally to ordinary small molecule, thermotropic nematics [3]. However, \(\frac{K_{11}}{K_{22}}\) and \(\frac{K_{33}}{K_{22}}\) are about an order of magnitude higher in the
Figure 5.7  Ratio of amplitudes for the twist and splay director relaxation modes at temperature $T = 21$ °C. The slope of the straight line fit gives $\frac{K_{11}}{K_{22}}$. 

$A_2/A_1$ versus $\tan^2 \theta_{st}/2$.
Figure 5.8 Ratio of the amplitudes for the twist and bend director relaxation modes obtained from the normalized amplitudes $A_2$ and $A_3$ at temperature $T = 21 \, ^\circ\text{C}$. 
Figure 5.9  Ratio of the amplitudes for the splay and bend director relaxation modes obtained from the normalized amplitudes $A_1$ and $A_3$ at temperature $T = 21 \, ^{\circ} \text{C}$. 
chromonic LC than in typical calamitic nematics, such as PAA and MBBA, but are rather more comparable to lyotropic, hard-rod polymer nematic liquid crystals such as poly-γ-benzyl-glutamate (PBG) [9]. Table 5.1 summarizes values for the elastic constant ratios for 14 wt% cromolyn and the other nematic liquid crystals.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Temperature (°C)</th>
<th>$T_{NI}$ (°C)</th>
<th>$\frac{K_{11}}{K_{22}}$</th>
<th>$\frac{K_{33}}{K_{22}}$</th>
<th>$\frac{K_{33}}{K_{11}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PAA [3]</td>
<td>120</td>
<td>135</td>
<td>1.6</td>
<td>2.7</td>
<td>2.0</td>
</tr>
<tr>
<td>MBBA [3]</td>
<td>22</td>
<td>47</td>
<td>2.4</td>
<td>3.4</td>
<td>1.4</td>
</tr>
<tr>
<td>PBG [9]</td>
<td>Just below $T_{NI}$</td>
<td>11.4</td>
<td>11.4</td>
<td>13.0</td>
<td>1.17</td>
</tr>
<tr>
<td>DSCG</td>
<td>21</td>
<td>27.8</td>
<td>22.0</td>
<td>43.0</td>
<td>1.8</td>
</tr>
</tbody>
</table>

Table 5.1 Ratio of elastic constants of some different nematic liquid crystals.

We are now in a position to check our assignment of $[A_3, \Gamma_3]$ to bend, utilizing additional techniques available in Dr. Lavrentovich’s lab. These were mainly carried out by Dr. Yuriy Nastishin, but as part of a general collaborative study of chromonic nematics between Dr. Sprunt’s and Dr. Lavrentovich’s research groups. We first obtained an independent measurement of $K_{33} / K_{22}$, using the magnetic Freedericksz transition for both twist and bend geometries at a temperature of 23 °C (Figure 5.10). For bend, since the diamagnetic susceptibility anisotropy is negative ($\chi_\parallel - \chi_\perp < 0$) [6], the magnetic field is applied along the director in a homeotropically-aligned sample of thickness $d_{33} = 67$ μm, and a field-induced bend distortion was observed at a critical field measured to be
Figure 5.10 Experimental set up to measure critical magnetic fields for bend and twist Freedericksz transitions. Upper panel: bend geometry in which magnetic field is applied along the director to a homeotropic cell. Critical magnetic field can be measured by measuring the transmitted light intensity through the crossed polarizers for different magnetic fields. At the critical magnetic field, there is a steep increase in the intensity of the transmitted light due to Freedericksz transition. Lower panel: twist geometry in which magnetic field is applied along the director to a planar cell.
\[ H_{c33} = 4.8 \text{ kG}. \] For twist, the field is applied along the director in a homogeneously-aligned planar sample of thickness \( d_{33} = 50 \text{ μm} \); the critical field for induced twist was determined to be \( H_{c22} = 1.1 \text{ kG}. \) \( K_{33} / K_{22} \) can then be calculated using the expression

\[
\frac{K_{33}}{K_{22}} = \left( \frac{H_{c33}d_{33}}{H_{c22}d_{22}} \right)^2 [3]; \]

this gives \( K_{33} / K_{22} = 34 \), which agrees well with the light scattering result, 37 at 23 °C, assuming our assignment of the mode \( [A_3, \Gamma_3] \) to bend fluctuations of the director. On the other hand, the ratio would be 7 times larger, if calculated by considering the slower, weaker \( [A_4, \Gamma_4] \) mode, detected in the bend geometry, to be the director mode. In a second experiment, the optical texture surrounding defects in the director field in an unaligned nematic sample of 14 wt% cromolyn was examined in order to estimate \( K_{33} / K_{11} \), following the procedure described by Hudson et al. [10]. This technique is less accurate compared to the light scattering approach, and yields data in the broad range \( K_{33} / K_{11} \sim 1-8 \), which nevertheless is closer to the value \( K_{33} / K_{11} = 2.5 \) we calculated by assigning \( [A_3, \Gamma_3] \) to bend fluctuations. If \( [A_4, \Gamma_4] \) were assigned to director bend, \( K_{33} / K_{11} \) would be 18 – definitely outside the range set by the optical study of defects. The two independent experiments just described clearly confirm our assignment of the director bend fluctuations. This leaves the question of the identity of the additional hydrodynamic mode \( [A_4, \Gamma_4] \) observed in the bend scattering geometry, which we will return to at the end of this Chapter.

We now turn to light scattering experiments to probe the temperature dependence of the viscoelastic parameters of our LCLC system. The experiments were typically
started at 21 °C, from which freshly prepared samples were heated towards the nematic to isotropic phase transition \( T_{NI} = 27.8 \, ^\circ C \). Near \( T_{NI} \), a coexistence of the isotropic and nematic phases – manifested by small domains (islands) of the isotropic phase developing in the nematic – was observed through an optical microscope. During the light scattering experiments, these islands were detected by the appearance of a circular diffraction pattern of the transmitted laser beam. The experiments were stopped when the diffraction pattern appeared, and any data very taken in the coexistence region were not analyzed further.

Figure 5.11 shows the relaxation rates \( \Gamma_1 \) and \( \Gamma_2 \) for splay and twist fluctuations as functions of temperature. Both increase with the increase in temperature toward \( T_{NI} \). The average scattered intensity of both modes also increases while approaching \( T_{NI} \) (Figure 5.12), but as Figure 5.13 reveals, this increase is selectively due to splay; the amplitude corresponding to twist remains constant throughout the nematic region. The temperature dependence of corresponding parameters for the bend geometry are plotted in Figure 5.14 \( (\Gamma_3, \Gamma_4) \), Figure 5.15 (average intensity), and Figure 5.16 \( (A_3, A_4) \). The increase in the average scattered intensity with temperature in the bend geometry is evidently due to an increase in the amplitudes contributed by both the bend director mode and the additional detected mode.

Using equations (5.15), (5.16), and (5.17) for the amplitudes at fixed lab scattering angles \( (40^\circ \) for the splay+twist geometry and \( 15^\circ \) for the bend geometries, respectively), we obtained the temperature dependences of the elastic moduli ratios;
Figure 5.11  Temperature behavior of relaxation rate of the splay ($\Gamma_1$) and twist ($\Gamma_2$) modes ($q = 78000 \text{ cm}^{-1}$).
Figure 5.12 Temperature behavior of the scattered intensity in the splay-twist geometry ($q = 78000 \text{ cm}^{-1}$).
Figure 5.13 Temperature behavior of the amplitude of splay mode $A_1$ (squares) and twist mode $A_2$ (circles) ($q = 78000 \text{ cm}^{-1}$).
Figure 5.14 Temperature behavior of $\Gamma_3$ and $\Gamma_4$ observed in bend geometry ($q = 29200$ cm$^{-1}$).
Figure 5.15  Temperature behavior of the scattered intensity in bend geometry ($q = 29200$ cm$^{-1}$).
Figure 5.16 Temperature behavior of the amplitude of the bend mode, $A_3$ (squares) and the amplitude of the additional mode, $A_4$ (circles) ($q = 29200$ cm$^{-1}$).
results are displayed in Figure 5.17. $\frac{K_{11}}{K_{22}}$ and $\frac{K_{33}}{K_{22}}$ decrease with the temperature, while $\frac{K_{33}}{K_{11}}$ increases.

We should point out that, in the course of our initial temperature scans, we noticed an interesting ageing effect of the samples. In particular, we found that the magnitude of $\frac{K_{11}}{K_{22}}$ increased by a factor ~2 over a few days; the qualitative temperature dependence of this ratio, however, remained the same. As shown in Figure 5.18, the relaxation rates corresponding to splay and twist decrease as the sample ages, while relaxation rate corresponding to bend increases. Figure 5.19 and Figure 5.20 reveal that the ageing effects saturate a sufficient time after initial sample preparation. We thus performed our $q$ and $T$ scan experiments only after at least 48 hours of ageing our samples (at room temperature). After this preliminary period, and over the <12 hr interval of subsequent experiments, the impact of ageing was observed to be minimal.

The temperature dependence of the individual elastic constants, normalized to their values at the lowest temperature investigated (21°C), was extracted from our data for the scattering amplitudes $A_i(T)$ and the relation $K_{ii}(T) \propto \frac{\Delta n^2(T)}{A_i(T)}$, where $\Delta n$ is the refractive index anisotropy. Data for the temperature dependence of the latter were obtained by Dr. Nastishin [11]. We then defined reduced values of the material constants by $\delta C(T) = \frac{C(T)}{C(T = 21^\circ C)}$. For example, $\frac{\Delta n(T)}{\Delta n(T = 21^\circ C)} = \frac{S(T)}{S(T = 21^\circ C)} = \delta S(T)$.
Figure 5.17 Temperature behavior of the ratio of the elastic constants.
Figure 5.18 Relaxation rates of a fresh and an old (after a few days) sample of DSCG at temperature $T = 21$ °C. When the sample gets older both splay and twist relaxation rates get slower while the bend relaxation rate gets faster.
Figure 5.19 Time evolution of relaxation rate in splay and twist geometry ($T = 21 \, ^{\circ}\text{C}$ and $q = 29200 \, \text{cm}^{-1}$).
Figure 5.20  Upper panel: time dependence of the ratio of splay and twist relaxation rates and lower panel: normalized amplitudes corresponding to splay and twist ($T = 21$ °C and $q = 29200$ cm$^{-1}$).
The values of $\delta S(T)$ and $\delta K_{ii}(T)$ are plotted in Figure 5.21. It is clear from the figure that the bend and splay elastic constants decrease on heating far more strongly than the twist elastic constant, and that the splay elastic constant is the most dependent on temperature.

Next, we determined absolute values of elastic moduli by calibrating the scattered intensity due to chromonic LC against an identical cell filled with 5CB for a pure bend geometry at 21 °C. For the twist-bend geometry, pure bend mode can be achieved setting $q_\perp = 0$ at the so called magic angle $\theta_{ab} = \sin^{-1}\left[\frac{n_\perp}{\sqrt{1 - \frac{n_\perp^2}{n_\parallel^2}}}\right]$. For 5CB the magic angle is 45.8° (calculated with literature values of $n_\perp = 1.536$, $n_\parallel = 1.737$ [12]). The intensity of the scattered light in this geometry is given by $I \propto \frac{\Delta n^2 T \cos^2 \theta_b}{K_{33} q_z^2} = \frac{\Delta n^2 T \cos^2 \theta_b}{K_{33} q_z^2}$, where $\bar{n} = \frac{1}{3}(2n_\perp + n_\parallel)$. Taking the ratio of intensities due to identical cells of 5CB and the lyotropic nematic liquid crystals, LNLC, we determined the bend elastic constant of LNLC by $(K_{33})_{LNLC} = \left(\frac{\Delta n^2 \cos^2 \theta_b T}{I q_z^2}\right)_{LNLC} \left(\frac{K_{33} I q_z^2}{\Delta n^2 \cos^2 \theta_b T}\right)_{5CB}$ for homodyne scattering. For this calculation, we made use of $n_\perp = 1.536$, $n_\parallel = 1.737$, and $K_{33} = 9.8$ pN [13] for 5CB at 21°C. The value of $K_{33}$ determined this way for our LNLC is 15 pN. With this value of $K_{33}$ at 21°C and $\delta K_{33}(T)$, we obtained the absolute value of the bend elastic constant at different temperatures; the result is plotted in Figure 5.22. From the value of
Figure 5.21 Temperature dependence of the reduced values of the scalar order parameter, $\delta S$ and elastic constants: $\delta K_{11}$, $\delta K_{22}$, and $\delta K_{33}$. 
Figure 5.22 Temperature dependence of splay, twist, and bend elastic constants.
and the ratios $K_{33}/K_{22}$ and $K_{33}/K_{11}$ previously determined, we calculated $K_{11}(T)$ and $K_{22}(T)$; these results are also displayed in Figure 5.22.

Below $T_{NI}$, the amplitudes of the modes, which are inversely proportional to the ratios $\frac{K_{ii}}{(\Delta n)^2}(i=1,2,3)$, are expected to be approximately constant with temperature within standard Landau-deGennes theory (Section 2.5.2). However, as Figure 5.23 reveals, only $\frac{K_{22}}{(\Delta n)^2}$ follows this expected behavior; $\frac{K_{33}}{(\Delta n)^2}$ and $\frac{K_{11}}{(\Delta n)^2}$ decrease with increasing temperature. This unusual result can be explained by considering the possibility that the LCLC aggregates shorten in average length $L$ with increasing temperature [2]. In this scenario, $K_{11}$ and $K_{33}$ are affected by the change in the length of the aggregates, but $K_{22}$ essentially unchanged [14]. The argument for this, due to Meyer [15], is that as the length of the LCLC stacks increases, there is a significant change in the density of the system under splay or bend deformation. The density change is unremarkable for standard small molecule nematics with a length to diameter ratio $L/d$ of 3 or 4. But as the molecules become longer, there are fewer ends available to fill the gaps in the system produced by the splay or bend deformation making the splay or bend deformation much more costly in energy. However, when the length of the rods becomes greater than a certain limit, they can bend continuously, making the situation for the bend elasticity more complicated. Twist is unaffected with the increase in the length of the rods because during the twist deformation each rod or chain remains straight and closely packed with its neighbors, no matter how long it is. Meyer [15] predicted that for a
Figure 5.23 Temperature dependence of $K_{11}/\Delta n^2$, $K_{22}/\Delta n^2$, and $K_{33}/\Delta n^2$. 
completely ordered chromonematic ($S=1$), the splay elastic constant would stiffen according to

$$K_{11} = \frac{k_B T}{4d} \frac{L}{d}. $$

Here $L$ (the average length of the chromonic stack) has an activated temperature dependence (similar to the Arrhenius form for fluid viscosities),

$$L = L_0 \exp \frac{E_a}{2k_B T} \quad (5.18)$$

where $L_0$ is the intermolecular spacing in the aggregate, $E_a$ is the scission energy needed to split an aggregate into two, $k_B$ is the Boltzmann constant, and $d$ is the diameter of the stack, which is approximately fixed by the lateral size of the crotonolyn molecules. (Although the lateral features of the aggregates might also change somewhat with temperature, it is still of interest to apply the simplest available model to our data.)

To apply Meyer’s model to extract $L(T)$ from our elastic constant data, we must first separate out the possible role of the orientational order parameter $S$, which is generally $<1$. One way to do this is to examine the ratio $K_{11} / K_{22}$. Since according to Figure 5.23 $K_{22}$ scales as $(\Delta n)^2$ (i.e., as $S^2$), but does not apparently vary with $L$ (i.e., $K_{22} / (\Delta n)^2 \sim \text{constant}$) – in agreement with Meyer’s argument – the ratio should “scale out” the $S^2$ dependence of $K_{11}$, thereby isolating the dependence on $L(T)$ contained in Meyer’s expression, $K_{11} \propto L/d$. Explicitly, one may express the ratio as

$$\frac{K_{11}}{K_{22}} = \frac{1}{K_{22}^0} \frac{k_B T}{4d} \frac{L}{d},$$

where the coefficient $K_{22}^0$ is taken as the value of $\frac{K_{22}}{S^2}$ at a reference temperature ($T = 21^\circ\text{C}$). With the experimentally determined value of $K_{22} = 0.35 \text{pN}$ and value of $S = 0.7$ [6, 16] at $21^\circ\text{C}$, we get $K_{22}^0 = 0.71 \text{pN}$. Then using $d = 1.6 \text{nm}$ [17]
and our data for $K_{11}$ (Figure 5.22), we may extract $L(T)$; the result is plotted in Figure 5.24 (upper panel). $L$ decreases from 41 nm at 21 °C to 18 nm at 27 °C. Alternatively, $L(T)$ can be obtained from $\frac{K_{11}}{(\Delta n)^2}$ by using the measured $\Delta n(T)$ for our 14 wt% cromolyn sample [6], and the relation $(\Delta n)^2 \propto S^2$ to “scale out” the $S^2$ dependence of $K_{11}$. The values of $L$ so deduced are essentially identical to those obtained from the ratio $K_{11} / K_{22}$. The highest temperature value of $L$ obtained in our experiment is comparable to the value $L = 18$ nm measured by Nastishin et al. [2] in the isotropic phase at 32 °C, just above the $I-N$ phase coexistence region. Using equation (5.18) and $L_0 = 0.34$ nm [6], we calculated the scission energy $E_a(T)$. As shown in Figure 5.24 (lower panel), it is weakly temperature dependent, varying from $9.6 \kappa_B T$ at 21 °C to $8 \kappa_B T$ at 27.15 °C. This range is consistent with literature estimates for chromonic dyes and, an analogous system, DNA oligomers [16, 18].

It is more difficult to understand the behavior of bend elastic constant with respect to temperature. For the hard-rod systems, it is expected to depend on the length $L$ of the aggregates, while for a flexible system it should depend on the persistence length [19]. The persistence length is a basic mechanical property quantifying the stiffness of a long polymer. It is defined as the length over which correlations in the direction tangent to the polymer chain are lost. For a hard-rod system $K_{11} \sim \frac{L}{d}$ and $K_{33} \sim \left(\frac{L}{d}\right)^2$ [19], so that, $\frac{K_{33}}{K_{11}}$ is expected to vary as $\frac{L}{d}$. Thus, as the length of the aggregates decreases with increasing
Figure 5.24 Temperature dependence of the length $L$ of the aggregates and the scission energy $E_a$. 
temperature, \( \frac{K_{33}}{K_{11}} \) is expected to decrease. However, our data (Figure 5.17) tell a different story: \( \frac{K_{33}}{K_{11}} \) increases with temperature. For flexible rods, \( K_{33} \) is expected to be proportional to the persistence length (which is constant) [19]. In this model \( \frac{K_{33}}{K_{11}} \propto \frac{1}{L} \), so that, as the length of the aggregates decreases with temperature in this case, \( \frac{K_{33}}{K_{11}} \) would be expected to increase. Hence the observed increase of \( \frac{K_{33}}{K_{11}} \) with temperature suggests that chromonic aggregates behave more like flexible rods but as we presently do not have data for the persistence length, it is not possible to confirm this definitely.

We determined the orientational viscosity coefficients associated with splay, twist, and bend deformation of our 14 wt% cromolyn LCLC from the absolute values of elastic constants (Figure 5.22) and corresponding relaxation rates (Figure 5.14 and Figure 5.11) using equations (5.4), (5.5), and (5.13) respectively. Results are plotted in Figure 5.25 for different temperatures. All the viscosity coefficients decrease on heating. The viscosity coefficients of cromolyn measured at room temperature (21°C) are compared with those of the low molecular weight nematic 5CB [12] and the lyotropic polymer nematic PBG [9] in Table 5.2. The viscosities of the chromonic LC resemble the measured values for the polymer nematics [19]. We note that \( \eta_{\text{twist}} \) in both the lyotropic polymer nematic and the chromonematic is two orders of magnitude higher than the value in 5CB. For sufficiently extended aggregates, the viscosity \( \eta_{\text{bend}} \) is associated
<table>
<thead>
<tr>
<th></th>
<th>5CB (kgm^{-1}s^{-1}) [20]</th>
<th>PBG (kgm^{-1}s^{-1}) [9]</th>
<th>cromolyn (kgm^{-1}s^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \eta_{\text{splay}} )</td>
<td>0.08</td>
<td>3.5</td>
<td>14</td>
</tr>
<tr>
<td>( \eta_{\text{twist}} )</td>
<td>0.08</td>
<td>3.5</td>
<td>11.1</td>
</tr>
<tr>
<td>( \eta_{\text{bend}} )</td>
<td>0.028</td>
<td>0.016</td>
<td>0.007</td>
</tr>
</tbody>
</table>

Table 5.2 Viscosities associated with the splay, twist and bend deformation of different liquid crystals at 21°C.

mainly with the relatively easy process of sliding the aggregates along each other. \( \eta_{\text{twist}} \) on the other hand should involve shearing and thus rearrangements of the aggregates. We observe that the ratio \( \eta_{\text{twist}} / \eta_{\text{bend}} \) decreases (Figure 5.26) dramatically from about 1600 at room temperature to about 450 at 27 °C. This behavior can be explained by the fact that the aggregates become shorter at high temperature which should dramatically decrease \( \eta_{\text{twist}} \) (~ 9 times) and less so \( \eta_{\text{bend}} \) (~ 2 times).

To conclude our discussion of results, let us return to the issue of the identity of the additional hydrodynamic mode \([ A_4, \Gamma_4 ] \) detected in the bend geometry (see Figure 5.5). We found that this mode is not present in polarized scattering, so it is not likely to be associated with concentration fluctuations of the aggregates or with translational diffusion monomers or short aggregates. Could it be related to a leakage of splay or twist scattering? To answer this question, we can compare its relaxation rate with those of splay and twist measured in the splay+twist geometry for the same magnitude of
Figure 5.25 Temperature dependence of viscosities associated with splay, twist and bend deformation.
Figure 5.26 Temperature behavior of the ratio of the viscosity coefficients corresponding to splay, twist, and bend fluctuations.
scattering vector. We find that $\Gamma_4$ is about three orders of magnitude faster than $\Gamma_1$ and four orders of magnitude faster than $\Gamma_2$, thus ruling out the leakage scenario. This leaves us with the following hypothesis: In a system of flexible or semi-flexible aggregate, the mode $[A_4, \Gamma_4]$ may correspond to a transverse sliding of cromolyn molecules within the overall stack that forms an aggregate. Using the experimental data (Figure 5.6) for the slope $\Gamma_4 / q^2$ at $21^\circ C$ and setting this equal to a diffusion constant $D$ (i.e., $\Gamma_4 = Dq^2$), we calculated the size of a sliding element in the stack using a spherical-shape approximation and the Stokes-Einstein formula $D = \frac{k_B T}{\xi}$, where $\xi = 6\pi \eta R_H$, $\eta$ is the solvent (water) viscosity, and $R_H$ is the hydrodynamic radius of the sliding element. We then estimate that the hydrodynamic diameter ($2R_H$) to be $d_H = 3.2 \text{ nm}$, which is twice that of the aggregate diameter $d = 1.6 \text{ nm}$ [17]. However, in this calculation, we have not taken into account the dragging force on a sliding element due to the neighboring molecules (i.e., we assumed viscous drag only from the solvent). To account for the additional drag, we assume $\eta_{\text{eff}} = c\eta$, where parameter $c > 1$. Available hydrodynamic calculations, which have been tested in experiments such as the diffusion of actin filaments in an aqueous solution confined between rigid planar boundaries [21], give $c \approx 2$. Thus, if we use $\eta_{\text{eff}}$ instead of $\eta$ in the Einstein’s formula, we get $d_H \approx d$, the diameter of a single cromolyn molecule in the stack. It is then at least reasonable to consider that the mode $[A_4, \Gamma_4]$ corresponds to the sliding of molecules within the aggregates. This sliding can provide a bending flexibility mechanism for the aggregates that differs significantly from the
known bending mechanisms (those involving stretching or extension) in other rod-like nematics.

### 5.3 SUMMARY

In this Chapter, we reported results from what we believe to be the first systematic study of nematic orientational elastic constants and viscosities of a lyotropic chromonic liquid crystal (formed by a 14 wt% solution of cromolyn in water). While qualitatively similar to the large values found in hard-rod polymer lyotropic nematics, the elastic constant ratios, $K_{11}/K_{22}$ and $K_{33}/K_{22}$, and viscosity ratios, $\eta_{\text{twist}}/\eta_{\text{bend}}$ and $\eta_{\text{splay}}/\eta_{\text{bend}}$, are somewhat larger still in the LCLC. More intriguing is evidence from the increase in $K_{33}/K_{11}$ with increasing temperature for semiflexibility of the chromonic aggregates; detailed measurements of their persistence length would help confirm (and quantify) this characteristic. Finally, we identified a novel hydrodynamic fluctuation mode in the chromonic nematic, observed in depolarized scattering in a geometry corresponding predominantly to bend distortion of the director. We suggest that this mode may also be associated with flexibility of the aggregate – in particular, with a sliding motion of the disk-like cromolyn molecules transverse to the axis of an aggregate, a motion one might picture as similar to the sliding of a “stack of coins”.
REFERENCES


CHAPTER 6

CONCLUSION

In this dissertation, we have described results of light scattering experiments on two, heretofore relatively unexplored, nematic liquid crystalline mesogens: 3- and 4-ring organosiloxane Germanium tetrapodes and a lyotropic chromonic nematic liquid crystal. Our experiments probe specifically the thermal fluctuations of nematic orientational order. We used both static and dynamic results to establish a strong case for nematic biaxiality in the tetrapodic compounds; our findings also support the prior conclusions drawn from other experimental techniques. Our data from the chromonic liquid crystal constitute a first study of viscoelastic coefficients in these nematic materials.

We employed temperature scans at fixed wave vector ($\vec{q}$) and $q$-scans for a constant temperature in specific light scattering geometries, which, based on appropriate Landau-deGennes theory and optical scattering theory for an anisotropic fluid, probe different elastic deformations of the director (optic axis), selectively isolate biaxial order parameter fluctuations in a uniaxial nematic, and/or separate contributions of uniaxial and biaxial director fluctuations in a biaxial phase.

In both tetrapodes we detected two distinct relaxation modes in the uniaxial nematic, utilizing scattering geometries in which the uniaxial director fluctuations are, in
principle, dark. The faster mode was shown to be distinct from uniaxial order parameter fluctuations (which were separately characterized in the isotropic phase) and consistent with the expected nonhydrodynamic (\(q\)-independent) behavior and distinct temperature dependence expected for biaxial order parameter fluctuations. In particular, we observed that these fluctuations slow down with temperature, in a manner consistent with a uniaxial-biaxial phase transition that is weakly first order in the 4-ring tetrapode and second order in the 3-ring tetrapode. The slower of the two modes observed in the “dark” geometry is hydrodynamic (having a relaxation rate that is linear with \(q^2\)), and has the character of a uniaxial director mode, which are intrinsically strongly scattering and consequently can, in a real sample with imperfections in optical axis alignment, “leak” into the scattering in the dark geometry. By comparing this “leakage” mode with standard director modes probed in conventional nematic scattering geometries, we confirmed its identity.

We additionally studied the temperature dependence of the intensity scattered (\(I_{sc}\)) by coupled director modes in the lower temperature nematic phase of the 4-ring tetrapode, and confirmed that the pretransitional temperature dependence of \(I_{sc}\) is consistent with light scattering theory for a biaxial phase. In particular, based on the predicted scaling of the dielectric anisotropies and elastic constants with uniaxial (\(S\)) and biaxial (\(P\)) order parameters near a uniaxial-biaxial transition, we confirmed that the scattered intensity scales as \(I_{sc} \sim \frac{(\Delta \varepsilon)^2}{K} \frac{S^2}{S^2} \), \(\frac{P^2}{S^2}\), or \(\frac{P^2}{P^2}\) (or certain combinations) for an appropriately chosen scattering geometry.
The ratio of elastic constants to viscosities measured in the uniaxial nematic phase is about 100 times lower in the 4-ring tetrapode and about 1000 times lower in the 3-ring tetrapode than those of typical small molecule thermotropic nematics. This indicates much higher orientational viscosities in the tetrapodic mesogens compared to standard thermotropics, suggesting substantially hindered rotations due to tethering of the mesogenic groups and their interdigitation between neighboring tetrapodes. Additionally, orientational fluctuations are significantly slower in the 3-ring compound than in the 4-ring compound: the $P$ order parameter fluctuations are about 30 times slower and the director fluctuations are about 50 times slower. This indicates that orientational motion of mesogens is more significantly hindered in the tetrapode with smaller mesogenic cores. One unifying explanation for our results on the tetrapodes is the development of tilt of the mesogenic groups relative to the average average director in the uniaxial phase; such a phenomenon could promote both biaxiality and further hinder orientational fluctuations of the tetrapodes.

The viscoelastic coefficients measured in a uniformly aligned sample of a lyotropic chromonic nematic formed by a solution of cromolyn in water show significant anisotropies and interesting temperature dependences. In particular, the bend ($K_{33}$) and splay ($K_{11}$) elastic moduli are an order of magnitude higher than the twist modulus $K_{22}$. Only the twist modulus shows a temperature dependence similar to that expected for ordinary (small molecule thermotropic) nematic liquid crystals – i.e. $\frac{K_{22}}{(\Delta n)^2} = \frac{S^2}{S'^2}$ is constant with temperature in agreement with standard Landau-deGennes mean-field
theory. On the other hand, $K_{33}$ and $K_{11}$ in the chromonic both decrease with increasing temperature in the nematic phase. The ratio $\frac{K_{33}}{K_{11}}$ is similar to that of the simple thermotropic calamitic liquid crystals, however the ratios $\frac{K_{11}}{K_{22}}$ and $\frac{K_{33}}{K_{22}}$ are about an order of magnitude higher and are closer to those characteristic of hard-rod lyotropic polymer nematic liquid crystals. The ratio $\frac{K_{33}}{K_{11}}$ shows an anomalous increase in temperature, which we attributed to the shortening of the aggregates. This anomalous temperature behavior of $\frac{K_{33}}{K_{11}}$ is explained by considering chromonic aggregates as flexible rods with $K_{33}$ proportional to a persistence length, approximately constant over the temperatures studied, and $K_{11}$ proportional to the length of the aggregates. We then deduced the length of the aggregates using the prediction of Meyer for a self-assembled chromonematic, $K_{11} = \frac{k_B T L}{4d^3 d}$, for fully aligned rods, and by removing the order parameter dependence of $K_{11}$ (for less than fully aligned rods) using the temperature dependence of the birefringence or, alternatively, the observed scaling of $K_{22}$ with $S^2$. We found that the length of the aggregates varies from 41 nm at 21 °C to 18 nm at 27 °C in a 14 wt% cromolyn solution. We estimated the scission energy $E_a$ required for splitting an aggregate in two. $E_a$ varies from 9.6 $k_B T$ to 8.0 $k_B T$ for the same temperature range. The scission energy calculated from our experiments is in the same range with that of chromonic dyes and DNA oligomers.
We also determined the orientational viscosity coefficients associated with the splay, twist, and bend deformation. The bend viscosity coefficient is three orders of magnitude smaller than the splay and twist viscosity coefficients. The splay and twist viscosity coefficients are of the same order of magnitude as found in lyotropic polymer nematic liquid crystals and two orders of magnitude higher than simple thermotropic calamitic nematic liquid crystals. All the viscosity coefficients decrease on heating. In particular, \( \frac{\eta_{\text{twist}}}{\eta_{\text{bend}}} \) decreases dramatically, from 1600 at 21 °C to 450 at 27 °C, a fact which can be explained by the aggregates becoming shorter on average at higher temperature in the nematic phase. In addition, we observed a new hydrodynamic mode in a depolarized geometry in which bend fluctuations of the director are dominant. We attributed this to the lateral sliding of chromonic molecules within the stacked configuration of the individual aggregates (which corresponds to an effective “bending” of the aggregates). The size of the sliding element estimated from the Stokes-Einstein formula for diffusing spheres, and accounting for an additional drag due to the presence of neighboring elements in the stack (through a rough analogy to the sliding of rods near a planar confining boundary), gave a value comparable to the size of a single chromonic molecule.
APPENDIX A

The following codes are written in Mathematica compatible form. Copy and paste in Mathematica notebook and compile to get the result.

A.1 Simplification of Order Parameter Tensor in Matrix form with Biaxial Director on XY Plane

\[ n = \{0, 0, 1\}; m = \{\text{Cos}[\phi], \text{Sin}[\phi], 0\}; \]
\[ a = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}; "a is a unit tensor" \]

CellPrint[
  Cell[
    "Uniaxial Part of the Order Parameter"
  ]]
MatrixForm[S* (Transpose[{n}].{n} - \frac{a}{3})]

CellPrint[
  Cell["Biaxial Part of the Order Parameter"]]
MatrixForm[
  TrigReduce[
    P* (Transpose[{m}].{m} - 
      Transpose[{\text{Cross}[m, n]}].{\text{Cross}[m, n]})]]]
A.2 Matrix Simplification for Dielectric Constant Tensor with Biaxial Director along X-axis

\[
\begin{align*}
R_x &= \{(1, 0, 0), (0, 1, \delta \phi_x), (0, -\delta \phi_x, 1)\}; \\
R_y &= \{(1, 0, -\delta \phi_y), (0, 1, 0), (\delta \phi_y, 0, 1)\}; \\
R_z &= \{(1, \delta \phi_z, 0), (-\delta \phi_z, 1, 0), (0, 0, 1)\}; \\
A &= R_x.R_y.R_z / . \{\delta \phi_x \delta \phi_y \to 0, \delta \phi_y \delta \phi_z \to 0, \delta \phi_z \delta \phi_x \to 0\}; \\
B &= \text{Inverse}[R_x.R_y.R_z] / . \{\delta \phi_x \delta \phi_y \to 0, \delta \phi_y \delta \phi_z \to 0, \delta \phi_z \delta \phi_x \to 0, \\
&\quad \delta \phi_y^2 \to 0, \delta \phi_z^2 \to 0\}; \\
\delta \varepsilon &= \{\{\varepsilon_{\text{perp}} + \Delta \varepsilon^b \ (P_0 + \delta P), 0, 0\}, \\
&\quad \{0, \varepsilon_{\text{perp}} - \Delta \varepsilon^b \ (P_0 + \delta P), 0\}, \{0, 0, \varepsilon_{\text{par}}\}\}; \\
\text{Expand}[A.\delta \varepsilon.B] / . \\
&\{\delta \phi_x \delta \phi_y \to 0, \delta \phi_y \delta \phi_z \to 0, \delta \phi_z \delta \phi_x \to 0, \delta \phi_x^2 \to 0, \\
&\quad \delta \phi_y^2 \to 0, \delta \phi_z^2 \to 0\}
\end{align*}
\]

A.3 Optical Selection Rules for Biaxial Director along X-axis

\[
\begin{align*}
\delta \varepsilon_U &= \{\{\Delta \varepsilon^b * \delta P, -2 \Delta \varepsilon^b * P_0 * \delta m_y, (-\Delta \varepsilon^u + \Delta \varepsilon^b * P_0) * \delta n_x\}, \\
&\quad \{-2 * \Delta \varepsilon^b * P_0 * \delta m_y, -\Delta \varepsilon^b * \delta P, -(\Delta \varepsilon^u + \Delta \varepsilon^b * P_0) * \delta n_y\}, \\
&\quad \{-\Delta \varepsilon^u + \Delta \varepsilon^b * P_0\} * \delta n_x, -(\Delta \varepsilon^u + \Delta \varepsilon^b * P_0) * \delta n_y, 0\}\};
\end{align*}
\]
Planar Alignment (n on yz scattering Plane and m normal to the scattering plane: Geometry 1),

\[ \text{Background} \rightarrow \text{RGBColor}[1, 0, 0] \]

\[ iV = \{(1), (0), (0)\}; \]
\[ iH = \{(0), \{\sin(\theta_i)\}, \{\cos(\theta_i)\}\}; \]
\[ fV = \{1, 0, 0\}; \]
\[ fH = \{0, -\sin(\theta_s), \cos(\theta_s)\}; \]

\[ \text{CellPrint[Cell["VH Scattering", Background \rightarrow \text{RGBColor}[0, 1, 1]]]} \]
\[ \text{MatrixForm[fH . \delta e_U . iV]} \]

\[ \text{CellPrint[Cell["HV Scattering", Background \rightarrow \text{RGBColor}[0, 1, 1]]]} \]
\[ \text{MatrixForm[fV . \delta e_U . iH]} \]

\[ \text{CellPrint[Cell["HH Scattering", Background \rightarrow \text{RGBColor}[0, 1, 1]]]} \]
\[ \text{MatrixForm[fH . \delta e_U . iH]} \]

\[ \text{CellPrint[Cell["VV Scattering", Background \rightarrow \text{RGBColor}[0, 1, 1]]]} \]
\[ \text{MatrixForm[fV . \delta e_U . iV]} \]

Planar Alignment (n in xz Scattering Plane and m normal to the scattering plane: Geometry 2),

\[ \text{Background} \rightarrow \text{RGBColor}[1, 0, 0] \]

\[ iV = \{(0), (1), (0)\}; \]
\[ fV = \{0, 1, 0\}; \]
\[ iH = \{\{-\sin(\theta_i)\}, (0), \{\cos(\theta_i)\}\}; \]
\[ fH = \{\sin(\theta_s), 0, \cos(\theta_s)\}; \]

\[ \text{CellPrint[Cell["VH Scattering", Background \rightarrow \text{RGBColor}[0, 1, 1]]]} \]
\[ \text{MatrixForm[fH . \delta e_U . iV]} \]

\[ \text{CellPrint[Cell["HV Scattering", Background \rightarrow \text{RGBColor}[0, 1, 1]]]} \]
\[ \text{MatrixForm[fV . \delta e_U . iH]} \]

\[ \text{CellPrint[Cell["HH Scattering", Background \rightarrow \text{RGBColor}[0, 1, 1]]]} \]
\[ \text{MatrixForm[fH . \delta e_U . iH]} \]

\[ \text{CellPrint[Cell["VV Scattering", Background \rightarrow \text{RGBColor}[0, 1, 1]]]} \]
\[ \text{MatrixForm[fV . \delta e_U . iV]} \]
CellPrint[
  Cell["Planar Alignment(n normal to the xy scattering
  and m parallel to the substrate and on the scattering
  plane: Geometry 3) ", Background→ RGBColor[1, 0, 0]]
  iV = {{0}, {0}, {1}};
  iH = {{Cos[θ_i]}, {Sin[θ_i]}, {0}};
  fV = {0, 0, 1};
  fH = {Cos[θ_s], Sin[θ_s], 0};
  CellPrint[Cell["VH Scattering", Background→ RGBColor[0, 1, 1]]]
  MatrixForm[fH . δε_U . iV]
  CellPrint[Cell["HV Scattering", Background→ RGBColor[0, 1, 1]]]
  MatrixForm[fV . δε_U . iH]
  CellPrint[Cell["HH Scattering", Background→ RGBColor[0, 1, 1]]]
  MatrixForm[fH . δε_U . iH]
  CellPrint[Cell["VV Scattering", Background→ RGBColor[0, 1, 1]]]
  MatrixForm[fV . δε_U . iV]
]

CellPrint[
  Cell["Planar Alignment(n normal to the xy scattering
  and m normal to the substrate and on the scattering
  plane: Geometry 4) ", Background→ RGBColor[1, 0, 0]]
  iV = {{0}, {0}, {1}};
  iH = {{-Sin[θ_i]}, {-Cos[θ_i]}, {0}};
  fV = {0, 0, 1};
  fH = {Sin[θ_s], -Cos[θ_s], 0};
  CellPrint[Cell["VH Scattering", Background→ RGBColor[0, 1, 1]]]
  MatrixForm[fH . δε_U . iV]
  CellPrint[Cell["HV Scattering", Background→ RGBColor[0, 1, 1]]]
  MatrixForm[fV . δε_U . iH]
  CellPrint[Cell["HH Scattering", Background→ RGBColor[0, 1, 1]]]
  MatrixForm[fH . δε_U . iH]
  CellPrint[Cell["VV Scattering", Background→ RGBColor[0, 1, 1]]]
  MatrixForm[fV . δε_U . iV]
]
CellPrint[
  Cell["Homeotropic Alignment: n in zx scattering Plane
       and m parallel to the substrate and on the scattering
       plane: Geometry 5 \), Background -> RGBColor[1, 0, 0]]
  iV = {{0}, {-1}, {0}};
  iH = {{Cos[\[Theta]1]}, {0}, {-Sin[\[Theta]1]}};
  fV = {0, -1, 0};
  fH = {Cos[\[Theta]3], 0, Sin[\[Theta]3]};
CellPrint[Cell["VH Scattering", Background -> RGBColor[0, 1, 1]]]
MatrixForm[fH . \[Delta] \[Epsilon] U . iV]
CellPrint[Cell["HV Scattering", Background -> RGBColor[0, 1, 1]]]
MatrixForm[fV . \[Delta] \[Epsilon] U . iH]
CellPrint[Cell["HH Scattering", Background -> RGBColor[0, 1, 1]]]
MatrixForm[fH . \[Delta] \[Epsilon] U . iH]
CellPrint[Cell["VV Scattering", Background -> RGBColor[0, 1, 1]]]
MatrixForm[fV . \[Delta] \[Epsilon] U . iV]

CellPrint[
  Cell["Homeotropic Alignment: n in yz scattering Plane
       and m parallel to the substrate and normal to the
       scattering plane: Geometry 6 \), Background -> RGBColor[1, 0, 0]]
  iV = {{1}, {0}, {0}};
  iH = {{0}, {-Cos[\[Theta]1]}, {-Sin[\[Theta]3]}};
  fV = {1, 0, 0};
  fH = {0, Cos[\[Theta]3], Sin[\[Theta]3]};
CellPrint[Cell["VH Scattering", Background -> RGBColor[0, 1, 1]]]
MatrixForm[fH . \[Delta] \[Epsilon] U . iV]
CellPrint[Cell["HV Scattering", Background -> RGBColor[0, 1, 1]]]
MatrixForm[fV . \[Delta] \[Epsilon] U . iH]
CellPrint[Cell["HH Scattering", Background -> RGBColor[0, 1, 1]]]
MatrixForm[fH . \[Delta] \[Epsilon] U . iH]
CellPrint[Cell["VV Scattering", Background -> RGBColor[0, 1, 1]]]
MatrixForm[fV . \[Delta] \[Epsilon] U . iV]
A.4 Matrix Simplification for Dielectric Constant Tensor Fluctuation with Biaxial Director on XY Plane

\[ R_x = \{1, 0, 0\}, \{0, 1, \delta \phi_x\}, \{0, -\delta \phi_x, 1\}; \]
\[ R_y = \{1, 0, -\delta \phi_y\}, \{0, 1, 0\}, \{\delta \phi_y, 0, 1\}; \]
\[ R_z = \{1, \delta \phi_z, 0\}, \{-\delta \phi_z, 1, 0\}, \{0, 0, 1\}; \]
\[ A = R_x.R_y.R_z / \{ \delta \phi_x \delta \phi_y \to 0, \delta \phi_y \delta \phi_z \to 0, \delta \phi_z \delta \phi_x \to 0 \}; \]
\[ B = \text{Inverse}[R_x.R_z.R_x] / . \{ \delta \phi_x \delta \phi_y \to 0, \delta \phi_y \delta \phi_z \to 0, \delta \phi_z \delta \phi_x \to 0 \}; \]
\[ \delta \varepsilon = \{ \{ \varepsilon_{\text{perp}} + \Delta \varepsilon^b (P_0 + \delta P) \cos[2 \phi], \Delta \varepsilon^b (P_0 + \delta P) \sin[2 \phi], 0 \}, \]
\[ \{-\Delta \varepsilon^b (P_0 + \delta P) \sin[2 \phi], \varepsilon_{\text{perp}} - \Delta \varepsilon^b (P_0 + \delta P) \cos[2 \phi], 0 \}, \]
\[ \{0, 0, \varepsilon_{\text{par}}\} \}; \]
\[ \text{MatrixForm}[\text{Expand}[A.\delta \varepsilon.B]] / . \{ \delta \phi_x \delta \phi_y \to 0, \delta \phi_y \delta \phi_z \to 0, \delta \phi_z \delta \phi_x \to 0, \delta \phi_x^2 \to 0, \]
\[ \delta \phi_y^2 \to 0, \delta \phi_z^2 \to 0, \delta P \delta \phi_x \to 0, \delta P \delta \phi_y \to 0, \delta P \delta \phi_z \to 0 \} \]
A.5 Optical Selection Rules for Biaxial Director on XY Plane

\[ \delta \varepsilon_U = \left\{ \begin{align*}
\Delta e^b \cdot \delta P \cdot \cos(2\phi) &+ 2\Delta e^b \cdot P_0 \cdot \sin(2\phi) \cdot \delta m_{\perp}, \\
\Delta e^b \cdot \delta P \cdot \sin(2\phi) &- 2\Delta e^b \cdot P_0 \cdot \cos(2\phi) \cdot \delta n_x, \\
(-\Delta e^u + \Delta e^b \cdot P_0 \cdot \cos(2\phi)) \cdot \delta n_y &+ \Delta e^b \cdot P_0 \cdot \sin(2\phi) \cdot \delta n_y, \\
\{-\Delta e^b \cdot \delta P \cdot \sin(2\phi) &- 2\Delta e^b \cdot P_0 \cdot \cos(2\phi) \cdot \delta m_{\perp}, \\
-\Delta e^b \cdot \delta P \cdot \cos(2\phi), \\
-(\Delta e^u + \Delta e^b \cdot P_0 \cdot \cos(2\phi)) \cdot \delta n_y &+ \Delta e^b \cdot P_0 \cdot \sin(2\phi) \cdot \delta n_y, \\
\{-\Delta e^b \cdot P_0 \cdot \sin(2\phi) &+ \Delta e^u \cdot P_0 \cdot \cos(2\phi) \cdot \delta n_x, \\
\Delta e^b \cdot P_0 \cdot \sin(2\phi) \cdot \delta n_x &- (\Delta e^u + \Delta e^b \cdot P_0 \cdot \cos(2\phi)) \cdot \delta n_y, \\
0 \right\}; \\
iV = \{\{0\}, \{1\}, \{0\}\}; \\
fH = \{\sin[\theta_s], 0, \cos[\theta_s]\};
\]
iV = {{1}, {0}, {0}};
fH = {0, Cos[θs], Sin[θs]};
CellPrint[Cell["Homeotropic Alignment(H1 Geometry) ",
    Background -> RGBColor[1, 0, 0]]]
CellPrint[Cell["VH Scattering",
    Background -> RGBColor[0, 1, 1]]]
MatrixForm[fH . δεU . iV]
iV = {{1}, {0}, {0}};
fV = {1, 0, 0};
CellPrint[Cell["Homeotropic Alignment(H2 Geometry) ",
    Background -> RGBColor[1, 0, 0]]]
CellPrint[Cell["VV Scattering",
    Background -> RGBColor[0, 1, 1]]]
MatrixForm[fV . δεU . iV]