# TABLE OF CONTENTS

List of Figures ......................................................................................................................... vi
Acknowledgement ................................................................................................................... xii

CHAPTER

## CHAPTER 1: INTRODUCTION AND LIQUID CRYSTAL BASIC

1.1 Introduction .................................................................................................................... 1
1.2 Thermotropic and lyotropic liquid crystals ................................................................. 2
1.3 Phase diagram for Thermotropic liquid crystals ....................................................... 6
1.4 Nematic phase .............................................................................................................. 8
1.5 Smectic phase ............................................................................................................. 10
1.6 Elastic free energy density of a nematic--------------------------------------------- 17
1.7 Elastic free energy of a Smectic-A ----------------------------------------------- 19
1.8 Smectic liquid crystals films ................................................................. 22
1.9 Objective of this dissertation------------------------------------------------------ 27
1.10 References............................................................................................................. 30

## CHAPTER 2: DYNAMIC LIGHT SCATTERING AND OTHER

### EXPERIMENTAL DETAILS

2.1 Introduction .................................................................................................................. 32
2.2 Light Scattering Spectroscopy................................................................................. 34
2.3 Light scattering from liquid crystals...................................................................... 37
2.4 Photon correlation spectroscopy (PCS)................................................................. 40
2.5 Novel hardware for PCS: Subnanosecond Digital Electronic
CHAPTER 3: LIGHT SCATTERING FROM SURFACE FLUCTUATIONS
ON A SMECTIC FILMS

3.1 Light scattering from thermal corrugations of a fluid surface

3.2 Diffraction of light from a corrugated thin film bounded by identical Media

3.3 Smectic liquid crystal layer hydrodynamics

3.4 Elastic modes of a smectic-A film

3.5 Time correlation function for surface layer fluctuations of a smectic-A Film

3.6 Reference

CHAPTER 4: RESULT ON LAYER DYNAMICS OF “THIN” AND “THICK” SMECTIC –A FILMS OF 9CB AND 8CB

4.1 “Thin” film limit of smectic layer dynamics

4.2 Results for “thin” 8CB and 9CB smectic-A films: Time correlation data

4.3 Dispersion of the frequency and damping of layer fluctuations in 8CB
4.4 Origin of the additional, overdamped mode observed in the layer dynamics of “thin” films
4.5 Surface light scattering measurements on a “thick” smectic-A film of 9CB
4.6 Reference

CHAPTER 5: RESULTS ON LAYER DYNAMICS IN “THIN” SMECTIC-C AND HEXATIC-B FILMS

5.1 Light scattering from layer fluctuations in a “thin” smectic-C film
5.2 Light scattering from layer modes in a “thin” hexatic-B film
5.3 Reference

CHAPTER 6: SUMMARY AND CONCLUSION
LIST OF FIGURES

Fig.1.1 Schematic illustration of the solid, liquid crystal and liquid phases ---------------2
Fig.1.2 General structural template for calamitic (rod-like) liquid crystals------------------4
Fig.1.3 Typical example of thermotropic liquid crystals---------------------------------5
Fig.1.4 Classification of phase occurrences in thermotropic liquid crystals-------------7
Fig.1.5 Schematic illustration of phase sequence of a liquid crystal-------------------7
Fig.1.6 Schematic diagram of nematic liquid crystal and the direction of orientation-----8
Fig.1.7 Schematic diagram of chiral nematic liquid crystals---------------------------9
Fig. 1.8 Smectic-A phase showing director orientation and density distribution along the layer normal $z$. (Sinusoidal density wave is not accurately depicted on the left.)---------12
Fig.1.9 Structure of the smectic-C plane. $\theta$ is the polar (tilt) angle, $\varphi$ is the azimuthal angle, and $c$ is the in-plane projection of the molecular director $n$ (and is sometimes referred to as the $c$-director). -----------------------------------------------13
Fig.1.10 Chiral smectic structure and layer rotation to form helical a structure---------15
Fig.1.11 Illustration of $C_{2h}$ symmetry in achiral smectic C and $C_2$ symmetry in the chiral smectic phase---------------------------------------------------------------16
Fig.1.12 Typical splay, bend and twist deformation in liquid crystals-------------------18
Fig.1.13 Schematic picture of bending (undulation) and compression of smectic layers. $u(r)$ is the displacement from equilibrium position, and dashed lines represent the equilibrium position. $q_{\perp}$, $q_z$ are wavevector components of the distortions in the indicated directions. (The equilibrium layer normal corresponds to the $z$ axis).---------------------------19
Fig 1.14 Typical *smectic-A* and *smectic-C* freely suspended film structure.----------------------23

Fig.1.15 Layer distortion corresponding to the ansatz discussed in the text, for \( n = 0 \) and \( n = 1 \).---------------------------------------------------------------------------------------------------25

Fig.1.16 The bracketed term in the film elastic free energy (Eq.1.8) plotted as a function of film thickness for \( n = 0 \) and \( n = 1 \). Typical values of \( B \) (10\(^8\) erg/cm\(^3\)), \( \gamma \) (25 erg/cm\(^2\)), and \( K \) (10\(^{-6}\) erg/cm) were used, and \( q_0^2 \) was fixed at a typical optical value of 10\(^9\) cm\(^{-2}\).-26

Fig. 2.1 Light scattering from small scatter centre ---------------------------------------------36

Fig. 2.2 Light scattering geometry from freely suspended film-------------------------------39

Fig. 2.3 Experiment schematic---------------------------------------------------------------52

Fig. 2.4 (a) Picture showing microscopic hot stage mounted at the top of a goniometer. The green arrow represents incoming incident laser and the reflected beam is collected through the detector and the red line is a line from film normal. (b) Picture of the wiper blade on the substrate on copper block in which the thermistor is placed by drilling a hole. (c) Close look of microscopic hot stage when top surface is covered. The film hole is also seen partially---------------------------------------------------------------55

Fig. 2.5 Thermistor calibration curve---------------------------------------------------------56

Fig. 2.6 Structures and the transition temperatures liquid crystal compounds studied---58

Fig. 2.7 An arrangement for the on site thickness measurement and the left figure shows how the film is made.-----------------------------------------------59

Fig. 2.8 Calculation of the thickness of thin films------------------------------------------62

Fig. 2.9 The interference pattern produced by laser reflections from thick films of 8CB, photographed against a distant screen. The thin, narrowly spaced lines are the
interference produced by the front glass window and the thicker, widely spaced lines by liquid crystal films of thickness in the range 10 – 100 μm.

Fig. 3.1 Corrugation of a free surface at liquid (medium 2) – air (medium 1) interface.

Fig 3.2 Scattering from air-liquid boundary.

Fig 3.3 Smectic film with notation for the surface layer displacements.

Fig 3.4 Multiple reflections and refractions/transmissions and associated wave amplitudes for a fluid film.

Fig. 3.5 Elastic stresses on surface elements of a smectic film.

Fig. 3.6 Plot for $q_z s$ for dimensionless parameter $q_z l_d = \sqrt{2}$. The intersection of dashed line and solid line gives the value of $q(q_1, n)d / \pi$ for $n$ even and odd respectively.

Fig. 4.1 Measured time correlation functions of the intensity of light scattered from layer undulations in a 90 nm thick *SmecticA* film of 9CB ≈ 0.5°C below the nematic phase, for various values of the wave vector $q_x$ (in cm$^{-1}$) parallel to the layer.

Fig. 4.2 Analysis of the data for 90 nm 9CB film for $q_x = 14300$ cm$^{-1}$ from Fig. 4.1. The solid line is a fit to the hydrodynamic theory for a smectic-A film in the underdamped regime (Eq. (4.4)). The dashed line is the damping envelope.

Fig. 4.3 Analysis of the data for 90 nm 9CB film for $q_s = 32000$ cm$^{-1}$ from Fig. 4.1. The solid blue line is a fit to the standard hydrodynamic theory for a smectic-A film in the underdamped regime (Eq. (4.4)). The blue line is a fit incorporating an additional, overdamped mode (Eq. (4.5)).
Fig. 4.4 Measured time correlation functions of the intensity of light scattered from layer undulations in a 100 nm thick $Smectic_A$ film of $8CB \approx 7^0C$ below the nematic phase, for various values of the wave vector $q_z$ (in cm$^{-1}$) parallel to the layers.

Fig. 4.5 Intensity time correlation functions measured on a 230 nm thick $9CB$ film $\approx 0.5^0C$ below the $Smectic_A$ to nematic transition. The solid lines are fits to Eq. (4.5), the sum of a single underdamped undulation mode plus a purely overdamped mode, whose impact is clearly seen at intermediate $q_z$ where the oscillations ride on top of the additional mode.

Fig. 4.6 Intensity time correlation functions measured on a 240 nm thick $8CB$ film $\approx 7^0C$ below the $Smectic_A$ to nematic transition. The solid lines are fits to a single underdamped undulation mode plus a purely overdamped mode (Eq. (4.5)).

Fig. 4.7 Dispersion of the frequency and damping for the $n = 0$ layer fluctuation modes of a 90 nm $9CB$ $Smectic_A$ film. Solid lines are a fit based on Eqs. (4.6).

Fig. 4.8 Dispersion of the frequency and damping for the $n = 0$ layer fluctuation modes of a 100 nm $8CB$ $Smectic_A$ film. Solid lines are a fit based on Eqs. (4.6).

Fig. 4.9 Dispersion of the frequency and damping for the $n = 0$ layer fluctuation modes of a 230 nm $9CB$ $Smectic_A$ film. Solid lines are a fit based on Eqs. (4.6).

Fig. 4.10 Dispersion of the frequency and damping for the $n = 0$ layer fluctuation modes of a 240 nm $8CB$ $Smectic_A$ film. Solid lines are a fit based on Eqs. (4.6).

Fig. 4.11 Dispersion of the additional, overdamped mode from fits of the correlation data in Fig. 4.5 for the 230 nm $9CB$ film. Solid lines indicate a “hybrid” origin for this mode,
i.e., a combination of hydrodynamic and nonhydrodynamic modes, as discussed in the text. The data interpolates between these modes.

Fig. 4.12 Measured correlation functions for the 8CB 95nm film exposed to Propanol at different temperatures. Solid lines are the fit to the hydrodynamic theory discussed in Eq. (4.5).

Fig. 4.13 Dispersion of relaxation mode, amplitude of relaxation mode, surface tension and layer sliding viscosity of 95 nm 8CB film exposed to propanol at different temperatures.

Fig. 4.14 Measured correlation data and fits for the 9CB 110μm thick films. The solid lines are the fit to Eq. (4.10) of the text.

Fig. 4.15 The relaxation rates $\Gamma_0$ and $\Gamma_1$ for the fitted correlation data of the thick films and the solid line shows the fits for $\Gamma_0 = \frac{2\gamma}{\eta_3d}$ and $\Gamma_1 = \frac{B(\pi/d)^2}{\eta_3q_s^2}$ respectively.

Fig. 4.16 Amplitudes of compression mode and pure undulation with the increasing $q_s$.

Fig. 5.1 Intensity time correlation function measured on 270nm 85 film at different temperatures at $q_s = 6887cm^{-1}$. The solid lines are the fit to undulation mode plus additional overdamped mode discussed in Eq.(4.5).

Fig. 5.2 Dispersion of the frequency and damping rate for the underdamped mode and additional overdamped mode with temperature at $q_s = 6887cm^{-1}$. 
Fig. 5.3 Intensity time correlation function measured on 270nm 8S5 film. The solid lines are the fit to undulation mode plus additional overdamped mode discussed in Eq.(4.5)----------------------------------143

Fig. 5.4 Top panel is dispersion of the frequency and damping rate for the underdamped mode. Fit gives $\eta = 0.045$ g cm$^{-1}$ s$^{-1}$ and $\gamma = 27.61$ erg cm$^2$. Bottom panel shows damping rate for the additional overdamped mode. Fit gives $\eta = 0.015$ g cm$^{-1}$ s$^{-1}$ at T= 46.0$^0$C for a 8S5 film of thickness 270nm.------------------------------------------144

Fig. 5.5 Measured intensity time correlation function measured on a 55nm thin 64COOBC film at 64$^0$C. Solid line are the fit based on Eq.(4.4).------------------------146

Fig. 5.6 Top panel is dispersion of the frequency and damping rate for the underdamped mode. Fit gives $\eta = 0.02690$ g cm$^{-1}$ s$^{-1}$ and $\gamma = 27.61$ erg cm$^2$. Bottom panel shows damping rate for the additional overdamped mode. Fit gives $\eta = 0.02060$ g cm$^{-1}$ s$^{-1}$ for 55nm thin 64COOBC film at 64$^0$C ------------------------------------------147

Fig. 5.7 Intensity time correlation function measured for 55nm thin 64COOBC film at a fixed wave vector $q_x = 77215.12 cm^{-1}$. Solid line are the fit based on Eq.(4.4).----------149

Fig. 5.8 Temperature dependence of the frequency and damping rate for the overdamped mode and additional underdamped mode at a fixed wavevector ($q_x = 7712.12 cm^{-1}$)----150
ACKNOWLEDGEMENTS

I would like to express my deep and sincere gratitude to my supervisor, Professor Dr. Samuel Sprunt. His help, stimulating suggestions and encouragement helped me in all the time of research.

I would like to thank Dr. A. Baldwin for the novel sub-nanosecond correlator. I wish to express my sincere thanks to Prof. Ellman, Prof James Gleeson and Prof. Sateyendra Kumar for their help and encouragement. I would like to thank my dissertation graduate committee members Prof. David Allender, Prof. Elizabeth Mann, Prof. Alex Seed and Prof. Deng Ke Yang.

I thank all of my fellow graduate students who worked in my professor’s group, Anthony Adorjian, Strahinja Stojadinovic and Krishna Neupane. I would also like to thank Staff members of physics department for their help.

Finally, I am forever indebted to my parents for their understanding and endless patience and encouragement. I owe my loving thanks to my wife Uma Sharma and son Swarup Sharma.
CHAPTER 1

INTRODUCTION AND LIQUID CRYSTAL BASICS

1.1 Introduction

Liquid crystals (LCs), discovered more than 120 years ago by an Austrian botanist Friedrich Reinitzer, are a separate phase of matter, distinct from the liquid and crystalline phase, but exhibiting certain properties of each (e.g., flow of a liquid; partial orientational or positional order of the types characteristic of a crystal). For this reason, the LC phases are termed *mesophases* (meaning `in-between' phases) \(^1\). In conventional crystals, atoms or molecules are arranged on a regular three-dimensional lattice of points (or sites) in space, and the group of atoms or molecules associated with each site point in well-defined directions. The crystal thus possesses both positional (translational) and orientational order. In liquid, by contrast, the constituent molecules are spatially and orientationally disordered. Liquid crystals, typically composed of rod shaped molecules having a rigid cores with flexible hydrocarbon tails, exhibit at least one dimensional orientational order (i.e., alignment along a preferred direction) but at most only partial positional order Fig.1.1) \(^3\).
Fig.1.1 Schematic illustration of the solid, liquid crystal and liquid phases.
1.2 Thermotropic and lyotropic liquid crystals

Liquid crystals are classified into two major classes: Thermotropic and lyotropic liquid crystals. They are distinguished by the mechanisms that drive their self-organization. Thermotropic liquid crystals are those, in which the transitions to the liquid crystalline state are induced thermally, i.e., the liquid crystalline states are formed by raising the temperature of a solid and/or lowering the temperature of a liquid. Thermotropic liquid crystals can further be classified into two types: enantiotropic liquid crystals, which can be changed into the liquid crystal state from either lowering the temperature of a liquid or raising of the temperature of a solid, and monotropic liquid crystals, which possess the liquid crystal state only upon a unidirectional change in temperature cooling from the isotropic liquid. Long range orientational order exists in the liquid crystal state in spite of random distribution of the centers of mass of the molecules. Maier and Saupe suggested that in thermotropic liquid crystals, whose molecules are anisotropic, the dominant intermolecular interaction maintaining orientational order is the anisotropic dispersion force. And their model only accounts for orientational order\textsuperscript{4-6}. At the same time there is ordering of the centers of masses (positional ordering) in a lattice due to the intermolecular repulsive force, which is called a molecular packing interaction. Many theoretical works have been put forward to account for ordering (isotropic-nematic, nematic-smectic) taking into account whether attractive or repulsive potentials play the dominant role i.e., anisotropic dispersion force or molecular packing interaction or both\textsuperscript{7-11}. In general, the thermotropic mesophase can be understood by considering the anisotropic dispersion force between molecules and the molecular packing interaction\textsuperscript{12}. 
The general structure of a thermotropic liquid crystal is shown in Fig. 1.2. There are four principal structural components (Fig.1.2): Core unit, Linking group, Terminal group and Lateral group.

![Diagram of general structural template for calamitic (rod-like) liquid crystals](image)

- A, B - Core unit,
- X, Y, Z - Linking group,
- R, R’ - Terminal group,
- M, N - Lateral group

Fig.1.2 General structural template for calamitic (rod-like) liquid crystals

The rigidity required to produce molecular shape anisotropy is produced by a ring system in the core. In Fig.1.2, A and B denote core units joined by a linking group Y. The terminal substituents R, R’ are alkyl or alkoxy chains attached to the core via linking groups X, Z. The lateral substituents M and N may enhance properties such as dielectric anisotropy, and suppress phase transition temperatures. The structural template of Fig. 1.2 corresponds to rod-shaped molecules, which have an elongated, anisotropic geometry that, when close packed, allows for preferential alignment along one spatial direction. Some specific examples of thermotropic liquid crystal are shown in following diagram (Fig.1.3):
Fig. 1.3 Typical example of thermotropic liquid crystals

Thermotropic LC molecules such as those shown in Fig. 1.3 are typically 3 nm (3×10^{-7} cm) long and 0.5 nm across.
Lyotropic liquid crystals are those in which the transitions take place due to change in concentration of amphiphilic molecules in a solvent. Amphiphilic molecules usually consist of a polar head group attached to one or more non-polar chains and are often known as surfactants (surface active agents). When they are dissolved in an appropriate solvent they self-assemble so the polar (hydrophilic) heads protect the non-polar (hydrophobic) tails, producing small, essentially spherical aggregates (~ 5 nm in diameter) known as micelles at low surfactant concentration, and various LC phases at higher concentrations.

In this dissertation, I shall only be concerned with thermotropic LCs of relatively simple molecular types – primarily the cyanobiphenyls shown at the bottom of Fig. 1.3.

1.3 Phase diagram for thermotropic liquid crystals

Thermotropic LCs exhibit an amazingly rich variety of mesophases (Fig.1.5). Transitions between different phases shown in Fig. 1.4 are characterized by breaking of a specific rotational or translational symmetry. Fig. 1.5 shows the simplest physically occurring sequence that illustrates the types of symmetry breaking in the most elementary way.
Fig. 1.4 Classification of phase occurrences in thermotropic liquid crystals

Fig. 1.5 Schematic illustration of phase sequence of a liquid crystal
1.4 Nematic phase

The simplest liquid crystal phase is the nematic liquid crystal. The nematic liquid crystal phase is characterized by molecules that have no positional order but they tend to point in the same direction. In the following diagram, the molecules point vertically but are arranged with no particular positional (or center-of-mass) order.³

Fig. 1.6 Schematic diagram of nematic liquid crystal and the direction of orientation

In uniaxial nematic LCs, the axis of orientational order is characterized by a unit vector called the director \( \hat{n} \) (Fig.1.6). The degree of uniaxial order is defined by the orientational order parameter \( S \), which is the thermal average \( \left \langle \frac{3}{2} \cos^2 \theta - \frac{1}{2} \right \rangle \), where \( \theta \) is the angle between a molecule’s long axis and the director \( \hat{n} \). The nematic phase of typical rod-like thermotropics is uniaxial, that is, the orientational ordering takes place along only one direction in space (a single axis \( \hat{n} \)), with no long range ordering of
molecular axes in the plane perpendicular to $\hat{n}$. An important symmetry is that the properties of the nematic are invariant under director inversion ($\hat{n} \rightarrow -\hat{n}$).

Chiral nematic liquid crystals are nematics composed of molecules which differ from their mirror images (“handed” LC molecules). In this phase chiral packing induces a helical director configuration – typically one in which $\hat{n}$ rotates or twists along an orthogonal axis (Fig. 1.7).

![Fig. 1.7 Schematic diagram of chiral nematic liquid crystals](image)

The chiral nematic phase (sometimes called “cholesteric”) is characterized by the pitch $P$ of the helical rotation. The pitch is generally temperature dependent, and usually strongly near to a transition to a smectic phase.
1.5 Smectic phase

The word "smectic" is derived from the Greek word for soap. Molecules in this phase show a degree of translational order that is not present in the nematic phase. In the smectic phase molecules possess not only the general orientational order of nematics, but also they tend to position themselves in layers or planes. In the smectic-A and –C phases, the molecules behave as a liquid within the smectic planes and there is no elastic penalty for separate planes to flow past each other. The one-dimensional positional ordering in smectic-A or –C may be described in terms of a density wave of the centers of mass of the molecules,\(^1\),\(^3\),\(^14\)

\[
\rho(z) = \rho_0(1 + |\psi| \cos(2\pi z/a)) \tag{1.1}
\]

where \(z\) is the coordinate parallel to the layer normal, the average density of the fluid is \(\rho_0\), \(a\) is the distance between layers, and \(\psi\) denotes a scalar smectic order parameter. When \(|\psi|=0\), the density is uniform, and there is no layering. The smectic density wave in Eq. 1.1 is characterized by a single harmonic (wavenumber \(2\pi a\)). This in fact has a profound significance: Spatial correlations of the molecular positions decay algebraically at long distances (or separations) to zero, instead of to a finite constant as is characteristic of a conventional 3D crystalline solid. The smectic phase also exhibits anisotropy in the translational diffusion processes, with the exchange between the layers being slower than lateral diffusion in a layer. X-ray scattering experiments confirm the algebraic decay of the correlations, which also implies that thermal fluctuations destroy the smectic order.
over sufficiently long length scales (Landau-Peierls instability)\(^{15,16}\). However, in practice smectic layering is rather easily stabilized by confinement of samples between solid substrates or, in the case of freestanding smectic films, even by free interfaces.

In the simplest orthogonal smectic phase, the *smectic-A* phase, the director \( \mathbf{n} \) is perpendicular to the smectic plane (Fig. 1.8). In each layer, the molecular centers of mass are arranged randomly, and the molecules have liquid-like freedom of translation and of rotation about their long axis\(^3,17\). The *smectic-A* phase is optically uniaxial with the optical axis being normal to the layer plane. The direction of \(+z\) and \(-z\) (\(z\) corresponding to the layer normal) are totally equivalent.

![Fig. 1.8 Smectic-A phase showing director orientation and density distribution along the layer normal \(z\). (Sinusoidal density wave is not accurately depicted on the left.)](image-url)
Similarly, in a smectic-B phase, the molecules orient with the director perpendicular to the smectic plane, but the molecules are arranged such that the bonds they make with their nearest in-plane neighbors exhibit a sixfold (hexagonal) orientational order. In a smectic-C phase, depicted in Fig. 1.9, the molecular centers of mass are arranged as in the smectic-A (with no in-plane order), but the director is inclined at an average angle $\theta$ called the tilt angle$^{3, 18}$, which is measured from the smectic layer normal. The smectic-C is optically biaxial as opposed to the smectic-A plane, which is optically uniaxial.

![Diagram of smectic phases](image)

**Fig. 1.9** Structure of the smectic-C phase. $\theta$ is the polar (tilt) angle, $\varphi$ is the azimuthal angle, and $c$ is the in-plane projection of the molecular director $n$ (and is sometimes refereed to as the c-director).

In the smectic-A plane, the layer normal corresponds to an axis of continuous rotational symmetry. Any axis lying in the layers is an axis of twofold rotational
symmetry, and any plane containing the layer normal is a mirror plane. The smectic-A plane is optically uniaxial with \( T(2) \times D_\infty \) symmetry i.e., the appropriate point group is \( D_{\infty h} \), and the optical axis is parallel to the molecular long axis. The viscous stress associated with it is described by five independent viscosities. In a smectic-C phase, the rotational symmetry around the layer normal is broken. There is only a single in-plane twofold axis, and only a single mirror plane – the corresponding point group is \( C_{2h} \). This phase has \( T(2) \times C_{2h} \) symmetry which corresponds to the appearance of tilting of molecules with respect to layers. In this case, 20 different viscosity coefficients are needed to describe the phase.\(^{19}\)

The smectic-C phase typically forms on cooling from the smectic-A. Just above the transition, strong fluctuations of smectic-C order parameter – the tilt angle \( \theta \) – may be observed in the polarizing microscope.

There are also bond-orientationally ordered tilted smectic phases – the smectic-F and –I phases. Together with the untilted smectic-B, these phases are sometimes labeled “hexatic” – a term which refers to the sixfold coordination of bond angles, but avoids any connotation of positional order usually associated with the term “hexagonal”.

### Chiral smectics

If chirality is introduced into a LC molecule which possesses a smectic-C phase, the latter will convert into a chiral smectic-C phase, denoted by smectic-C* (Fig. 1.10). Analogous to the twisted structure of a chiral nematic, in the smectic-C* phase the c-
director rotates from layer to layer in a helicoidal fashion, with the “handedness” of the helix determined by the molecular chirality. The introduction of chirality in the smectic-\textit{C} phase causes a further reduction in symmetry. If molecules are chiral then there will be no mirror plane and center of inversion symmetry\textsuperscript{20}. The corresponding point group is $C_2$, with a single polar two fold axis parallel to the layer plane and normal to the tilt plane. This situation is explained in Fig. 1.11\textsuperscript{21}. 
Fig. 1.10 Chiral smectic structure and layer rotation to form a helical structure
This reduction of symmetry in *smectic-C* phase establishes a spontaneous polarization in the smectic layers. The broken mirror symmetry reflects hindered rotational symmetry of the transverse dipole moments of the molecules, and thus an alignment of dipoles along the $C_2$ axis, which corresponds to a ferroelectric phase. R. B. Meyer first predicted that the reduced symmetry of a chiral smectic-C phase will produce ferroelectricity, and later Strzelecki et al synthesized the first ferroelectric liquid crystal verifying Meyer’s prediction.
Smectics with in-plane positional order

*Smectics*-E, -G, -H, -J, and -K are in-plane positionally-ordered phases (plastic crystals) that occur at temperatures below the orthogonal (*smectic*-B) and tilted (*smectics*-F, -I) bond-orientationally ordered phases\(^{25}\).

1.6 Elastic free energy density of a nematic

In this dissertation, the role of thermally-induced fluctuations of the uniaxial director and smectic layers will be paramount. Such fluctuations are entropically favored, but incur a penalty in intermolecular interaction energy. On length scales much greater than the molecular spacing (e.g., visible optical length scales), and on time scales much slower than individual molecular motions, one may describe the free energy of the system as an elastic free energy, in terms of the director \(\mathbf{n}\) and/or smectic layer displacement from equilibrium \(u\) along the average layer normal, and one may treat the dynamics as a collective motion involving many molecules. We may then take \(\mathbf{n}\) and \(u\) to be continuous functions of space and time, \(\mathbf{n} = \mathbf{n}(x,y,z,t)\) and \(u = u(x,y,z,t)\).

In a nematic phase, the elastic free energy arises due to spatial gradients in \(\mathbf{n}\). Since the energy must be invariant under \(\mathbf{n} \rightarrow -\mathbf{n}\), the lowest order terms are of the form \((\nabla \mathbf{n})^2\). These terms are also restricted by the fact that \(\mathbf{n}\) is a unit vector. One then finds that the lowest order elastic free energy reduces to a combination of three terms corresponding to three basic elastic distortions of \(\mathbf{n}\) – splay, twist, and bend – which are depicted in Fig. 1.12.
For a non-chiral, uniaxial nematic phase, the elastic free energy density is given as

\[ f_N = \frac{1}{2} \left[ K_1 (\nabla \cdot n)^2 + K_2 (n \cdot \nabla \times n)^2 + K_3 (n \times \nabla \times n)^2 \right] \]  \hspace{1cm} (1.2)

Since \( f_N \) must always be positive for the stability of the uniformly aligned state, all the elastic constants \( K \) must be positive. The relative strength of the \( K \)'s depends on the type of liquid crystal. For typical calamitic nematics, all \( K \)'s are \( \sim 10^{-6} \) dyne, and typically one finds \( K_3 \geq K_1 > K_2 \). In orthogonal smectics (e.g., smectic-A), neither twist nor bend director distortions are compatible with a uniform layer spacing, and so one expects and observes a divergence of the corresponding elastic constants, \( K_2 \) and \( K_3 \), at the nematic-smectic-A transition. Director splay, on the other hand, corresponds to a simple
undulation of layers in a smectic-A that maintains uniform layer spacing. Thus the splay constant $K_1$ is essentially temperature independent across the nematic-smectic-A transition.$^{26}$

### 1.7 Elastic free energy of a Smectic-A

![Diagram of bending undulation and compression of smectic layers.](image)

**Fig. 1.13** Schematic picture of bending (undulation) and compression of smectic layers. $u(r)$ is the displacement from equilibrium position, and dashed lines represent the equilibrium position. $q_\perp$, $q_z$ are wavevector components of the distortions in the indicated directions. (The equilibrium layer normal corresponds to the $z$ axis).

In the continuum limit the smectic-A phase is equivalent to 2D layers, and these layers can slide with no elastic restoring force parallel to each other. Smectics-A are liquid-like in the plane of the layers and behave like solids to a force perpendicular to the layers. Therefore there are certain restrictions on the types of deformations that can be possible in smectics-A.
An undeformed smectic has parallel and equidistant layers. When small distortions are imposed (or thermally excited) on the smectic layers, the layers may get displaced and curved (Fig. 1.13). Let \( u(x, y, z) \) represent displacements along \( z \) of the layers (assumed to lie in the \( x-y \) plane in equilibrium). A layer at \( z_0 \) before displacement is now at

\[
z(x, y) = z_0 + u(x, y, z)
\]  

(1.3)

The first order derivatives of \( u \) parallel to the smectic layers, i.e., \( \frac{\partial u}{\partial x} \) and \( \frac{\partial u}{\partial y} \) correspond to the rigid rotation of the layers. Since the director \( \mathbf{n} \) is normal to the layers in smectic-A liquid crystals, we can write

\[
\begin{align*}
    n_x &= -\frac{\partial u}{\partial x}, \\
    n_y &= -\frac{\partial u}{\partial y}
\end{align*}
\]

and

\[
    n_z = 1 - \frac{1}{2} (\nabla \parallel u)^2
\]

(1.4)

to lowest order in the gradients, where \( (\nabla \parallel u) = \left\{ \begin{array}{l}
    \frac{\partial u}{\partial x} \\
    \frac{\partial u}{\partial y}
\end{array} \right\} \)  

Elastic distortions in a smectic-A liquid crystal can be described by two elastic constants, one for compression (\( B \)) and one for bending (\( K \)) of the layers. From Fig. 1.13, the former will depend on the first derivative of \( u \) on \( z \), and the latter on the layer curvature controlled by second derivatives of \( u \) with respect to \( x \) and \( y \). The elastic free energy density of a smectic-A is
The compression modulus $B$ has dimensions of $(\text{energy})/(\text{length})^3$ and typical magnitude $10^8 \text{ erg/cm}^3$ in calamitics, while the bending elastic constant $K$ has dimensions of energy/length and a typical value $10^{-6} \text{ erg/cm (dyne)}$. What about the contributions to $f_{SA}$ due to director distortions? From Eqs. 1.4 and 1.5, we see that the layer curvature is identical to director splay to lowest order – i.e., $\nabla \cdot n = \frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial y^2}$ – so splay is already included. As we have already noted, bend and twist director distortions are expelled from a defect-free smectic-A, so they are not included.

However, in the vicinity of a smectic-A to -C transition, one must introduce the director explicitly in order to describe director tilt $\theta$ away from the layer normal. The additional, lowest order contribution to the elastic free energy is $\frac{1}{2}D\theta^2$, where $D$ is a temperature dependent elastic constant with units of $(\text{energy})/(\text{length})^3$. In a Landau theory, with $\theta$ the smectic-C order parameter, the temperature dependence of $D$ near the smectic-A to -C transition is expected to be $D = D_0[(T - T^*)/T^*]$, where $T^*$ is the supercooling limit of the smectic-A phase. For small variations, one can express $\theta$ in terms of $n_x$, $n_y$, $\partial u/\partial x$, and $\partial u/\partial y$ as: $\theta^2 = (n_x + \frac{\partial u}{\partial x})^2 + (n_y + \frac{\partial u}{\partial y})^2$. The full elastic free energy density near $T^*$ is:

$$
\begin{align*}
\mathcal{F}_{SA} &= \frac{1}{2}B\left(\frac{\partial u}{\partial z}\right)^2 + K(\nabla^2 u)^2
\end{align*}
$$

(1.5)
\[ f_{\text{SAC}} = \frac{1}{2} \left[ B \left( \frac{\partial u}{\partial z} \right)^2 + D(\vec{n}_1 + \vec{V}_1 u)^2 + K(\nabla_1^2 u)^2 \right] \] (1.6)

1.8 Smectic liquid crystals films

Smectic liquid crystals form free-standing (FS) films similar to soap bubbles. Planar FS smectic films may be prepared using a thin blade to wipe smectic LC across a hole in a thin, rigid substrate, in a similar way to the suspension of a soap film over an open frame. Soap films are stabilized by the hydrophilic/hydrophobic anisotropy of a surfactant monolayer, while in the case of a thermotropic smectic LC, the line tension energy penalty associated with opening a hole substantially exceeds the interfacial energy saved. In planar free-standing smectic films, the layers are parallel to the film surface (Fig. 1.14), and the film thickness is quantized \( d = Na \) where \( N \) is number of layers and \( a \) is the layer spacing (~2.5 nm). These films can be made of well controllable size and high degree of uniformity, with thicknesses varying from two to over hundreds of layers. Therefore they are ideal systems to study the crossover from three dimensional to two-dimensional behavior, as well as the influence of the surfaces on the physical properties\(^{27,28}\).

The combination of smectic layering and surface tension at a film-air boundary leads to a smectic monodomain in FS films. Formation of defects such as layer dislocations are ultimately penalized by increased surface energy. The high degree of homogeneity in layering, confirmed by X-ray diffraction studies that reveal resolution limited reflections associated with the layering, makes FS films the sample geometry of choice for studying static and dynamic properties of smectics\(^{29}\).
The simplest continuum model for the surface energy of a smectic film involves one parameter, the surface tension $\gamma$ [dimensions: energy/(length)$^2$; typical magnitude: 25 erg/cm$^2$]. The free energy of a smectic-A film that includes the possibility of director tilt distortions is then,

$$
F_{\text{SmA film}} = \int dV \frac{1}{2} \left[ B \left( \frac{\partial u}{\partial z} \right)^2 + D(\vec{n}_\perp + \vec{\nabla}_\perp u)^2 + K(\nabla_u^2)^2 \right] + \int dA \frac{1}{2} \gamma \left[ (\nabla_u^2)^2 \right]_{z=-d/2} + (\nabla_u^2)^2 \Big|_{z=d/2} \right]
$$

(1.7)

where the integrals are over volume and surface area of the film, respectively. Now let us consider this free energy in terms of distortions in $u$, assuming layer displacements are locked to director distortions – i.e., $\vec{n}_\perp = -\vec{\nabla}_\perp u$ (to lowest order in the gradients) – and taking the ansatz $u = u_0 \cos q_0 x \cos(n\pi z / d)$, where $z$ is normal to the film, $d$ is the film
thickness, \( z = 0 \) corresponds to the mid plane of the film, and \( n \) is an integer, for a film of size \( L \) in the \( x \) direction. We also assume the boundary condition \( u(x = \pm L/2) = 0 \), which implies \( \cos(q_0 L/2) = 0 \). Plugging the ansatz into Eq. 1.7 and applying the boundary condition, we calculate:

\[
F_{\text{SAfilm}} = \frac{u_0^2 L^2}{8d} \left[ B(n\pi)^2 + 4\gamma q_0^2 d \cos^2(n\pi/2) + Kq_0^4 d^2 \right]
\]  

(1.8)

As shown in Figs. 1.15 and 1.16, this result reveals that for sufficiently thin films \((d \ll B/(\gamma q_0^2))\), the \( n = 0 \) distortion (simple undulation mode with no bulk compression, or “surface” mode) is the lowest energy excitation of the film, while in sufficiently thick films \((d \gg B/(\gamma q_0^2))\), the \( n = 1 \) distortion, involving bulk compression, is the lowest energy mode. Alternatively, for fixed \( d \), longer wavelength distortions (small \( q_0 \)) are dominated by surface tension, whereas short wavelength fluctuations (large \( q_0 \)) involve bulk compression.
Fig. 1.15 Layer distortion corresponding to the ansatz discussed in the text, for $n = 0$ and $n = 1$. 
Fig. 1.16 The bracketed term in the film elastic free energy (Eq. 1.8) plotted as a function of film thickness for $n = 0$ and $n = 1$. Typical values of $B \left(10^8 \text{erg/cm}^3\right)$, $\gamma \left(25 \text{erg/cm}^2\right)$, and $K \left(10^6 \text{erg/cm}\right)$ were used, and $q_0^2$ was fixed at a typical optical value of $10^9 \text{cm}^2$. 
1.9 Objective of this dissertation

The foregoing discussion indicates that by probing layer fluctuations of a smectic film one can expect to probe extremes of surface-dominated and bulk-dominated behavior as a function of film thickness. However, the problem is enriched – and made more complicated – by the fact that the dynamical response is governed by inertia and damping (dissipation) in addition to elasticity. The inertia is, of course, characterized by the mass density of the LC, while damping is parametrized by dynamical viscosities of the system (such as the viscosity associated with sliding smectic layers parallel to one another).

Dynamic light scattering (DLS) is a well established, powerful and essentially noninvasive probe of LC dynamics. Strong dynamic scattering from smectic films is produced either by dielectric fluctuations (e.g., fluctuations in the optic axis or director $\mathbf{n}$) or by thermal fluctuations of the film surface orientation (e.g., corrugations of the film surface). In general, the scattered light will contain a combination of discrete frequency-shifted components and a continuous band due simply to broadening of the incident frequency. In terms of collective fluctuations of $\mathbf{n}$ and $\mathbf{u}$ in smectics, the frequency-shifted light provides information primarily on the combined effect of inertia and elasticity (underdamped fluctuation modes), while the unshifted central band of scattering reflects predominantly damping and elastic properties (overdamped modes).

Most DLS studies have been confined to either frequency-domain measurements above $\sim$1 GHz, which probe sound waves in a limit where damping is a weak effect, or by photon correlation spectroscopy (PCS), performed in the time-domain below 10 MHz.
(i.e., for times $\geq 0.1\mu \text{sec}$) and usually designed to study purely overdamped fluctuations of the smectic layer orientation when inertia is negligible. The interesting crossover regime, where inertia, damping, and elastic forces all contribute significantly in the hydrodynamic description, has posed a long standing challenge to scattering experiments.

In this dissertation, we present experimental results on the dynamics of smectic films obtained by extending the PCS technique down to unprecedented subnanosecond resolution and thereby fully closing a historical gap between frequency and time domain scattering techniques. This allows us to determine, for optical scattering wavevectors $\sim 10^{-4}$-$10^{-5}$cm$^{-1}$, both the propagation frequency and damping rate for undulatory motion of thin free-standing smectic films (a few tens of molecular layers), as well as to probe the overdamped dynamics of bulk films (thousands of layers thick) over time scales never before accessible to PCS.

We will report results on films of standard thermotropic compounds in different smectic phases. We will compare our results from the extended PCS technique as a function of scattering vector with relevant hydrodynamic theory for smectic films, and determine values of such important parameters as the surface tension, layer compression modulus, layer sliding viscosity, layer bending modulus, and relaxation rate for director tilt fluctuations.

The body of this dissertation is organized as follows:

Chapter 2 will discuss the newly developed ultra fast correlation technique, the procedure of making thick and thin smectic films, the film thickness monitoring technique and other features of the experimental setup.
In chapter 3 we will review relevant theoretical background on light scattering from surface fluctuations of smectic films, and calculate (and relate to the scattering cross-section) the layer displacement correlation function for freely suspended smectic films with the aid of hydrodynamic theory. This will be used to analyze and interpret our experimental observations.

Chapter 4 will present measured light scattering correlation data and analysis from layer fluctuations in freely suspended liquid crystal films of standard cyanobiphenyl LCs in “thin” and “thick” film limit.

Chapter 5 will describe results obtained on layer fluctuations in thin hexatic B and crystal B phase films.

Chapter 6 will summarize our work and discuss the possible applications and advantages of our theoretical and experimental approach to future studies of smectic films.
1.10 Reference


Chapter 2

DYNAMIC LIGHT SCATTERING AND OTHER EXPERIMENTAL DETAILS

2.1 Introduction

The interaction of electromagnetic waves with matter is studied in light scattering experiments by measuring the intensity, angular distribution, polarization, frequency shift, and frequency broadening of scattered light. These measurements in turn give the information about the dynamic as well as the structural properties of system under study. In liquid crystals, due to strong molecular anisotropy, the light scattering due to thermal fluctuations at equilibrium is much more intense than from ordinary liquids\(^1\). The wavelength of visible light corresponds to fluctuation length scales on which the liquid crystal system can be described by continuum elastic theory and hydrodynamics. The theoretical understanding of hydrodynamics of both simple fluids and liquid crystals is well described by Martin, Parodi and Pershan\(^2\) and by Berne and Pecora\(^3\).

The hydrodynamics of a liquid or liquid crystal are described in terms of conserved properties\(^4\) of the system such as mass, energy, and momentum, as well as fluctuations in variables that arise from particular broken symmetries – e.g., the nematic director \(\mathbf{n}\) or smectic layer displacement \(u\). For a system undergoing thermal fluctuations from equilibrium, and if \(\delta\) represents the fluctuations, then we can write the equation of continuity for a general property \(A\) as
\[
\frac{\partial}{\partial t} \delta A(\mathbf{r}, t) + \nabla \cdot \delta \mathbf{J}_A(\mathbf{r}, t) = \delta \sigma_A(\mathbf{r}, t) \tag{2.1}
\]

where \(\mathbf{J}_A\) is a current density describing the transport of \(A\), and \(\sigma_A\) is a source if \(A\). The Fourier transform of the above equation is

\[
\frac{\partial}{\partial t} \delta A(\mathbf{q}, t) - i\mathbf{q} \cdot \delta \mathbf{J}_A(\mathbf{q}, t) = \delta \sigma_A(\mathbf{q}, t) \tag{2.2}
\]

Since \(A\) is a conserved quantity therefore \(\delta \sigma_A(\mathbf{q}, t) \equiv 0\), hence,

\[
\frac{\partial}{\partial t} \delta A(\mathbf{q}, t) = i\mathbf{q} \cdot \delta \mathbf{J}_A(\mathbf{q}, t) \tag{2.3}
\]

This suggests as \(\mathbf{q} \to 0\) also \(\frac{\partial}{\partial t} \delta A(\mathbf{q}, t) \to 0\). The limit \(\mathbf{q} \to 0\) is called the long wavelength limit since \(|\mathbf{q}| \sim \lambda^{-1}\). This means that the frequency \(\omega(\mathbf{q})\) of fluctuations in the conserved densities vanishes, i.e., \(\omega(\mathbf{q}) \to 0\) as \(\mathbf{q} \to 0\) for a conserved variable. Any fluctuation with this property is called a hydrodynamic mode. The frequency can have both a real part (corresponding to a propagating mode) and an imaginary part (corresponding to damping)\(^5,6\). The inverse of the latter is the fluctuation lifetime, which grows to infinity as \(\mathbf{q} \to 0\). Additional fluctuating variables that are “long lived” as \(\mathbf{q} \to 0\) are those arising from spontaneous breaking of symmetry. Such fluctuation modes, called Goldstone modes, tend to restore the broken symmetry.

Consider, for example, the transition from an isotropic liquid to nematic liquid crystal. The isotropic fluid phase has five conserved variable modes – density, energy, and three components of momentum – but full translational and rotational symmetry. The nematic phase, however, is an orientationally anisotropic phase where the molecules
align along the direction of the director \( \hat{n}(\vec{r}) \). The director describes a broken orientational symmetry. From Goldstone’s theorem, we expect two new variables with hydrodynamic behavior to describe director rotations about two axes normal to the average \( \mathbf{n} \) that tend to restore the full rotational symmetry of the isotropic phase. These two symmetry-restoring modes plus the five conserved variable modes of the isotropic fluid add up to seven hydrodynamic modes in nematic liquid crystals. A detailed hydrodynamic analysis for the nematic phase leads to the following normal modes: two propagating, longitudinal sound waves, and five diffusive (non-propagating) ones representing thermal conduction, two transverse shear waves and two transverse orientational order waves.

The Goldstone mode of a smectic-A phase is described by the displacement \( u \) of smectic layers from equilibrium. When the layers are formed, below a nematic to smectic phase transition, there are layer undulating fluctuations that tend to alter the layered structure in order to restore nematic random positional order.

### 2.2 Light scattering spectroscopy

Light is an oscillating electromagnetic field and when monochromatic light interacts with matter it induces an electric dipole within each constituent atom, which oscillates at the frequency of the incident light and acts as a secondary source of electromagnetic radiation. There will be interference between the radiation emitted from individual atoms or molecules of a system separated by a vector, \( \mathbf{r} \). The net effect of this interference (after summation over the illuminated volume of the system) results in
scattering over various angles away from the direction of propagation of the incident light. The intensity of scattered light ultimately depends on the magnitude of the dipole induced in the constituent atoms or molecules.

Light scattering is classified into two classes:

**Inelastic Scattering:** When a photon falls on a molecule, inelastic scattering may occur, either by transfer of energy from the photon to the molecule (resulting in lower frequency secondary or scattered photons) or the reverse (resulting in higher frequency scattered photons). These energy changes are associated with the translational, rotational, vibrational, and electronic degrees of freedom of the molecule. The frequency spectrum of the scattered light will give the resonance at the frequencies corresponding to specific transitions, described by quantum mechanics, among these degrees of freedom. This type of scattering is *Raman scattering*. Usually Raman scattering is used in the study of rotational and vibrational energy spectra of the molecules, or lattice vibrations in crystalline solids.

**Quasi-elastic / Elastic scattering:** In quasi-elastic scattering the frequency of the scattered light is broadened by the finite lifetime of thermal fluctuations in the medium that scatter light. The center frequency of scattered light is unaltered; this type of scattering is called Rayleigh scattering. It may be accurately described by classical scattering theory (classical electromagnetic theory). Pure elastic scattering is the “ideal” or limiting case where the scattered light has the same frequency as the incident light, and there is no broadening imposed by damping effects (friction) on fluctuations in the medium.
The optical behavior of a medium is described by the dielectric constants associated with it. Fluctuations in dielectric behavior are produced by the fact that the molecules are constantly vibrating, rotating and translating in the medium. The dielectric constant, at any time at any point in the medium, depend on local averages of the positions and orientations of the molecules.

Important parameters describing light scattering from a small scattering centre are schematically shown in Fig.2.1.

![Fig. 2.1 Light scattering from small scatter centre](image)

The plane containing the incident light wavevector \( (\vec{k}_i) \) and the wavevector \( (\vec{k}_s) \) for a particular direction of the scattering define the scattering plane and hence the scattering angle \( \theta \). In quasi-elastic scattering, the center frequency of the incident and scattered light is the same, i.e., \( \omega_i = \omega_s \), and the incident and scattered wave vectors have equal
amplitude, i.e. $|\vec{k}_i|^2 = |\vec{k}_s|^2$. Then the resulting $\vec{q}$ vector – or wavevector transfer – is given as

$$\vec{q} = \vec{k}_s - \vec{k}_i$$

$$|\vec{q}|^2 = |\vec{k}_s - \vec{k}_i|^2 = |\vec{k}_s|^2 + |\vec{k}_i|^2 - 2\vec{k}_s \cdot \vec{k}_i$$

$$= 2k_s^2(1 - \cos \theta)$$

which gives

$$|\vec{q}| = \frac{4\pi}{\lambda} \sin(\frac{\theta}{2})$$

(2.5)

where $k_i = 2\pi / \lambda$. Here $\lambda$ is the wavelength of light in the scattering medium, $\lambda = \lambda_0/n$, where $n$ is the refractive index of the medium and $\lambda_0$ is the vacuum wavelength.

### 2.3 Light scattering from liquid crystals

Due to their optical anisotropy (a consequence of orientational order), liquid crystals are generally strong scatterers of light. In fact, the anisotropic dielectric properties are simply related to the orientational order parameter, which due to symmetry under inversion of the optic axis is a traceless second rank tensor $Q_{\alpha\beta}$

$$\varepsilon_{\alpha\beta} = \varepsilon + \frac{2}{3} \Delta \varepsilon \, Q_{\alpha\beta}$$

(2.6)

where, for a uniaxial medium, $\varepsilon = \frac{2}{3} \varepsilon_\perp + \frac{1}{3} \varepsilon_\parallel$, $\Delta \varepsilon = \varepsilon_\parallel - \varepsilon_\perp$, and $\varepsilon_\perp, \varepsilon_\parallel$ are the saturated principal values of $\varepsilon_{\alpha\beta}$ – or the dielectric constants corresponding, respectively, to light polarized along the optic axis (axis of orientational order) and perpendicular to it. In the uniaxial case, $Q_{\alpha\beta} = \frac{3}{2} S(n_\alpha n_\beta - \frac{1}{3})$, where $n_\alpha$ are the components of the director taken in
some arbitrary choice of coordinate system, and $S$ is the scalar order parameter specifying
the magnitude of the orientational order. Then one may obtain:

$$\varepsilon_{\alpha\beta} = \varepsilon_{\perp} \delta_{\alpha\beta} + \Delta \varepsilon S n_\alpha n_\beta$$ (2.7)

This expression reveals that the fluctuations in $S$ (order parameter fluctuations) or
$n$ (director fluctuations) may be responsible for dynamic light scattering from ordered
liquid crystal phases. Writing $S = S_0 + \delta S$, $n = n_0 + \delta n$, where the subscripts “0” indicate
equilibrium values, “$\delta$” represents a fluctuation, and $n_0 \cdot \delta n = 0$ to lowest order in $\delta n$
(since $|n| = |n_0| = 1 + \delta n^2$), one may isolate the lowest order fluctuating part of $\varepsilon_{\alpha\beta}$ as:

$$\delta \varepsilon_{\alpha\beta} = \Delta \varepsilon \delta S n_0^2 \delta_{\alpha\beta} + \Delta \varepsilon S_0 (n_0\alpha \delta n_\beta + n_0\beta \delta n_\alpha)$$ (2.8)

In a single scattering process, the scattered electric field is related to the incident field
by $E_s^i \propto \delta \varepsilon_{\alpha\beta} E_\beta^i$, where (as usual) the labels $i, s$ denote incident and scattered. Thus, the
scattering from bulk director fluctuations depends crucially on the quantity $s_\alpha \delta \varepsilon_{\alpha\beta} \delta n_\beta$, where $i$ and $s$ are the polarizations of the incident and scattered light.

Another strong source of scattering from liquid crystals can arise from the
interfaces the sample makes with its surroundings. In a conventional liquid crystal sample
cell, the liquid crystal director is “clamped” to the surfaces of rigid, parallel substrates
(typically treated with different types of alignment layers). In this case, the interfaces
simply produce a specular reflection (no dynamic scattering). However, in a free-standing
liquid crystal film, the “soft” interface can fluctuate significantly (in thin films the
fluctuation amplitude is predominantly controlled by surface tension), leading to a spatio-temporal modulation of the reflectivity, and to light scattering at off specular angles. Fig. 2.2 illustrates such a situation for a smectic film. The scattering is reasonably strong because of the fairly large film reflectivity (the refractive index contrast between the film and air being typically 1.5-1.7 to 1.0). One can analyze the intensity of the scattering in terms of the amplitude of fluctuations of the surface normal, which can be expressed in terms of an angular deviation $\theta$ from the equilibrium normal (corresponding to a flat surface – see Fig. 2.2). For small layer displacements $u$, the angle $\theta$ may be expressed as

$$\theta(\hat{r}, t) = -\hat{q} \cdot \hat{V}_\perp u(\hat{r}, t)$$

(2.9)

where $\hat{r}$ spans the (equilibrium) plane of the film, the gradient is taken in this plane, and $\hat{q}$ is the in-plane direction along which $u$ varies.

The general combination of light scattering from bulk dielectric and surface fluctuations involves a rather complicated analysis. Since our main interest in the following chapters will be on scattering from surface motion of smectic films (and the consequent coupling to $u(\hat{r}, t)$), we chose a particular scattering geometry for which bulk
Fig. 2.2 Light scattering geometry from freely suspended film. $k_i, k_r, k_s$ are the incident, specular reflected, and scattering wavevectors, respectively. The light polarization is out of the page, as indicated. (Coordinate system on the lower left is used for an argument, below, in the text.)
scattering from $\delta \varepsilon_{\alpha\beta}$ is negligible. Using the coordinates indicated in the Fig. 2.2, we selected the scattering vector $\vec{q}$ to lie in the $x$-$z$ plane, so that for a smectic-$A$, hexatic-$B$, or crystal-$B$ phase with the average director along the layer normal ($z$ axis), we have $\vec{n}_0 = (0,0,1)$. We then set both polarizer and analyzer parallel to the $y$ axis, so that from Eq. 2.8, the component of bulk scattering selected is $\delta \varepsilon_{yy}$, which vanishes since $n_{0y} = 0$. This geometry corresponds to polarized light scattering, or in the language of an optically isotropic medium, “ordinary-ordinary” scattering, since the polarizations are both “ordinary” ($\varepsilon = \varepsilon_\perp$). In this case, there is no significant contribution from bulk dielectric scattering.

The dominant contribution to the scattering collected in our experiment, coming from surface fluctuations of a smectic film, will be calculated at the beginning of the next chapter.

2.4 Photon correlation spectroscopy (PCS)

In typical dynamic light scattering experiments, scattered light is detected by converting the energy of light quanta (photons) into kinetic energy of photoelectrons, and hence into electric current pulses, via a photomultiplier tube (or other suitable type of photodetector). The most that can be measured is the record of photon arrival times, limited on the short end by the time resolution associated with the combination of detector and pulse processing electronics, and on the long end by the data acquisition time. In photon correlation spectroscopy, one processes electronically the photon record (either in terms of differences in single photon arrival times or in terms of photons
counted in various arrays of different length intervals) in order to construct the time correlation function of the scattered intensity, defined as

\[
G^{(2)}(\tau) \equiv \langle I_s(0)I_s(\tau) \rangle \equiv \frac{1}{T_\infty} \int_0^{T_\infty} I_s(t)I_s(t+\tau)dt
\]  

(2.10)

where \( \tau \) is a time delay associated with the correlation between the state of the system that scatters light intensity \( I(t) \) at time \( t \) with that scattering \( I(t+\tau) \) at time \( t+\tau \), and \( T_\infty \) is the duration time of the experiment. (As seen below, the scattered field correlation function is actually the quantity of prime interest; but this can only be obtained through intensity correlations. It cannot be measured directly because the photodetectors do not sense the phase of the electric field.) If the scattering is collected at some well defined scattering vector \( q \), then \( G^{(2)}(\tau) \) gives information on the amplitude, frequency, and lifetime of collective fluctuations of the system with wavevector \( q \) (or wavelength \( 2\pi/q \)). We shall discuss this connection in detail for smectic layer fluctuations in the next chapter. In the following, we confine ourselves to some important general comments.

\( G^{(2)}(\tau) \) measured for a specific \( q \) may be related to the relevant fluctuation spectrum of the system under study in two steps, subject to rather general assumptions. In the first step, one assumes that the statistics governing the random process of the thermal fluctuations of the system are stationary in time – this is typically true of a system in thermodynamic equilibrium. In this case, the time average in Eq. 2.10 is equivalent to a statistical ensemble average, and the angular brackets can be taken as an ensemble (thermodynamic) average.
The volume illuminated by incident beam is called “scattering volume” and it does not have sharp boundaries; it is the region with in the sample where majority of single scattering occurs. The number of molecules in this scattering volume will be larger than the number of molecules that falls on the narrowly focused beam. The intensity fluctuation associated with fluctuating molecules in this narrowly focused region is detected and correlated at any time. In the second step, we assume that the illuminated volume of the system is much larger than the volume over which the fluctuations are correlated at any instant in time. Then the Central Limit Theorem of probability theory applies, and the scattered field at any \( q \) can be considered a Gaussian Random Process (i.e., characterized by a Gaussian probability distribution of zero mean). Under such circumstances, and using \( I_s(q, \tau) = E_s^*(q, \tau)E_s(q, \tau) \), the intensity-intensity correlation function can be expressed in terms of the field-field correlation function as

\[
G^{(2)}(\tau) = \left\langle E_s^*(q, 0)E_s(q, \tau) \right\rangle^2 + \left\langle |E_s(q)|^2 \right\rangle^2
\]

(2.11)

or

\[
G^{(2)}(q, \tau) = \left\langle I_s(q) \right\rangle^2 (1 + |g^{(1)}(q, \tau)|^2)
\]

(2.12)

where

\[
g^{(1)}(q, \tau) = \frac{\left\langle E_s^*(q, 0)E_s(q, \tau) \right\rangle}{\left\langle |E_s(q)|^2 \right\rangle}
\]

(2.13)

and \( \left\langle I_s(q) \right\rangle \) is the average intensity of light collected at wavevector \( q \). A normalized form of \( G^{(2)} \) may be defined by
Eq. 2.14 is the Siegert relation.

In “factoring” the intensity-intensity correlation in Eq. 3.11, we also assumed the scattered light collected over the detection aperture to be spatially coherent. For typical lasers used in dynamic light scattering, the incident light is coherent over length scales far greater than the size of the illuminated volume of the sample. Spatial incoherence then mainly arises from choosing too large a detection solid angle, and it reduces the first term in Eq. 2.11 relative to the second when one integrates over both the sample volume and solid angle to obtain the net $E_s$ that contributes at a particular scattering vector. This reduction can be taken into account by rewriting Eq. 2.14 as

$$g^{(2)}(\tilde{q}, \tau) = \frac{G^{(2)}(\tilde{q}, \tau)}{\langle I_s(\tilde{q}) \rangle} = 1 + |g^{(1)}(\tilde{q}, \tau)|^2$$

(2.14)

where $\beta$ is the “coherence” factor; $\beta \sim 1$ for spatially coherent detection and $\beta \to 0$ in the limit of a mixture of scattered light.

Eqs. (2.11)-(2.15) apply to scattering purely due to thermal fluctuations, the so-called “homodyne” limit in photon correlation spectroscopy. Additional contributions from sources of scattering unrelated to sample fluctuations – e.g, “static” light from immobile defects or sample cell inhomogeneities, or stray unscattered laser light – modify the form of Eq. (2.15) and also reduce the signal term relative to the background. In the extreme case where substantial unscattered laser light is deliberately introduced onto the photodetector (the “heterodyne” limit), one can derive a simple replacement for Eq. 2.15 by replacing $E_s(\tilde{q}, \tau)$ with $E_s(\tilde{q}, \tau) + E_l$ and $I_s(\tilde{q}, \tau)$ with $|E_s(\tilde{q}, \tau) + E_l|^2$, 

$$g^{(2)}(\tilde{q}, \tau) = \frac{G^{(2)}(\tilde{q}, \tau)}{\langle I_s(\tilde{q}) \rangle} = 1 + |g^{(1)}(\tilde{q}, \tau)|^2$$

(2.15)
where $E_L$ is the field contributed by unscattered light and $E_L \gg E_s$. Going through the steps leading from Eq. 2.10 to 2.15 in this case gives,

$$g^{(2)}(q, \tau) = 1 + \beta^{1/2} \frac{\langle I_s(q) \rangle}{I_L} g^{(1)}(q, \tau)$$

(2.16)

where $I_L = E_L^2$. Although in the heterodyne case the relation between $g^{(2)}$ and $\langle E_s^*(q, 0) E_s(q, \tau) \rangle$ is simpler (i.e., linear), the signal to background is significantly reduced for $E_L \gg E_s$. In our experiments on smectic films, we focused on the homodyne limit in order to obtain the best signal statistics for a given experiment duration.

Homo- or heterodyne intensity correlation measurements of the light scattered from a fixed illuminated volume can be performed in two modes: auto-correlation and cross-correlation. In auto-correlation, one photodetector is used, and the collected scattered light is correlated with itself in time. In cross-correlation (or, more properly, pseudo-cross-correlation if a single illuminated volume is used), the scattered light is divided into equally intense components, which are fed to two separate photodetectors, whose outputs are cross-correlated in time.

Cross-correlation has key advantages for performing PCS experiments at short delay times. The performance of single photomultiplier tubes in auto-correlation 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 tubes. The typical resolving time (commonly 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; these typically range from \(\sim 50\) nanosec to \(\sim 1\) microsec. 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. Cross-correlation was exclusively employed in our studies of smectic films.

2.5 Novel hardware for PCS: Subnanosecond Digital Electronic Correlator

A correlator is an electronic device that computes the time correlation function of one or two input electrical signals. In PCS, these signals are trains of electrical pulses; the pulses are typically the output from an amplifier/discriminator circuit that processes the raw signal from a photodetector into regular shaped pulses at conventional logic levels.

In the experiments presented in this dissertation, we used two different correlators designed and built by Dr. A. Baldwin of Kent State University for the express purpose of extending PCS measurements down to the subnanosecond regime. The first one is a nanosecond digital correlator, which was utilized to measure the time correlation function of the scattered intensity down to a resolution of 1 nanosecond. The second correlator is a redesigned and improved version of the first with an ultimate resolution of 60 picosec. One might ask why subnanosecond PCS would be useful generally, and what is its particular value for studies of smectic layer fluctuations in thin films. Subnanosecond PCS fills a historical gap between frequency-domain light scattering techniques based on optical interferometry, which becomes extremely challenging for frequencies less than
~500 MHz, and traditional, commercially available time-domain PCS systems, which are effective for frequencies up to ~10 MHz. In the particular case of smectic films, as we will see in the next Chapter, the frequency of propagating modes associated with surface or bulk layer motion in a film is \( \omega \sim \sqrt{\frac{2\sigma}{\rho d}} q_\perp \sim 10-100\) MHz or \( \omega \sim \sqrt{\frac{B}{\rho d}} \pi \sim 100\) MHz, and the relaxation rate due to damping is \( \Gamma \sim \frac{\eta}{\rho} q_\perp^2 \sim 100\) MHz. (Here \( \sigma, \rho, B, \eta, d, \) and \( q_\perp \) are typical values of, respectively, film surface tension, mass density, layer compression modulus, layer sliding viscosity, film thickness, and optical scattering vector.) Accurate time-domain measurements require a minimum delay time at least 10 times shorter than these time scales, and thus clearly motivate the development of a very fast correlator.

Both correlators constructed for our studies are based on commercially available time-digitizing integrated circuits that encode the arrival times of incoming pulses, limited by a specified minimum resolution and by a maximum overall time span – the latter is typically an 8 to 16 bit binary number times the minimum resolution. In the nanosecond correlator, two LeCroy model MTD135 time digitizers record arrival times at a resolution of either 0.5 or 1 nanosec up to either ~16 or 33 microsec (or more precisely 32768 times the resolution). Acquiring many separate arrival time records of this length in a single scattering experiment, one can build a histogram and calculate either two auto-correlations or a single cross-correlation. To extend the correlations to longer times than 16 or 33 microsec, hardware was added to take the same incoming pulse streams
processed by the digitizers and perform a “traditional” calculation of the intensity
correlation function, using pulse counters, shift registers, and multipliers. This method is
actually more computationally efficient than building arrival time histograms, when delay
times exceed ~1 microsec. The “hybrid” hardware architecture gives complete correlation
functions consisting of 32768 0.5/1 nanosecond channels (which are normally rebinned in
software to a more manageable size – e.g., 10 channels for each decade in time), plus 128
contiguous channels at each of the following delays: 1, 10, 100 microsec; 1, 10, 100
millisecond; 1, 10 sec. Data from the “nano”-correlator is processed by a 9-unit PMP8A DSP
board running inside a Pentium PC.

The “pico”-correlator uses improved time-digitizers (Acam Gmbh, model TDC-
F1) to achieve an order of magnitude higher time resolution, switchable between 60 and
120 picosec. An upgraded PC controls the correlator and processes the data, without need
for a DSP board. The full channel layout on the “pico”-correlator is 204800 62.5 picosec
or 102800 125 picosec channels in the “fast” section that utilizes the time-digitizers (these
channels are typically rebinned to a more manageable number), plus 128 channels at each
of the same delays used in the “nano”-correlator. Note that the resolution of the our
correlator is 125 or 62.5 picosecond even though the time to digital converter chips have
resolution of 120 or 60 picoseconds respectively. The clocking of the chip must be
selected properly to set channels of desired resolutions. The resolution is defined as

$$\text{res} = \frac{T_{\text{ref}} \times 2^r_{\text{refclk}}}{152 \times D_{\text{adc}}}$$

(2.17)
$D_{hsdv}$ is the high resolution divider setting, $refclk$ is reference clock divider and $T_{ref}$ is the external clock period in nanoseconds. The defined range of the external clock is 1 to 40 MHz. The calculation shows that, for 8 measuring channels, the TDC F1 chip clock should be $T_{ref} = 38 \text{ ns (} f_{freq} = 26.3158 \text{ MHz)}$ which suggests optimum resolution $(1/8)\text{ns i.e. 125 picosecond.}$ Similarly in high resolution mode, 4 measuring channels, it will be $(1/16)\text{ ns i.e., 62.5 picosecond resolution.}$

Powerful but user friendly software controls the operation of the correlators, manages data acquisition, updates the display of the full correlation function at 1 sec intervals, and saves data to disk. The software also contains extensive diagnostics to monitor proper functioning of the correlators, photodetectors, and associated electronics as a system. A software interface for National Instruments LabVIEW was created to allow incorporation of the correlators into automated experiments that include separate instruments to control and monitor other experimental parameters (temperature, laser power, incident and scattering angles, etc).

The unprecedented time resolution of both correlators would be wasted if the amplifier/discriminator circuits conditioning the raw output from the photodetectors introduced distortion or ringing on the pulse trains on time scales significantly greater than the time-digitizer resolution, or if the pulse rise time of the photodetectors was much longer than this resolution. The photodetectors were selected for an optimal combination of performance, reliability, and price. We used two Hamamatsu model HC120-08\textsuperscript{11} single photon counting photomultiplier modules, which have a quantum efficiency of $\sim 16 \%$ at the wavelength (532 nm) used in our experiments, and a rise time of 700 picosec. The
amplifier/discriminator circuits were designed and constructed by Dr. Baldwin. These use a modified version of constant fraction discrimination, where a fixed fraction of the height of each photopulse is used as the basis for discrimination. This allows one to maintain timing resolution at a fraction of the rise time (i.e., down to the ~100 picosec level of the “pico”-correlator). Extensive testing and confirmation of performance of the amplifier/discriminators and correlators was carried out down to the time resolution limits with a fast electronic pulse generator. The combination was then tested with the photomultipliers using a high-speed pulsed LED light source (that produces ~1 nanosec FWHM optical pulses).

Subsequently, the LED was installed into the optical path of the photomultipliers, and its drive electronics integrated into the correlator control software, so that a calibration of zero delay time could be conveniently performed at the beginning of any correlation run. The calibration involved comparing a fixed period between LED pulses with the position of the associated correlation peak recorded for these pulses. “Zero time” calibration is important since temperature-dependent variations in signal cable lengths, electronic propagation times, and/or detector transit times can cause a spurious delay to be added to (or subtracted from) the photon arrival time record, shifting the position of zero delay in the correlation calculation. A variable delay built into the correlator provided compensation for these drifts, which were significant only over times (~8-12 hr) long compared to the acquisition time of a single correlation function. During experiments, data were always simultaneously acquired for forward and backward time
correlations. Time-reversal symmetry of the correlogram could then be visually or quantitatively tested, providing another check on the proper setting of zero delay time.

Another feature of the correlation system is a count-rate audio tuner. It is an audio amplifier – i.e., it produces sound whose audible frequency is proportional to the rate of photopulses received from the detectors. This device proved to be quite useful for “peaking up” – or properly adjusting the focusing and spot position – of the collected light scattering on the tip of an optical fiber, which was used to carry the light from the scattering setup to the photodetectors.

2.6 Light scattering setup

The experimental set up for our light scattering studies of freely suspended films is shown schematically in Fig. 2.3.

The liquid crystal film was illuminated by a diode-pumped solid state laser (Coherent, model Verdi V8), which produces a Gaussian single mode (TEM\(_{00}\)) output at a wavelength of 532 nm and a maximum power of 8 watts. The beam waist (diameter at 1/e\(^2\) intensity levels) is (1.2 \(\pm 5\%\)) mm. The laser was typically run at 1 – 1.5 watts, and the power was further reduced by two sequential \(\sim8\%\) reflections off of fused silica optical flats, which were also used to steer the beam to the film samples, and by a polarizer / half wave plate combination. The final power incident on the film ranged from \(\sim1\) to \(\sim150\) mW, depending on scattering angle. The Verdi laser produces extremely coherent light (coherence length > 60 meters) and has extremely low optical noise (<0.003 \%rms\(^2\)). The laser power was independently monitored by a Newport model
1815-C optical power meter\textsuperscript{13}, placed to intercept the beam transmitted through the sample. Before passing to the incident polarizer (a Glan-Laser air-spaced calcite prism pair, labeled P1 in Fig. 3.3), residual non-Gaussian light from the laser or subsequent optics was removed by a spatial filter (SF), which also served to expand the beam waist to \( \sim 5 \) mm. Polarizer P1 was adjusted for vertical incident polarization (i.e., polarization perpendicular to the horizontal plane in which scattering was collected). After the polarizer, the beam was focused to a spot size of \( \sim 50 \) microns on the film using a best form lens (L1).
Fig. 2.3 Experiment schematic
The angle of incidence on the film surface (lab angle $\theta_i$), and the angle ($\theta_s$) with respect to the film normal at which the scattering was collected, were controlled by a two stage goniometer (Huber, model 415) to a precision of 0.01°. As shown in Fig. 2.3, the scattering geometry corresponds to back-scattering, and the range of values of $q_\perp$ (component of $q$ in the plane of the film) probed in our experiment was $\sim 5000 – 75000$ cm$^{-1}$. In terms of the geometry defined in Fig. 2.2, $q_\perp$ is given by

$$q_\perp = \frac{2\pi}{\lambda_0} (\sin \theta_i - \sin \theta_s).$$

[In our experiments, we used negative values of $\theta_s$ (ranging from 0 up to $-\theta_i$).] The component $q_z$ along the film normal is determined by the surface boundary conditions, as will be discussed in Chapter 3. The main uncertainty in $q$, which sets a lower bound on $q_\perp$, comes from the cone of focusing of the incident light, and its effect will be discussed in Chapter 4. The scattered light was collected through a 600 micron pinhole at a distance of 205mm from the illuminated volume of the film. The pinhole diameter was selected to optimize the coherence factor in Eq. 2.15 to a typical value $\beta = 0.9$, corresponding nearly to the homodyne maximum of PCS. The uncertainty in $q_\perp$ introduced by the finite pinhole size was ±300cm$^{-1}$.

The collection pinhole was mounted to the scattering arm, which rotated on one stage of the goniometer. Behind the pinhole on the scattering arm were an analyzer (a Glan-Thompson calcite prism pair with axis adjusted vertical to the scattering plane), an imaging lens, and the tip of a 200 micron optical fiber, whose position could be adjusted in two dimensions perpendicular to the scattered wavevector to optimize coupling of the light into the fiber. The combination of polarizer and analyzer selected a polarized (VV)
over depolarized (VH) scattering process by approximately $10^5$:1. The imaging lens produced a real image of the illuminated volume of the film on the fiber tip. In this way, the fiber admitted only scattering from the illuminated volume (center of the film) and excluded light scattered from film edges or other surfaces arising from reflections (e.g., due to the windows on the sample chamber). The light from the optical fiber was passed to 50/50 beam splitter, which divided the beam into two beams of equal intensity, which were focused onto the active areas of the two photomultipliers used for cross-correlation.

2.7 Temperature controlled hot stage for liquid crystal films

Freestanding liquid crystal films were produced and housed in a modified commercial hot stage (Instec, model HS1)$^{14}$, which can be computer controlled for temperatures between ambient room temperature (~22°C) and 150°C. Fig. 2.4 shows the modified hot stage and typical scattering geometry.
Fig. 2.4 (a) Picture showing microscopic hot stage mounted at the top of a goniometer. The green arrow represents the incoming incident laser and the reflected beam is collected through the detector the and red line is a line from film normal. (b) Picture of the wiper blade on the substrate on copper block in which the thermistor is placed by drilling a hole. (c) Close look of microscopic hot stage when top surface is covered. The film hole is also seen partially.
The temperature was recorded once per second and displayed as a function of time in LabVIEW on the same PC used to control the correlators. During correlation runs (and for each wavevector $q$), the average measured temperature and standard deviation were computed and saved.

![Thermistor Calibration Graph](image)

**Fig. 2.5** Thermistor calibration curve

The Instec hot stage had sealed front and back windows (BK7 optical glass) placed on either side of the film to allow access and egress for the laser beam. The front (incident) window was anti-reflection coated for the 532 nm laser wavelength used; the
average reflectivity for 0-45° incident angle was 0.3%. The front window was rectangular, and covered a narrow (2 mm) slit in the Aluminum front cover of the hot stage. For back-scattering, the slit accommodated incident and scattering angles up to ±70°. However, the incident angle in typical experiments was fixed at a value between 25° and 30°, and the scattering angle was varied between ~-4° and -30° (see Fig. 2.2). Experiments were done under LabVIEW automation whenever possible. A comprehensive data file of experiment conditions (temperature, incident and scattering angles, laser power, film thickness), as well as the full correlation function, average scattered intensity and standard deviation, was saved for analysis after each run.

2.8 Liquid crystal samples

The structure, chemical names, and the transition temperatures of the thermotropic liquid crystal studied are listed below. The cyanobiphenyl compounds were obtained from a commercial supplier (Merck) and used without further purification. The compounds 8S5 and 64COOBC were provided by the Liquid Crystal Institute’s Organic Synthesis Lab and were purified according to standard facility procedures.
Fig. 2.6 Structures and the transition temperatures liquid crystal compounds studied.
2.9 Film making and thickness measurement

Smectic films of uniform thickness were prepared in a standard way by depicted in Fig. 2.7

Fig. 2.7 An arrangement for the on site thickness measurement and the left figure shows how the film is made.

The hot stage was raised to a temperature close to the nematic phase (or to the isotropic phase, in the case of a direct isotropic-smectic transition), and then a small amount of sample was melted onto the bottom edge of a 6 mm diameter circular hole in a 0.5 mm thick, 19 mm by 25 mm flat stainless steel film holder, which was fixed to a copper substrate in the hot stage that was adjustable in two dimensions (parallel to the plane of the film, so as position the incident laser beam in the center of the film and away
from the circular meniscus at the edge, where the thickness is not uniform). The hot stage was then sealed, and a free standing film was pulled over the hole in the film holder by a stainless steel wiper blade actuated from outside the sealed chamber (see Figs. 2.4 and 2.7). Once a stable film was pulled over the hole, the wiper blade was retracted, and the temperature was lowered to the desired temperature for experiments in smectic phases. It is important to note that before sample loading, all parts of the hot stage coming in contact with the sample were ultrasonicated in reagent grade acetone and dried, assembled into the hot stage using similarly cleaned tools; the entire interior of the hot stage was then baked out for 1 hour at 100°C.

Among the liquid crystals studied (see previous section), 8CB, 9CB, and S5 readily produced both thick and thin films, in the range ~50 nm to 110 μm (20 to 44,000 layers assuming single layer thickness~ 2.5nm of a smectic layers), that were stable and uniform for days to weeks. With the other liquid crystal studied, 64COOBC, we could not produce stable films above several 100 nm thickness. Our experiments were performed on vertically standing films (film plane perpendicular to the scattering plane), although the films were usually drawn in a horizontal geometry, cooled down to the desired temperature in the smectic phase, and then rotated into a vertical orientation and allowed to stabilize for ~24 hr.

Film thickness and stability were measured and continuously monitored in situ by two different methods. For films of thickness ~50 nm to 1 μm, we measured the spectrum of light from a broadband source (a fiber coupled tungsten-halogen lamp, Analytical Instruments, model DT1000) that was reflected from the film. The spectrum
was recorded using a computer interfaced fiber optic spectrometer (Ocean Optics, model USB2000\textsuperscript{19}) sensitive from 200 to 850 nm. A schematic of this method, together with typical results, is shown in Fig. 2.7. Collimated broadband light is shone through the uncoated back window of the hot stage onto the film, via a fiber optic/lens combination, at an angle of 25°. (The collimated beam diameter is slightly smaller than the film diameter.) The light reflected from the window and from the film is separately collected by additional lens/fiber combinations, and transmitted to the spectrometer. The spectra are displayed by a LabVIEW routine, which also calculates and displays their intensity ratio (film/window). Factoring in the known index of refraction and dispersion of the BK7 window, the reflectivity ratio effectively normalizes out the spectral variation of the light source, and reveals the normalized film reflectivity \( R \). This can then be fit to a standard expression, given the incident angle and known refractive indices for the liquid crystal (plus reasonable estimates of their dispersion) as inputs, and using the film thickness as the single variable parameter. The expression for \( R \) is,

\[
R = |r_0(1 - \frac{t_0' e^{2i\delta_0}}{1 - r_0^2 e^{-2i\delta_0}})|^2 = \frac{4r_0^2 \sin 2\delta_0}{(1 + r_0^2 - 2r_0^2 \cos 2\delta_0)}
\]

where \( r_0 = \frac{\cos \theta_0 - n \cos \theta_0'}{\cos \theta_0 + n \cos \theta_0'} \), \( \delta_0 = \frac{2\pi d \cos \theta_0'}{\lambda} \), \( n \) is the average refractive index of the film \((2n_o/3 + n_e/3)\), where \( n_o = n_{\perp} = \sqrt{\varepsilon_{\perp}}, n_e = n_{\perp} \left[1 + \left(\frac{1 - \frac{n_{\parallel}^2}{n_{\perp}^2}}{n_{\parallel}^2}ight) \sin^2 \theta_0 \right], n_{\parallel} = \sqrt{\varepsilon_{\parallel}} \), and \( d \) is the film thickness\textsuperscript{20, 21}. 
Typical results for the fit to $R$ are shown in Fig. 2.8, which demonstrates a thickness determination accuracy of ~5 nm. We found that the thickness of “thin” films (~60 – ~600 nm) could be roughly tuned (from thick to thin) by slowly heating the film toward the nematic phase, allowing it to thin layer by layer, and then abruptly cooling near the desired thickness, with the film thickness constantly monitored by reflectivity.
The thickness of very thick films \( (d \gg 1 \mu m) \) was measured by a second technique, which utilized the interference fringes\(^{22,23} \) observed on a distant screen from laser light reflected off the two film surfaces, calibrated against the interference observed from the surfaces (parallel to the film) of the front window, whose thickness is 1.00 mm (±1%). The incident angle of the laser light in these measurements was 27°. Typical results of the method are shown in Fig. 2.9\(^{22,23} \).

![Interference pattern from thick films](image)

**Fig. 2.9** The interference pattern produced by laser reflections from thick films of 8CB, photographed against a distant screen. The thin, narrowly spaced lines are the interference produced by the front glass window and the thicker, widely spaced lines by liquid crystal films of thickness in the range 10 – 100 \( \mu m \).
2.10 References


CHAPTER 3
LIGHT SCATTERING FROM SURFACE FLUCTUATIONS AND
HYDRODYNAMIC MODEL OF SMECTIC-A FILMS

3.1 Light scattering from thermal corrugations of a fluid surface

When light falls on the surface of a fluid, it is scattered as well as reflected and refracted, due to thermal corrugations (fluctuations) of the surfaces. A quantitative theory of light scattering from a liquid surface was first developed by Mandlestam, who modeled the corrugations in terms of surface waves, whose mean square amplitude was calculated by Einstein using a simple free energy for the surface and classical equipartition. Later Andronov and Lorentowicz further extended the model by separately considering s and p polarization states of the incident light and directions of the diffracted light off the plane of incidence.

To describe fluctuations of a liquid surface, let us assume (see Fig. 3.1) that in equilibrium the surface is parallel to the $x$-$y$ plane, and that the thermally induced displacement of the surface along $z$ is given by $\xi = \xi(x,y)$ in the continuum approximation, where $|\xi| << \lambda$ (the optical wavelength). Also assume that the film has dimensions $a$ by $a$ in the $x$-$y$ plane. In terms of Fourier components, the function $\xi(x,y)$ may be expanded as

$$\xi(x,y) = \sum_{\rho,\sigma=-\infty}^{\infty} \xi_{\rho\sigma} e^{i(px+\sigma y)}$$  \hspace{1cm} (3.1)

where $p = \frac{2\pi}{a}$, $\rho$ are $\sigma$ integers, and $\xi_{\rho\sigma}$ are complex Fourier coefficients.
Fig. 3.1 Corrugation of a free surface at liquid (medium 2) – air (medium 1) interface.

The calculation\textsuperscript{4,5} of the intensities of light reflected, refracted and diffracted from a single corrugated surface described by Eq. (3.1), requires a solution to Maxwell’s equations, subject to appropriate boundary conditions. In the remainder of this section, we will consider the simple case of a single fluctuating surface occupying the $x$-$y$ plane ($z = 0$) and separating semi-infinite media labeled 1 and 2 (Fig. 3.1). Let $\varepsilon = \varepsilon_0$ and $\varepsilon'$ be the dielectric constants of media 1 (air) and 2 (non-absorbing, non-conducting fluid) and assume an incident plane wave of the form $A(A_x, A_y, A_z) e^{i[k(x\alpha_0 + z\gamma_0)]}$, where, as shown in Fig. 3.2,

\begin{equation}
\alpha_0 = -\sin \theta_0 \quad \gamma_0 = -\cos \theta_0
\end{equation}
are components of the incident wave propagation direction in the x-z plane, \( \theta_0 \) is the incident angle on the surface, and \( k = 2\pi / \lambda \). Now from Maxwell’s electromagnetic theory the electric fields in media 1 and 2 satisfy\(^4\)

\[
\nabla^2 \mathbf{E}(r) + k^2 \mathbf{E}(r) = 0 \quad \text{and} \quad \nabla \cdot \mathbf{E}(r) = 0
\]

\[
\nabla^2 \mathbf{E}'(r) + k'^2 \mathbf{E}'(r) = 0 \quad \text{and} \quad \nabla \cdot \mathbf{E}'(r) = 0
\]

where primes denote quantities in medium 2.

For \( |\xi| << \lambda \), one expects the fields to be linear in the surface displacement \( \xi \), so that we can express solutions for \( \mathbf{E}, \mathbf{E}' \) to Eqs. (3.3) and (3.4) as

\[
\mathbf{E} = A_0 \exp[i k (ct - (x\alpha_0 + z\gamma_0))] + A_k \exp[i k (ct - (x\alpha_0 - z\gamma_0))]
\]

\[
+ \sum_{\rho,\sigma=-\infty}^{+\infty} A_{12}^{\rho\sigma} \exp[i k (ct - (x\alpha + y\beta + z\gamma))]
\]

\[
\mathbf{E}' = A_r \exp[i k' (ct - (x\alpha'_0 + z\gamma'_0))] + \sum_{\rho,\sigma=-\infty}^{+\infty} A_{12}'^{\rho\sigma} \exp[i k' (ct - (x\alpha' + y\beta' + z\gamma'))]
\]

where \( A_0, A_k, \) and \( A_r \) are incident, reflected, and transmitted field amplitudes, while \( A_{12}^{\rho\sigma}, A_{12}'^{\rho\sigma} \) are Fourier components of the diffracted (scattered) field due to fluctuations \( \xi \) (see Eq. 3.1), and \( k' = 2\pi / \lambda' = 2\pi \varepsilon' / \lambda \varepsilon_0 \). The propagation direction components are \((\alpha_0', 0, \gamma_0')\) of the refracted wave, and \((\alpha, \beta, \gamma)\) and \((\alpha', \beta', \gamma')\), respectively, for waves diffracted into media 1 and 2 (see Fig. 3.2) by corrugations with wavevectors labeled by
Fig. 3.2 Scattering from air-liquid boundary
\( \rho, \sigma \). Here and in the following we suppress the subscripts \( \rho, \sigma \) needed to explicitly label the diffracted wavevector components. The detailed connection between the angular coordinates and the wavevector components defined in Fig. 3.2 is given by

\[
\begin{align*}
\alpha &= \sin \theta \cos \varphi \\
\beta &= \sin \theta \sin \varphi \\
\gamma &= \cos \theta \\
\alpha' &= \sin \vartheta' \cos \varphi' \\
\beta' &= \sin \vartheta' \sin \varphi' \\
\gamma' &= -\cos \theta'
\end{align*}
\]

(3.7)

(Again we suppress labels \( \rho, \sigma \) on the angles \( \theta, \vartheta, \varphi, \varphi' \) describing the diffracted waves.)

Assuming no free charge on the fluid surface, the normal component of electric field is continuous at the boundary

\[
\left( \mathbf{n} \cdot \mathbf{D} \right)_{z = \xi} = \left( \mathbf{n} \cdot \mathbf{D}' \right)_{z = \xi}
\]

or

\[
\varepsilon \left( \mathbf{n} \cdot \mathbf{E} \right)_{z = \xi} = \varepsilon' \left( \mathbf{n} \cdot \mathbf{E}' \right)_{z = \xi}
\]

(3.8) (3.9)

where \( \mathbf{n} \) is the normal vector to the surface, given as

\[
\mathbf{n} = \hat{i} \left( \frac{\partial \xi}{\partial x} \right) + \hat{j} \left( \frac{\partial \xi}{\partial y} \right) + \hat{k} \left[ 1 - \left( \frac{\partial \xi}{\partial x} \right)^2 - \left( \frac{\partial \xi}{\partial y} \right)^2 \right]^{\frac{1}{2}}
\]

(3.10)

Also at the boundary surface, the transverse component of \( \mathbf{E} \) is continuous,

\[
[ \mathbf{E} - (\mathbf{n} \cdot \mathbf{E}) \mathbf{n} ]_{z = \xi} = [ \mathbf{E}' - (\mathbf{n} \cdot \mathbf{E}') \mathbf{n} ]_{z = \xi}
\]

(3.11)

Finally, in the absence of free currents and assuming \( \mu \cong \mu' \), both components of \( \mathbf{B} \) are continuous, so that (from Faraday’s law),

\[
\nabla \times \mathbf{E} \bigg|_{z = \xi} = \nabla \times \mathbf{E}' \bigg|_{z = \xi}
\]

(3.12)

Applying these boundary conditions, we get the following four independent equations to first order in \( \xi \):
\[
E_y - E'_y + (E_z - E'_z) \frac{\partial \xi}{\partial y} = 0 \quad (3.13)
\]
\[
E_x - E'_x + (E_z - E'_z) \frac{\partial \xi}{\partial x} = 0 \quad (3.14)
\]
\[
\frac{\partial}{\partial z} (E_y - E'_y) + \frac{\partial}{\partial y} (E_z - E'_z) = 0 \quad (3.15)
\]
\[
\frac{\partial}{\partial z} (E_x - E'_x) + \frac{\partial}{\partial x} (E_z - E'_z) = 0 \quad (3.16)
\]

Inserting Eqs. (3.1), (3.5) and (3.6) into (3.12) – (3.15), one finds for each Fourier component \((\rho, \sigma)\) of the surface corrugation that

\[
\alpha_0 - \alpha = \rho \frac{p}{k} \quad \text{or} \quad -\sin \theta_0 - \sin \theta \cos \varphi = \rho \frac{p}{k}
\]
\[
-\beta = \sigma \frac{p}{k} \quad \text{or} \quad -\sin \theta \sin \varphi = \sigma \frac{p}{k}
\]
\[
\alpha'_0 - \alpha' = \rho \frac{p}{k'} \quad \text{or} \quad -\sin \theta'_0 - \sin \theta' \cos \varphi' = \rho \frac{p}{k'}
\]
\[
-\beta' = \sigma \frac{p}{k'} \quad \text{or} \quad -\sin \theta' \sin \varphi' = \sigma \frac{p}{k'}
\]

where (as defined above) \(p = \frac{2\pi}{a}\). Eqs. (3.17) and (3.18) are standard results from elementary diffraction theory, where the diffracted optical wavevector component along the grating axis (i.e., parallel to the surface of the film) matches a particular wavevector of the surface modulation.

Applying the above results to the field boundary conditions, and now assuming the conditions relevant to our experiment (see Chapter 2) – namely, that the incident wave is polarized perpendicular to the plane of incidence \((A_0 = A_0)\) and that the diffracted
(scattered) light is detected in the plane of incidence \((\varphi = \varphi' = 0)\) – one can obtain to linear order in \(\xi^{1-3,5}\)

\[
A_{\rho \sigma, y}^{12} = 2ikA_0\frac{\varepsilon}{\varepsilon'} \frac{\sin(\theta_0 - \theta'_0) \cot \theta_0 \sin \theta}{\sin(\theta + \theta')} = A_{\rho \sigma, y}^{12}'
\]

\[
A_{\rho \sigma, x}^{12} = A_{\rho \sigma, x}' = A_{\rho \sigma, z}^{12} = A_{\rho \sigma, z}' = 0
\]

Now let us recall the Fresnel coefficient for transmission of light polarized perpendicular to the plane of incidence and incident at angle \(\theta_0\) (or \(\vartheta_0\))

\[
t_0 = \frac{2 \cos \theta_0}{\cos \theta_0 + n \cos \theta'_0}
\]

\[
t = \frac{2 \cos \theta}{\cos \theta + n \cos \theta'}
\]

where the refractive index of medium 2 (the liquid) is given by \(n = \sqrt{\varepsilon'/\varepsilon_0}\). After some trigonometric calculation, Eq. (3.19) can be recast as

\[
A_{\rho \sigma}^{12} = \frac{ikA_0\varepsilon}{2 \cos \theta} (n^2 - 1)t_0t = A_{\rho \sigma}^{12}'
\]

for diffraction with the incident wave coming from medium 1 at angle \(\theta_0\). (Henceforth we drop the subscript \(y\) on the diffracted amplitude.) Recall that the superscript “prime” on the diffracted wave amplitude denotes the wave diffracted into the transmission medium, while “unprimed” denotes a wave diffracted back into the incident medium. This notation will be used repeatedly below.

In similar way, one can derive the diffracted amplitudes in the case of the incident wave coming from medium 2 at angle \(\theta_0'\). The result is
where

\[ A_{\rho \sigma}^{21} = \frac{ikA_{\rho \sigma}^o \varepsilon}{2 \cos \theta} (n^2 \sin \vartheta - 1) t_0' t = A_{\rho \sigma}^{21} \]  

(3.23)

The results in Eqs. (3.22) and (3.23) are very useful for calculating surface scattering from a finite thickness freestanding film, since in that case the problem will involve diffraction at successive air-film and film air interfaces. The main complication is interference among diffracted waves arising from multiple reflections/refractions of the incident wave.

### 3.2 Diffraction of light from a corrugated thin film bounded by identical media

In the previous section, we discussed the light scattered by surface fluctuations of a single interface. The intensities of diffracted waves are proportional to the square of respective Fourier coefficients. The mean square Fourier coefficients are calculated on the basis of Einstein’s fluctuation theorem. We now consider a transparent film (medium 2) with refractive index \( n_2 = n \) separated from surrounding air (media 1 and 3, with \( n_1 = n_3 = 1 \)). The average film surfaces are flat, parallel to the X-Y plane and located at \( z = \pm d/2 \) and \( -d/2 \) (so that the film thickness is \( d \)). We again suppose that the surfaces undergo small amplitude fluctuations (compared to \( \lambda \)), as depicted in Fig. 3.3, with the surface displacements given by
Fig. 3.3 Smectic film with notation for the surface layer displacements.

\[ \xi^I(x, y, t) \quad \text{at } z = d/2 \]

\[ \xi^{II}(x, y, t) \quad \text{at } z = -d/2 \]

\[ \xi^I (x, y) = \sum_{\rho, \sigma = -\infty}^{+\infty} \xi^I_{\rho \sigma} e^{ip(x+\sigma y)} \quad (\text{at } z = +d/2) \]

\[ \xi^{II} (x, y) = \sum_{\rho, \sigma = -\infty}^{+\infty} \xi^{II}_{\rho \sigma} e^{ip(x+\sigma y)} \quad (\text{at } z = -d/2) \]

where \( p = \frac{2\pi}{a} \) (\( a \) being the film lateral dimension) and \( \xi^I_{\rho \sigma}, \xi^{II}_{\rho \sigma} \) are complex Fourier amplitudes.

We assume the incident light, with field \( E_0 = A_0 \exp[i(k(ct - x\alpha_0 - z\gamma_0))] \), is polarized perpendicular to the plane of incidence. As shown in Fig. 3.4, the light will undergo multiple reflections and refractions at the two surfaces, with reflected and transmitted amplitudes indicated in the figure. Summing up terms for the reflected ray into medium 1, we get

\[ A' = A_0 \left( r_0 + r_0' t_0 e^{-2i\delta_0} + r_0' t_0' e^{-4i\delta_0} + r_0' t_0' e^{-6i\delta_0} + \ldots \right) = A_0 r_0 \left( 1 - \frac{t_0' e^{-2i\delta_0}}{1 - r_0' e^{-2i\delta_0}} \right) \]
where \( r_0 \) is the Fresnel reflection coefficient for light propagating from 1 to 2 and polarized perpendicular to the plane of incidence\(^8, 9\)

\[
r_0 = \frac{\cos \theta_0 - n \cos \theta'_0}{\cos \theta_0 + n \cos \theta'_0}
\]  
(3.27)

And we have used the fact that \( r_0' \), the Fresnel coefficient for reflection of a wave propagating from 2 to 1 and incident at angle \( \theta'_0 \), equals \(-r_0 \). \( \delta \) is the optical path given by
\[
\delta_0 = \frac{2\pi n}{\lambda} d \cos \theta_0'
\]  

(3.28)

and \(t_0, t_0'\) are given by Eqs. (3.20) and (3.24). Similarly, we can obtain

\[
A^3_T = A_0 (t_0' t_0 e^{-i\delta_0} + r_0^2 t_0' t_0' e^{-3i\delta_0} + r_0^4 t_0' t_0' e^{-5i\delta_0} + ... ) = A_0 t_0' t_0 e^{-i\delta_0} \frac{1}{1 - r_0^2 e^{-2i\delta_0}}
\]  

(3.29)

The calculation of \(A^2_R\) and \(A^2_T\) also follows in the same way, with the results

\[
A^2_R = A_0 \frac{t_0 r_0'}{1 - r_0^2 e^{-2i\delta_0}} = -A_0 \frac{t_0 r_0 e^{2i\delta_0}}{1 - r_0^2 e^{-2i\delta_0}}
\]  

(3.30)

\[
A^2_T = A_0 \frac{t_0 e^{-i\delta_0}}{1 - r_0^2 e^{-2i\delta_0}}
\]  

(3.31)

Now let us turn to the light diffracted (scattered) from thermal fluctuations of the two surfaces, described by \(\xi^I\) and \(\xi^{II}\) in Eq. (3.25). The incident light (amplitude \(A_0\)) will give rise to diffraction at the boundary 1-2, the internally reflected light (amplitude \(A^2_T\)) will give diffraction at 2-1, and the internally transmitted light (amplitude \(A^2_T\)) will give diffraction at 2-3. The waves that diffract into the film also undergo multiple reflection and refraction; however, a major simplification is achieved if we neglect multiple diffraction, since its amplitude will be of higher than linear order in \(\xi/\lambda\) (assumed \(<<1\)).

To find the diffracted wave amplitudes (including interference), we restrict our consideration to diffraction in the plane of incidence only (i.e., \(\varphi = \varphi' = 0\) in Fig. 3.3), and only to diffraction into medium 1 (i.e., to the back-scattering geometry used in our experiment – recall Fig. 2.2). Following Vrij et al\(^7,10\), we may then proceed as follows:
(1) The incident wave gives rise to one wave diffracted into medium 1 and one into medium 2, with amplitudes given by Eq. (3.22):

\[
A_{ρσ}^{12} = \frac{ikA_0^\prime \rho \sigma}{2\cos \theta} (n^2 - 1)^t_0 t = A_{ρσ}^{12}\prime
\]  

(3.32)

for each Fourier component \((\rho, σ)\). The wave diffracted into 2 gives after multiple reflection and interference a wave transmitted back into medium 1, whose amplitude is:

\[
A_{ρσ}^{12}\prime (−r' t e^{-2iδ} − r'^2 t e^{-4iδ} − r'^4 t e^{-6iδ} − ...) = -A_{ρσ}^{12} \frac{r' t e^{-2iδ}}{1 − r^2 e^{-2iδ}}
\]  

(3.33)

where

\[
r = \frac{\cos \theta - n \cos \theta'}{\cos \theta + n \cos \theta'}
\]  

(3.34)

\[
t' = \frac{2n \cos \theta'}{\cos \theta + n \cos \theta'}
\]  

(3.35)

and

\[
δ = \frac{2\pi n}{λ} d \cos \theta'
\]  

(3.36)

The angles \(\theta, \theta'\) are defined in Fig. 3.2.

(2) The internal wave in the film propagating back toward the incident interface 2-1, with amplitude \(A_{r}^{2}\) given by Eq. (3.30), gives rise to a diffracted wave in medium 1. Accounting for multiple reflection, interference, and refraction/transmission
into medium 1 of the singly diffracted components, this contribution has amplitude

\[ A^2_{r_{\rho\sigma}} \left( \frac{A^2_{r_{\rho\sigma}}}{A_0} \right) (1 + r't'e^{-2i\delta} + r^3t'e^{-4i\delta} + r^5t'e^{-6i\delta} + \ldots) = \frac{A^2_{r_{\rho\sigma}}}{A_0} \left( 1 - \frac{r't'e^{-2i\delta}}{1 - r^2e^{-2i\delta}} \right) \quad (3.37) \]

where \( A^2_{r_{\rho\sigma}} \) is given by Eq. (3.23) for each Fourier component \((\rho, \sigma)\).

(3) The internal wave in the film propagating toward the “transmission” interface 2-3 (bottom interface in Fig. 3.4), with amplitude \( A^2_r \) given by Eq. (3.31), gives rise to diffracted waves propagating back into the film from interface 2-3. After accounting for multiple reflections, interference, and transmission into medium 1, we get a contribution to the diffraction into medium 1 given by

\[ A^2_{r_{\rho\sigma}} \left( \frac{A^2_{r_{\rho\sigma}}}{A_0} \right) (t'e^{-i\delta} + r^2t'e^{-3i\delta} + r^4t'e^{-5i\delta} + \ldots) = \frac{A^2_{r_{\rho\sigma}}}{A_0} \frac{t'e^{-i\delta}}{1 - r^2e^{-2i\delta}} \quad (3.38) \]

where \( A^2_{r_{\rho\sigma}} = -\frac{ikA_0\bar{\bar{\varepsilon}}}{2\cos\theta} (n^2 - 1)t_0't = A^2_{r_{\rho\sigma}} \)

Combining the results from (1) – (3) [specifically Eqs. (3.32), (3.33), (3.37), (3.38)], we may obtain the total amplitude diffracted into medium 1 (the incident medium, air) by fluctuations of the film surfaces:

\[ A^1_{r_{\rho\sigma}} = A_0 \frac{ik(n^2 - 1)t_0't}{2\cos\theta} \left( 1 - r_0e^{-2i\delta} \right) (1 - re^{-2i\delta}) \bar{\bar{\varepsilon}}_{r_{\rho\sigma}} - t_0't'e^{-i\delta}e^{-i\delta} \bar{\bar{\varepsilon}}_{r_{\rho\sigma}} \frac{A^2_{r_{\rho\sigma}}}{A_0} \left( 1 - r^2e^{-2i\delta} \right) \quad (3.39) \]

This result may be written in terms of in phase and out of phase surface fluctuations, defined by

\[ \bar{\bar{\varepsilon}}_{r_{\rho\sigma}} = (\bar{\bar{\varepsilon}}_{r_{\rho\sigma}} + \bar{\bar{\varepsilon}}_{r_{\rho\sigma}})/2 \]

\[ \bar{\bar{\varepsilon}}_{r_{\rho\sigma}} = (\bar{\bar{\varepsilon}}_{r_{\rho\sigma}} - \bar{\bar{\varepsilon}}_{r_{\rho\sigma}})/2 \quad (3.40) \]
as

\[ A_{\rho\sigma}^t = \frac{ik(n^2-1)}{2\cos\theta}(A^+_{\rho\sigma} + A^-_{\rho\sigma}) \]  

(3.41)

where

\[ A^\pm = t_0^\pm \frac{(1-r_0 e^{-2i\delta})(1-re^{-2i\delta}) \mp t_0' e^{-i\delta} e^{-i\delta}}{(1-r_0 e^{-2i\delta})(1-r e^{-2i\delta})} \]  

(3.42)

The electric field diffracted into medium 1 for Fourier component \((\rho,\sigma)\) of the surface fluctuations is

\[ E_{\rho\sigma}^1(x,z,t) = A_{\rho\sigma}(t) \exp[ik(ct-x\alpha_0 + z\gamma_0)] \]  

(3.43)

Here we have explicitly displayed the time dependence that arises from the dependence of the fluctuations \(\xi^I, \xi^{II}\) on \(t\).

Now, since the lateral size of the film is very much larger than an optical wavelength \((a>>\lambda)\), we may replace the discrete fluctuation wavevectors \(2\pi(\rho\hat{i} + \sigma\hat{j})/a\), indexed by integers \((\rho,\sigma)\), with a continuous wavevector \(\vec{q}_l = q_x\hat{i} + q_y\hat{j}\). From Eqs (3.41) and (3.43), we may then calculate the time correlation function of \(E^1\) as

\[ \langle E^{*}(\vec{q}_l,0)E^1(\vec{q}_l,t) \rangle = e^{ikc\tau} |A|^2 \{ \langle \xi^+(\vec{q}_l,0)\xi^+(\vec{q}_l,t) \rangle + |A|^2 \langle \xi^-(\vec{q}_l,0)\xi^-(\vec{q}_l,t) \rangle \} + A_{\rho}A_{\sigma} \{ \langle \xi^{II*}(\vec{q}_l,0)\xi^-\xi^+(\vec{q}_l,t) \rangle + A_{\rho}A_{\sigma} \{ \langle \xi^{II*}(\vec{q}_l,0)\xi^-\xi^+(\vec{q}_l,t) \rangle \} \]  

(3.44)

As discussed in Chapter 2, this correlation function is the quantity probed in our light scattering experiments. To relate it to specific properties of a smectic film, we need to utilize results from the hydrodynamic theory of smectics.
3.3 Smectic liquid crystal layer hydrodynamics

In Chapter 2, we pointed out that hydrodynamics describes the collective motion of equilibrium many-body systems in terms of “slow” variables – various conserved quantities supplemented by the Goldstone modes associated with relevant broken symmetries\textsuperscript{11-13}. The layer displacement \( u \) is the Goldstone mode of a \textit{smectic-A} liquid crystal and is also the fluctuating variable of interest in our experiments. Since mass density fluctuations in smectics have frequencies in the GHz range\textsuperscript{12, 14, 15}, which is well beyond any mode we detect and report in later chapters, we shall restrict ourselves to smectic hydrodynamics in the incompressible limit (density \( \rho = \) constant). Since temperature was kept constant in the experiments, we also assume isothermal conditions \((T = \) constant). Under these conditions, the equations of momentum, mass, and energy conservation that involve \( u \) reduce to\textsuperscript{12}:

\[
\rho \frac{\partial v_i}{\partial t} = -\partial_i p + \sum_j \partial_j \sigma_{ij} + h_u \delta_{ij} \tag{3.45}
\]

\[
\sum_i \partial_i v_i = 0 \tag{3.46}
\]

where \( i = x,y,z \), \( \partial_i = \partial / \partial x_i \), \( \bar{v} \) is the molecular velocity, \( p \) is effectively a pressure on the film that enforces the incompressibility condition, \( \sigma_{ij} \) is the viscous stress tensor of a \textit{smectic-A} liquid crystal, and \( h_u \) is the elastic force per unit volume conjugate to \( u \).

Taking the divergence of Eq. (3.45) and using Eq. (3.46), we get the following equation for the pressure:

\[
\sum_i \partial_i \partial_i p = \sum_{ij} \partial_i \partial_j \sigma_{ij} + \partial_z h_u \tag{3.47}
\]

The viscous stress is given by\textsuperscript{13}:
\[ \sigma'_{ij} = 2\eta_2 v_{ij}^2 + 2(\eta_3 - \eta_2)(v_{iz} \delta_{jz} + v_{jz} \delta_{iz}) + (\eta_4 - \eta_2)\delta_{ij}v_{kk} \]
\[ + \eta'\delta_{iz} \delta_{jz} v_{zz} + (\eta_5 - \eta_4 + \eta_2)(\delta_{iz} v_{zz} + \delta_{jz} v_{zz}) \]  
(3.48)

where \( v_{ij} = (\partial_i v_j + \partial_j v_i)/2 \), \( \eta' = \eta_1 + \eta_2 - 4\eta_3 - 2\eta_5 + \eta_4 \), and \( \eta_i (i = 1 - 5) \) are the independent viscosities arising from the broken orientational and translational symmetries of a smectic-\( A \). The conjugate force density \( h_u \) is

\[ h_u = \sum_i \frac{\partial}{\partial x_i} \frac{\partial f_{sA}}{\partial (\partial u / \partial x_i)} - \frac{1}{2} \sum_{i,j} \frac{\partial}{\partial x_i} \frac{\partial}{\partial x_j} \frac{\partial f_{sA}}{\partial (\partial^2 u / \partial x_i \partial x_j)} \]  
(3.49)

where \( F \) is the elastic free energy density of a smectic-\( A \) (see Eq. (1.5) of Chapter 1):

\[ f_{sA} = \frac{1}{2} B \left( \frac{\partial u}{\partial z} \right)^2 + \frac{1}{2} K \left( \frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial y^2} \right)^2 \]  
(3.50)

Eq. (3.49) then yields:

\[ h_u = B \frac{\partial^2 u}{\partial z^2} - K \left( \frac{\partial^4 u}{\partial x^4} + \frac{\partial^4 u}{\partial y^4} + 2 \frac{\partial^3 u}{\partial x^2 \partial y^2} \right) \]  
(3.51)

The hydrodynamic equations [Eq. (3.45) and (3.46)] must be supplemented by an equation connecting the speed \( \partial u / \partial t \) associated with layer displacement \( u \), molecular speed along the layer normal \( (v_z) \), and the possibility of molecular permeation (molecular movement along \( z \) that is independent of the layer motion):

\[ \frac{\partial u}{\partial t} = v_z - \xi_p h_u \]  
(3.52)

where \( \xi_p \) is the coefficient of permeation\(^1^2 \), which has dimensions of time/(mass density).

Eqs. (3.45) – (3.48), (3.51), (3.52) together form the basis of our analysis of the layer fluctuations in smectic films. However, for a film of finite thickness \( d \), they must be supplemented by boundary conditions at the surfaces, \( z = \pm d/2 \).
The appropriate boundary conditions are the following\textsuperscript{11}:

A) Liquid crystal molecules do not enter or leave the surface of the film from outside the medium (no permeation across the surface):

\[
\frac{\partial u}{\partial t} \bigg|_{z=\pm d/2} = v_z \bigg|_{z=\pm d/2}
\]  
\text{(3.53)}

B) The normal component of the permeation force vanishes at the surfaces. This requires\textsuperscript{12}:

\[
\frac{\partial u}{\partial z} \bigg|_{z=\pm d/2} = 0
\]  
\text{(3.54)}

C) The viscoelastic stresses (Fig. 3.5) acting on the film are continuous across the free surfaces:

\[
\begin{align*}
\sigma_{iz} + \sigma_{iz}' \big|_{z=\pm d/2} &= 0 \quad (i = x, y) \\
\sigma_{zz} + \sigma_{zz}' \big|_{z=\pm d/2} &= \sigma_{\text{surf}} \bigg|_{z=\pm d/2} = \pm \gamma \nabla^2 u \big|_{z=\pm d/2}
\end{align*}
\]  
\text{(3.55)}
Where $\sigma_{\text{surf}}$ is the pressure due to surface tension, and $\gamma$ is the surface tension of the film in air. Since the normal elastic stress $\sigma_{zz} = -p + B\partial_z u$, Eqs. (3.55) may be written

$$
(\partial_z v_z + \partial_z v_x) \bigg|_{z = \pm d/2} = 0
$$

(3.56)

$$
[-p + \sigma'_{zz} + B\partial_z u \mp \gamma (\partial_z^2 + \partial_y^2) u] \bigg|_{z = \pm d/2} = 0
$$

(3.57)

When permeation is included, the solution to the hydrodynamic equations plus boundary conditions is quite complicated. For small displacements ($u \ll \lambda$), $u$ is a superposition of Fourier components, each of which is the sum of an elastic and permeation term

$$
u = [u_{el}(\vec{q}_\perp, z) + u_p(\vec{q}_\perp, z)]\exp[i(\vec{q}_\perp \cdot \vec{r} - \omega t)]
$$

where $z$ is the direction along the layer normal. To simplify the analysis below, we argue that $|u_p| \ll |u_{el}|$ and therefore that permeation may be neglected. One can show that

$$
\sqrt{\langle u_p^2 \rangle / \langle u_{el}^2 \rangle} = \sqrt{(q_{z_{el}}^2 + \lambda_s q_{z_{p}}^2) / q_{z_p}^2},
$$

where $q_{z_{el}}$, $q_{z_p}$ are inverse lengths associated with elastic motion and permeation along $z$, and $\lambda_s$ is the smectic penetration length $\sqrt{K / B}$. One can estimate $q_{z_{el}}$ by equating layer compression and surface elastic energies,

$$
Bq_{z}^2 (Ad) \sim \gamma q_{z}^2 A,
$$

where $A$ is the film area. This gives $q_{z_{el}} \sim \sqrt{\gamma / Bd} q_{z_{p}}$. Previous results on smectics indicate that $q_{z_p}$ is typically $\sim 10^7$ cm$^{-1}$. Taking $d \sim 100$ nm $= 10^{-5}$ cm (a typical thickness of films studied in Chapter 4), $q_{z_p} \sim 10^4$ cm$^{-1}$, and typical values $B = 10^8$ dyne/cm$^2$, $K = 10^{-6}$ dyne, and $\gamma = 25$ dyne/cm, we get $\sqrt{\langle u_p^2 \rangle / \langle u_{el}^2 \rangle} \sim 10^{-4}$, which is negligible. Thus, in the following, we will specialize to the case of elastic modes only –
specifically, we will neglect the $\xi_p$ term in Eq. (3.52) and the constraint on the permeation force at the surfaces [i.e., we neglect boundary condition B) given above in Eq. (3.54)]. Then, as we shall see below, purely elastic modes can satisfy the remaining boundary conditions.

3.4 Elastic modes of a smectic-A film

We now focus on solutions to the hydrodynamic equations (Eqs. 3.45, 3.46, and 3.52 with $\xi_p \to 0$) of the form

$$u^{el} = u = u_0 \exp[iq_z(q_x, \omega)z] \exp[i(q_x x - \omega t)]$$

$$\vec{v}^{el} = \vec{v} = \vec{v}_0 \exp[iq_z(q_x, \omega)z] \exp[i(q_x x - \omega t)]$$

where, without loss of generality for a smectic-A film, we have taken $q_{z\perp} = 0$, and have anticipated that the elastic mode boundary conditions will set the value of $q_{z\perp}$ in terms of $q_x$ and $\omega$.

The Fourier transform of Eq.(3.57) for the pressure yields

$$p = \frac{q_i q_j}{q^2} \sigma'_{ij} - iq^2 h_{ij}$$

where  $h_{ij} = (-Bq_z^2 + K q_{z\perp}^4) u_{ij}$. Then in Fourier space Eqs. (3.45) and (3.52) with $\xi_p \to 0$ and $q_{z\perp} = q_x$ become:

$$-i\omega \nu_x = -iq_x p + iq_j \sigma'_{xj}$$

$$-i\omega \nu_z = -iq_z p + iq_j \sigma'_{zj}$$

$$-i\omega \nu_y = iq_j \sigma'_{yj}$$

$$-i\omega \nu = \nu_z$$

(3.60)
Combining Eqs. (3.59)-(3.61), the incompressibility condition \( \sum_i \partial_i v_i = \sum_i v_i \rho = 0 \), and the explicit form of \( \sigma'_i \) for a smectic-A (Eq. 3.48), one finds after considerable algebra

\[
-i \omega v_x - \eta_1 q_x^2 v_x + \eta_2 q_y v_y + C q_z u_0 \\
-i \omega v_z = -\eta_1 q_y v_x + \eta_2 q_x v_y - C q_z^2 u_0 \\
-i \omega v_y = -(\eta_2 q_x^2 + \eta_3 q_z^2) v_y \\
-i \omega u_0 = v_z
\]

(3.61)

where

\[
\eta_1(q) = \frac{\eta_1(q_x^2 - q_y^2)}{q^2} \\
\eta_2(q) = \frac{\eta q_y^2}{q^2} + \left(3 \eta_3 + \eta_q \right) \frac{q_z^2}{q^2} \\
C(q) = Bq_x^2 + K q_z^4
\]

(3.62)

and \( q^2 = q_x^2 + q_z^2 \).

In principle, one obtains four normal modes and four associated eigen frequencies from Eqs. (3.61). The \( v_y \) mode decouples, giving

\[
i \omega_{v_y} = \frac{\eta_2 q_x^2 + \eta_3 q_z^2}{\rho}
\]

(3.63)

This corresponds to an overdamped transverse shear wave (transverse since we assumed \( q_y = 0 \)); it is not coupled to \( u \) in a smectic-A phase, and thus will not contribute to light scattering produced by \( u \) fluctuations. The remaining three equations may be written in matrix form as
The secular equation of the above matrix is

$$i \omega [ \rho (i \omega)^2 - (\eta_x q_x^2 - \eta_z q_z^2) i \omega + C q_z^2 ] = 0$$

(3.65)

This gives three solutions

$$i \omega_0 = 0$$
$$i \omega_\pm = \frac{(\eta_x q_x^2 - \eta_z q_z^2)}{2 \rho} \pm \frac{\left[ (\eta_x q_x^2 - \eta_z q_z^2)^2 - 4 \rho C q_z^2 \right]^{1/2}}{2 \rho}$$

(3.66)

The eigenvalue $i \omega_0 = 0$ is trivial. It arises because the condition of incompressibility implies $q_x v_x = -q_z v_z$, so that are in fact only two independent variables $(v_x, u)$ or $(v_z, u)$, and there are only two non-trivial modes of the smectic-A film, with eigenvalues given by $i \omega_\pm$, that couple to $u$. We shall refer to these modes as “$u$-$v$” modes.

They are underdamped or overdamped, depending on the sign of the argument in the square root in Eq. (3.66). The frequencies $i \omega_\pm$ may be expressed in a form ultimately useful to our data analysis in Chapter 4 as

$$i \omega_\pm = \Gamma \pm i \sqrt{\Omega}$$

(3.67)

where
\[
\Gamma = \frac{\eta(q)}{2\rho} q^2
\]
\[
\Omega = \frac{C(q)}{\rho} q_x^2 - \Gamma^2 \tag{3.68}
\]
\[
\eta(q) = \eta_0 + \eta' \frac{q_x^2 q_z^2}{q^4}
\]
and \(C(q)\) is defined by Eq. (3.62). The \(u-v\) modes are underdamped when \(\Omega > 0\) and overdamped when \(\Omega < 0\).

One can write the time dependence of \(u\) in terms of the \(u-v\) normal modes as
\[
u(t) = c_+ e^{-i\omega t} + c_- e^{+i\omega t} \tag{3.69}
\]
Since \(v_z(t) = \partial u/\partial t\) (neglecting permeation), we may deduce that \(u(0) = c_+ + c_-\) and \(v_z(0) = -i\omega c_+ - i\omega c_-\), so that
\[
u(t) = \frac{(i\omega_+ e^{-i\omega t} - i\omega_- e^{+i\omega t})u(0) + (e^{-i\omega t} - e^{+i\omega t})v_z(0)}{i\omega_+ - i\omega_-} \tag{3.70}
\]
where \(u(0)\) is shorthand for \(u(q_x, q_z)e^{iq_x x} e^{iq_z z}\) and similarly for \(v_z(0)\).

It remains to apply the boundary conditions at the film surfaces, which in general will connect the amplitudes \(u(0)\) and \(\bar{v}(0)\), and determine the spectrum of allowed wavevectors \(q_z\). In the elastic limit \((u_e = 0)\) and provided the fluctuation frequencies are sufficiently low, the boundary condition Eq. (3.57) yields a fairly simple condition on \(q_z\).

To obtain this condition, we return to the original expression for \(u_{el}\) (Eq. (3.58)) and write it in terms of symmetric and anti-symmetric modes with respect to the mid-plane of the film (i.e., with respect to \(z = 0\)): 
\begin{align}
  u_{el}^S &= u_0 \cos q_z z e^{i(q_z x - \omega t)} \\
  u_{el}^A &= u_0 \sin q_z z e^{i(q_z x - \omega t)}
\end{align}
\tag{3.71}

and similarly for \( \ddot{v}_{el} \). If these are substituted into Eq. (3.57), and Eqs. (3.59) and (3.48), plus the incompressibility condition, are used to evaluate the pressure \( p \) and \( \sigma'_{zz} \), one finds after some algebra

\begin{align}
  B q_z \sin \left( \frac{q_z z}{2} \right) + O \left( \frac{(2\eta_s + \eta') |\omega|}{B} \right) &= \gamma q_s^2 \cos \left( \frac{q_z z}{2} \right) \\
  \frac{q_z}{2} &= \cot \left( \frac{q_z d}{2} \right) \left[ \frac{q_z}{B} \right]^{\pm 2}
\end{align}
\tag{3.72}

for symmetric modes, and

\begin{align}
  B q_z \cos \left( \frac{q_z z}{2} \right) + O \left( \frac{(2\eta_s + \eta') |\omega|}{B} \right) &= -\gamma q_s^2 \sin \left( \frac{q_z z}{2} \right) \\
  \frac{q_z}{2} &= \cot \left( \frac{q_z d}{2} \right) \left[ \frac{q_z}{B} \right]^{\pm 2}
\end{align}
\tag{3.73}

for anti-symmetric modes. Let us assume \( B \gg (2\eta_s + \eta') |\omega| \) (an assumption we will discuss critically in Chapter 4). Then Eqs. (3.72) and (3.73) may be written compactly as

\begin{align}
  q_z &= \pm \frac{\gamma q_s^2}{B} \left[ \cot \left( \frac{q_z d}{2} \right) \right]^{\pm 2}
\end{align}
\tag{3.74}

where +,− corresponds to \( S,A \) (symmetric, antisymmetric modes, respectively).
Fig. 3.6 Plot for \( q_z \)'s for dimensionless parameter \( q_z l_d = \sqrt{2} \). The intersection of dashed line and solid line gives the value of \( \frac{q(z,n)d}{\pi} \) for \( n \) even and odd respectively.

Eq. (3.74) is a transcendental equation for \( q_z \) values allowed in a finite thickness film. Fig. 3.6 displays graphical solutions, which may be indexed by a non-negative integer \( n \), where \( n = 0 \) denotes the smallest \( q_z^{(n)} \) and \( q_z^{(n)} < q_z^{(n+1)} \). There are two experimentally relevant limits:

**“Thin” film** \( (q_x^2 \gamma d / B \ll 1) \):

\[
q_z^{(n)} \approx \begin{cases} 
\sqrt{\frac{2 \gamma}{Bd}} q_x & (n = 0) \\
\frac{n\pi}{d} + \frac{2 \gamma}{Bn\pi} & (n > 0)
\end{cases}
\]  

(3.75)
“Thin” film ($q_z^2 \gamma d / B \gg 1$):

$$q_z^{(n)} \approx \frac{(n+1)\pi}{d} \left( 1 - \frac{2B}{\gamma d q_z^2} \right)$$  \hspace{1cm} (3.76)

One may note from Fig. 3.6 and the indexing above that for “thin” films, even $n$ corresponds to symmetric layer fluctuation modes, while odd $n$ refers to anti-symmetric modes.

### 3.5 Time correlation function for surface layer fluctuations of a smectic-A film

We close this chapter by performing a calculation of the time correlation functions for surface layer displacements and for the diffracted $E$ field relevant for light scattering. We will draw on various results of the foregoing sections. In the elastic limit, the general solution to the hydrodynamic equations considered in the previous section for $u$ at the film surfaces is

$$u(q_x, z = \pm d/2, t) = \left[ \sum_{n \text{ even}} u(q_x, n, t) \cos(q_z^{(n)} d / 2) \pm \sum_{n \text{ odd}} u(q_x, n, t) \sin(q_z^{(n)} d / 2) \right]$$  \hspace{1cm} (3.77)

where $u(q_x, n, t)$ is given by Eq. (3.70) with $i\omega_x, i\omega_\perp \rightarrow i\omega_z(q_x, q_z^{(n)}), i\omega_\perp(q_x, q_z^{(n)})$.

The correlation function we require will involve $\langle u(q_x, m, 0)u(q_x, n, t) \rangle$. From Eq. (3.70), we will therefore need $\langle u(q_x, m, 0)u(q_x, n, 0) \rangle$ and $\langle u(q_x, m, 0)v_z(q_x, n, 0) \rangle$. The Fourier transform of the smectic-A free energy density [from Eq. (3.50)] may be written

$$F_g = \left( \frac{1}{2} Bq_z^{(n)} + \frac{1}{2} K q_x^4 \right) |u(q_x, n, 0)|^2$$  \hspace{1cm} (3.78)
Since this expression does not involve any coupling of \( u \) to \( v_z = \partial u / \partial t \), the equipartition theorem implies

\[
\langle u(q_x,m,0)u(q_x,n,0) \rangle = \delta_{mn} \frac{k_B T}{Bq_{z}^{(n)^2} + Kq_{x}^{4}} \quad \text{(3.79)}
\]

\[
\langle u(q_x,m,0)v_z(q_x,n,0) \rangle = 0 \quad \text{(3.80)}
\]

In the elastic limit, the surface fluctuations are given by \( \xi^I(q_z,t) = u(q_x,z = d/2,t) \) and \( \xi^H(q_z,t) = u(q_x,z = -d/2,t) \). To calculate the electric field correlation function given at the end of section 3.2 [Eq. (3.44)] for scattering from smectic film surface fluctuations, we actually need the correlations of \( \xi^+ = (\xi^I + \xi^H)/2 \) and \( \xi^- = (\xi^I - \xi^H)/2 \). It is straightforward to combine the results above with Eq. (3.77) to obtain:

\[
\langle \xi^+ \ast (q_z,0) \xi^+ (q_z,t) \rangle = 4 \sum_{n \text{ even}} \cos^2(q_z^{(n)}d/2) \langle u(q_x,n,0)u(q_x,n,t) \rangle
\]

\[
\langle \xi^- \ast (q_z,0) \xi^- (q_z,t) \rangle = 4 \sum_{n \text{ odd}} \sin^2(q_z^{(n)}d/2) \langle u(q_x,n,0)u(q_x,n,t) \rangle
\]

\[
\langle \xi^+ \ast (q_z,0) \xi^- (q_z,t) \rangle = \langle \xi^- \ast (q_z,0) \xi^+ (q_z,t) \rangle = 0
\]

Then Eq. (3.44) gives:

\[
\langle E^{\ast I}(q_x,0)E^I(q_x,t) \rangle = 4e^{ikt} \sum_{n \text{ even}} \cos^2(q_z^{(n)}d/2) \langle u(q_x,n,0)u(q_x,n,t) \rangle +
\]

\[
|A|^2 \sum_{n \text{ odd}} \sin^2(q_z^{(n)}d/2) \langle u(q_x,n,0)u(q_x,n,t) \rangle
\]

(3.82)

where, from Eqs. (3.67), (3.70), (3.79), and (3.80), one may calculate
\[
\langle u(q_z, n, 0)u(q_z, n, t)\rangle = \frac{k_B T}{(Bq_z^{(n)2} + Kq_z^4)[i\omega_z(q_z, q_z^{(n)}) - i\omega_z(q_z, q_z^{(s)})]} k_B T \left[ e^{-i\omega_z(q_z, q_z^{(n)})t} - e^{-i\omega_z(q_z, q_z^{(s)})t} \right]
\]

\[
= \frac{k_B T}{Bq_z^{(n)2} + Kq_z^4} \sqrt{1 + \frac{\Gamma^2}{\Omega}} \cos \left[ \frac{\sqrt{\Omega}t - \tan^{-1} \left( \frac{\Gamma}{\sqrt{\Omega}} \right)}{\sqrt{\Omega}} \right] e^{-\Gamma t} \quad \Omega > 0 \quad (3.83)
\]

\[
\begin{cases}
1 + \frac{\Gamma}{\sqrt{\Omega}} e^{-(\Gamma - \sqrt{\Omega}) t} & \Omega > 0 \\
1 - \frac{\Gamma}{\sqrt{\Omega}} e^{-(\Gamma + \sqrt{\Omega}) t} & \Omega < 0
\end{cases}
\]

Recall that \( \Gamma \) and \( \Omega \) are defined by Eqs. (3.68), and, according to the definition, \( \Gamma > \sqrt{|\Omega|} \). Reiterating what was pointed out in the previous section, the above results reflect counter-propagating underdamped modes when \( \Omega > 0 \) (small \( q_z \) or \( d \)) and a pair of distinct overdamped modes when \( \Omega > 0 \) (large \( q_z \) or \( d \)). The latter are associated with “slow” elastic layer undulations (relaxation rate \( \Gamma - \sqrt{\Omega} \)) and “fast” molecular diffusion (relaxation rate \( \Gamma + \sqrt{\Omega} \)).

The role of the optical factors \( |A_+|^2 \) and \( |A_\perp|^2 \) in Eq. (3.82) is very important. From Eq. (3.42), we note that they are strong functions of the film thickness. For given incident and scattering angles (determining \( q_z \)), and a given wavelength of light, these factors will be selectively peaked for particular film thicknesses, essentially determined by the interference conditions between waves reflected from the two surfaces. This fact will be exploited in the choice of film thickness (and/or \( q_z \)) used in the experiments described in the next chapters.
3.6 References


CHAPTER 4

RESULTS ON LAYER DYNAMICS OF “THIN” AND “THICK” SMECTIC-A FILMS OF 9CB AND 8CB

In this chapter we will concentrate mainly on experimental results obtained on layer dynamics of “thin” smectic-A films of the liquid crystals 9CB and 8CB. Here we mean “thin” in the dynamical sense – the limit where the lowest energy and dominant mode contributing to the surface light scattering is nearly a pure undulation of the film, with surface tension being the primary elastic restoring force. In the final section, however, we will present results for a very thick film, where bulk modes involving layer compression contribute significantly to the scattering.

4.1 “Thin” film limit of smectic layer dynamics

As discussed in Chapter 3, the layer fluctuation modes contributing to polarized surface scattering from smectic films are characterized by a discrete set of wavevectors $q_z^{(n)}$ ($n = 0, 1, 2, \ldots$) along the layer normal, whose values are determined by the surface boundary conditions. When the film is sufficiently thin, the energy associated with layer compression (minimum $q_z^{(n)} = \pi / d$) will dominate the energy associated with increasing the surface area – i.e., $\left[ B(\pi / d)^2 u_0^2 \right] (Ad) \gg \gamma q_z^2 u^2 A$ for sufficiently small thickness $d$, where $u_0$ is the amplitude of the layer displacement, $A$ the film area, $B$ is the layer compression modulus, $\gamma$ the surface tension, and $q_z$ is the in-plane wavevector. In other
words, when $q_z^2(\gamma d / B) \ll 1$, the film is “thin”, and the lowest energy modes will correspond to nearly pure layer undulation, with minimal layer compression.

In this limit, Eq. (3.75) gives

$$q_z^{(n)} = \begin{cases} \frac{2\gamma}{Bd} q_z & (n = 0) \\ \frac{n\pi}{d} & (n > 0) \end{cases} \quad (4.1)$$

Then for the lowest frequency mode $(n = 0)$, Eq. (3.68) gives

$$\eta(\tilde{q}) \approx \eta_3 + \eta' \frac{2\gamma / B d}{(1 + 2\gamma / B d)^2} \approx \eta_3 + \eta' \frac{2\gamma}{B d} \approx \eta_3 \quad (4.2)$$

assuming $\eta' \sim \eta_3$ and taking typical $\gamma = 25$ erg/cm$^2$, $B = 10^8$ erg/cm$^3$, $d \geq 10^{-3}$ cm, so that $\gamma / Bd \leq 0.025$. The complex frequency for the $n = 0$ mode (obtained from combining Eqs. (3.67), (3.68), and (4.2)) is

$$i\omega_z^{(0)} = \Gamma \pm i\sqrt{\Omega}$$

$$\Gamma = \frac{\eta_3}{2\rho} q_z^2$$

$$\Omega = \frac{2\gamma}{pd} q_z^2 - \Gamma^2 = \frac{2\gamma}{pd} q_z^2 - \left( \frac{\eta_3}{2\rho} \right)^2 q_z^4$$

The associated fluctuation amplitudes are proportional to (see Eq. (3.82))

$$A_0 = \frac{k_BT}{Bq_z^{(0)} + Kq_z^4} \approx \frac{k_BT}{(2\gamma / d)q_z^2 + Kq_z^4}.$$  On the other hand, the lowest order $(n = 1)$ compression mode has amplitude proportional to $A_1 = \frac{k_BT}{B(\pi / d)^2 + Kq_z^4}$.

In this chapter, we will focus on smectic films satisfying the “thin” film limit. Taking values of $\gamma$ and $B$ given above, and maximum experimental $q_z^2 \approx 4 \times 10^9$ cm$^{-2}$, we
find that the limit applies for \( d \ll 10 \mu \text{m} \), which is well satisfied for films thinner than 300 nm, as are all the samples considered in this chapter. Also one finds the ratio of fluctuations amplitudes for \( n = 0 \) and \( n = 1 \) modes to be

\[
\frac{A_0}{A_1} = B(\pi/d)^2/(2\gamma/d) > 800 \quad \text{for} \quad d < 300 \text{ nm and } q_s^2 < 4 \times 10^9 \text{ cm}^{-2}.
\]

Thus, in the “thin” film limit, we expect the \( n = 0 \) modes to utterly dominate even at the largest experimental \( q_s \).

Employing the results of Chapters 2 and 3 (specifically, Eqs. (2.11-15), (3.82), (3.83)), we may express the normalized time correlation of the vertically polarized surface scattered intensity as

\[
\frac{\langle I_{VV}(0)I_{VV}(\tau) \rangle}{\langle I_{VV} \rangle^2} = \frac{\beta \langle E_{VV}(0)E_{VV}(\tau) \rangle^2}{\langle E_{VV}^2 \rangle^2} + 1 = \begin{cases} 
C_0 e^{-(\Gamma + \Omega)\tau} \cos(\sqrt{\Omega} \tau - \tan^{-1}(\Gamma/\sqrt{\Omega}))^2 + 1 & (\Omega > 0) \\
C_0 e^{-(\Gamma - \sqrt{\Omega})\tau} + C_0 e^{-(\Gamma + \sqrt{\Omega})\tau} & (\Omega < 0)
\end{cases}
\]

where \( \Gamma = \Gamma(q_s), \Omega = \Omega(q_s) \) for the \( n = 0 \) modes are given in Eq. (4.3). The amplitudes have maximum values of 1 when the coherence factor \( \beta \) of the scattered light is optimized. Eq. (4.4) indicates that for appropriate \( d \), one should observe and be able to quantitatively test the hydrodynamic theory of a crossover from under to overdamped dynamics, while from the dispersion \( (q_s \text{ dependence}) \) of the frequency and damping, a known film thickness and density, one may extract the quantities \( \gamma \) and \( \eta_B \).
4.2 Results for “thin” 8CB and 9CB smectic-A films: Time correlation data

Figs. 4.1 – 4.6 show measured correlation functions \( \langle I_{VV}(0)I_{VV}(\tau) \rangle \) (normalized as in Eq. (4.4)) for 90 and 230 nm films of 9CB, taken at a temperature of 44°C (0.5°C below the bulk smectic-A – nematic transition), and for 100 and 240 nm films of 8CB taken at 25.5°C (7°C below the Smectic-A – N transition). The actual transition temperatures of the films were determined by slowly heating the samples until the onset of film thinning, observed by monitoring the film reflectivity. A sequence of thinning transitions typically precedes collapse of free-standing films at the Smectic-A – N transition\(^2,^3\), and we found that the temperatures at which the films began to thin were within ~0.1°C of the bulk transitions. The data in Figs. 4.1-4.6 were taken as a function of in-plane wavevector \( q_x \) by varying the scattering angle in the backscattering geometry described in Chapter 2. We chose the film thicknesses 90-100 nm and 230-240 nm to correspond empirically to maxima in the interference factor that controls the unnormalized correlation amplitude in Eq. (3.82). For \( d < \lambda \) and \( q_x < 2\pi/\lambda \), is a periodic function of \( d \) and is fairly insensitive to \( q_x \) over the range studied. The first generation fast correlator, capable of nanosecond resolution, was used for the measurements reported in this section.

Let us first consider the data for 90 nm 9CB (Fig. 4.1 – 4.3). We clearly observe an underdamped time dependence; Fig. 4.2 shows that at least 13 oscillations with delay time \( \tau \) can be resolved at certain values of \( q_x \). With increasing \( q_x \), both the oscillation period and the damping time characterizing the underdamped behavior shift to shorter times \( \tau \). Note the importance of 1 – 10 nanosec resolution in defining the oscillatory
features in the data. The solid line in Fig. 4.2 is a fit to the $n = 0$ (lowest energy) underdamped modes, modeled by Eq. (4.4), with three variable parameters $C_0$, $\Gamma$, and $\Omega$. The fit is good, and represents a significant confirmation of the smectic hydrodynamic theory in the general case where inertia, dissipation, and elasticity all contribute importantly to the layer fluctuations. It is especially significant that the phase of the oscillatory term in Eq. (4.4) is not an independent, variable parameter, but is fully constrained in the theory and in the fit.
Fig. 4.1 Measured time correlation functions of the intensity of light scattered from layer undulations in a 90 nm thick SmecticA film of 9CB at 0.5°C below the nematic phase, for various values of the wave vector $q_x$ (in cm$^{-1}$) parallel to the layers.
Fig. 4.2 Analysis of the data for 90 nm 9CB film for $q_x = 14300$ cm$^{-1}$ from Fig. 4.1. The solid line is a fit to the hydrodynamic theory for a smectic-A film in the underdamped regime (Eq. (4.4)). The dashed line is the damping envelope.
especially at low \( q_x \), where one would normally expect static scattering from optical surfaces on either side of the film (or from the film holder) to be concentrated. Neither of

However, a closer examination of Fig. 4.2 reveals that the data alternate high and low with respect to successive peaks in the fitted curve. We find that this discrepancy between data and fit to Eq (4.4) is more pronounced at larger \( q_x (q_x \sim 26000 – 50000 \text{ cm}^{-1}) \), where the data are still underdamped but the peaks no longer decrease monotonically in height with increasing \( \tau \). As shown for the case of \( q_x = 32000 \text{ cm}^{-1} \) in Fig. 4.3, the simple hydrodynamic model of Eq. (4.4) (blue curve) fails significantly. The alteration in peak heights in the data can, however, be explained by a beating of the lowest energy (\( n = 0 \)) layer fluctuation mode with an additional, purely overdamped mode. The red line in Fig. (4.3) is a fit to Eq. (4.4) supplemented by such a mode,

\[
\frac{\langle I_{vv}(0)I_{vv}(\tau) \rangle}{\langle I_{vv} \rangle^2} = \left[ C_0 e^{-\Gamma \tau} \cos(\sqrt{\Omega} \tau - \tan^{-1}(\Gamma / \sqrt{\Omega})) + C' e^{-\Gamma' \tau} \right]^2 + 1
\]

The fit, using the two additional parameters – an amplitude \((C')\) and relaxation rate \((\Gamma')\), is excellent. The solid line fits to the full set of data in Fig. 4.1 include the additional overdamped mode. The amplitude \(C'\) ranges from a fairly small value, 0.0164, at low \( q_x \) to 0.263 at the largest \( q_x \), while \( \Gamma' \) ranges from 100 kHz to several MHz.

In principle, one could also get an alternation of peak heights by beating scattering from the \( n = 0 \) layer modes with static scattered light from some unrelated source (e.g., optical windows, film holder). However, there are three reasons that this is unlikely to be significant. First, beating with static light would produce a significant,
Fig. 4.3 Analysis of the data for 90 nm 9CB film for $q_x = 32000$ cm$^{-1}$ from Fig. 4.1. The solid blue line is a fit to the standard hydrodynamic theory for a smectic-A film in the underdamped regime (Eq. (4.4)). The blue line is a fit incorporating an additional, overdamped mode (Eq. (4.5)).
degradation in the ratio of signal (zero $\tau$ intercept) to baseline (intercept at $\tau = \infty$) for the data in Fig. 4.1, and also oscillation minima that drop systematically below the baseline, especially at low $q_x$, where one would normally expect static scattering from optical surfaces on either side of the film (or from the film holder) to be concentrated. Neither of these effects is observed in the data. Second, a model based simply on a contribution due to static scattering (i.e., putting $\Gamma' \rightarrow 0$ in Eq. (4.5)) fails in a quantitative fit of the data at large $q_x$. Finally, substantial efforts were made to eliminate static light, including the use of high quality anti-reflection coated windows, extensive shielding of the detector aperture from stray laser light, and the use of a lens to image the film on the detection fiber, which consequently admitted only light scattered from the illuminated volume in the center of the film.

For the 90 nm 9CB film, we also see in Fig. 4.1 that we do not quite reach the cross-over from underdamped to overdamped dynamics at the largest experimental $q_x$. This is expected for thinner films, since the cross-over is predicted when $\Omega = 0$ or, from Eq. (4.3), when $q_x^2 = 8\gamma\rho / \eta^2 d$, which increases with decreasing film thickness $d$.

Data and fitting for the 100 nm 8CB smectic-A film (Fig. 4.4) are qualitatively similar to the 90 nm 9CB results. One aspect deserves special mention, however. At the lowest $q_x$, fewer oscillations are evident and, in fact, the damping is faster than the single decaying exponential factor in Eq. (4.4). This effect is a manifestation of the finite $q_x$ resolution ($\Delta q_x$) of our scattering experiment, rather than any intrinsic physical phenomenon of the film. The main contribution to finite resolution comes from the focusing of the incident, collimated laser beam, from which we estimate $\Delta q_x \approx 1500 \text{cm}^{-1}$. 
We find that fits for a single valued $\Gamma$ (corresponding to a single value of $q_x$) break down noticeably when $q_x$ falls below \(~5\text{-}10\ \Delta q_x\). To account for $\Delta q_x$ in fitting the underdamped correlation data for smaller $q_x$, we averaged the expression

$$e^{-\Gamma(q_x)\tau} \cos[\sqrt{\Omega(q_x)}\tau - \tan^{-1}(\Gamma(q_x)/\sqrt{\Omega(q_x)})]$$

in Eq. (4.4) by applying the integral

$$\frac{1}{\Delta q_x} \int_{q_x - \Delta q_x/2}^{q_x + \Delta q_x/2} dq_x,$$

correctly weighted for the amplitude dependence on $q_x$ given in Eq. (3.83). Since $\Delta q_x$ is experimentally known, no new fitting parameters were introduced.

The resulting fits to the low $q_x$ data are very good, as seen in the examples in Fig. 4.4.
Fig. 4.4 Measured time correlation functions of the intensity of light scattered from layer undulations in a 100 nm thick smectic-A film of 8CB at 7°C below the nematic phase, for various values of the wave vector $q_x$ (in cm$^{-1}$) parallel to the layers.
Fig. 4.5 Intensity time correlation functions measured on a 230 nm thick 9CB film $\approx 0.5^\circ C$ below the smectic-A to nematic transition. The solid lines are fits to Eq. (4.5), the sum of a single underdamped undulation mode plus a purely overdamped mode, whose impact is clearly seen at intermediate $q_s$ where the oscillations ride on top of the additional mode.
Fig. 4.6 Intensity time correlation functions measured on a 240 nm thick 8CB film ≈ 7°C below the smectic-A to nematic transition. The solid lines are fits to a single underdamped undulation mode plus a purely overdamped mode (Eq. (4.5)).
Time correlation data for the intensity of light scattered from the surfaces of 230-240 nm 9CB and 8CB films, presented in Figs. 4.5 and 4.6, reveal a cross-over from under to overdamped layer fluctuation modes at large $q_x$. Also, particularly in the thicker (240 nm) film, we see striking evidence of the additional, overdamped mode (which is not accounted for in the simple hydrodynamic model), as its amplitude increases relative to the underdamped modes in the range $q_x > 16000$ cm$^{-1}$. Indeed, the underdamped modes “ride” on top of the overdamped mode in this range. From the data above $q_x \approx 35000$ cm$^{-1}$ in Fig. 4.6, we see that the relaxation rate of the additional mode is of MHz order, and is at least 10 times lower than relaxation rate of the faster decay associated with the hydrodynamic layer fluctuations. The fits to the highest $q_x$ correlation data in Figs. 4.5 and 4.6 are to a pair of simple exponential decays – the lowest frequency surface layer mode, corresponding to viscoelastic fluctuations in $u$ (relaxation rate $\Gamma - \sqrt{\Omega} \to 2\gamma/\eta_d$ for large $q_x$—see Eq. (4.3)), plus the additional, overdamped mode noted above. The faster layer mode (relaxation rate $\Gamma + \sqrt{\Omega} \approx \eta_s q_x^2/\rho$), associated with damped inertial molecular motion, is too weak to be detected in our experiments. In particular, the amplitude factor for this mode from Eqs. (3.83) and (4.3) is $1 - \Gamma/\sqrt{\Omega}$, which by Eq.(4.3) is very small for large $q_x$.

We summarize the results of this section as follows:

- The correlation function predicted by the standard hydrodynamic model of a smectic-A film is quantitatively successful in describing data obtained at low in-plane wavevector ($q_x < 15000$ cm$^{-1}$) in films of thickness ~100 nm (far within the
“thin” film limit described in section 4.1), and in the regime where inertial, viscous, and elastic forces are all important. In other words, the standard model is most accurate for small $q_d$.

- The standard model does not completely describe our experimental results at large $q_d$, where the contribution of an additional overdamped mode is observed. (However, this mode is not a consequence of higher order ($n \geq 1$) layer modes, involving significant layer compression, since these are of utterly negligible amplitude for $d$ below 1000 nm.)

- The predicted crossover from underdamped to overdamped layer dynamics is observed within the experimental range of $q_s$ for films above ~200 nm thickness.

We next discuss quantitatively the $q_s$ dependence of the fit parameters obtained from our analysis of the correlation data.

### 4.3 Dispersion of the frequency and damping of layer fluctuations in 8CB and 9CB films

The dispersion of the parameters $\Gamma$ and $\sqrt{\Omega}$ for the lowest energy ($n = 0$) underdamped layer modes, obtained from the fits to the correlation data 90-100 nm 9CB and 8CB films described in the previous section, is shown in Figs. 4.7 and 4.8. For small $q_s$, we expect from Eq. (4.3) that $\Gamma$ should be quadratic in $q_s$, $\Gamma = \eta q_s^2 / 2 \rho$, and $\sqrt{\Omega}$ linear in $q_s$ with a slope of $\sqrt{2\gamma / \rho d}$. Our experimental results bear out these predictions for sufficiently low $q_s$ ($q_s \leq 20000$ cm$^{-1}$). However, at larger $q_s$, the data show significant upward deviations: The dashed lines in the figures represent extrapolations of the linear
and quadratic fits for $\sqrt{\Omega}$ and $\Gamma$ at low $q_x$; they clearly underestimate the data at larger $q_x$. In the simple hydrodynamic model, there is no prediction for these deviations; in fact, the full expression for $\sqrt{\Omega}$ in Eq. (4.3) predicts a downward turn at larger $q_x$, which is associated with the crossover to overdamped layer dynamics.

![Fig. 4.7 Dispersion of the frequency and damping for the $n = 0$ layer fluctuation modes of a 90 nm 9CB smectic-A film. Solid lines are a fit based on Eqs. (4.6).]
However, we find that the entire range of data can be fit if we allow additional quartic \((q_x^4)\) terms in Eq. (4.3),

\[
\Gamma = \frac{\eta_3}{2\rho} q_x^2 + \tilde{\Gamma} q_x^4
\]

\[
\Omega = \frac{2\gamma}{\rho d} q_x^2 + \tilde{\Omega} q_x^4 - \Gamma^2
\]

(4.6)

where \(\tilde{\Gamma}\) and \(\tilde{\Omega}\) are coefficients of the quartic correction terms. The solid lines in Figs. 4.7 and 4.8 are four parameter, simultaneous fits of the dispersion data using Eq. (4.6).

With \(d = 90\) nm and the literature value \(\rho = 1.0\) g/cm\(^3\), we find \(\gamma = 29\) erg/cm\(^2\) and \(\eta_3 = 0.0098\) g/cm-s for the 90 nm 9CB film, and, similarly, \(\gamma = 28\) erg/cm\(^2\) and \(\eta_3 = 0.0083\) g/cm-s for the 100 nm 8CB film. The values of surface tension \(\gamma\) obtained here are 5-10\% higher than those reported from mechanical measurements on smectic films of the same compounds\(^5\). This difference is slightly larger than the \(\sim 5\%\) error bar estimated for our light scattering technique.

On the other hand, the values of layer sliding viscosity \(\eta_3\) obtained from our light scattering technique are dramatically lower – \(\sim 40\) to 50 times – than those reported for 9CB and 8CB by mechanical and ultrasonic techniques on thick samples contained between solid substrates\(^6\), or by X-ray photon correlation spectroscopy\(^4,7\) on thick free-standing films. Although one could attribute some reduction in \(\eta_3\) to the fact that free-standing films are essentially free of layer defects (which is certainly not the case with solid substrated samples), it is hard to imagine this accounting for such a large discrepancy (and, in any case, the X-ray studies were also performed on films). A better explanation,
to be amplified on below, is that our light scattering measurement is probing a surface layer viscosity, while the other methods are sensitive to the corresponding bulk viscosity. In the X-ray case, this is because the signal is coming from diffuse scattering off the layer Bragg peak – i.e., from fluctuations integrated over the full stack of layers, and not just the reflectivity from surfaces that give the dominant contribution in our light scattering experiment.

Fig. 4.8 Dispersion of the frequency and damping for the $n=0$ layer fluctuation modes of a 100 nm 8CB smectic-A film. Solid lines are a fit based on Eqs. (4.6).
Similar results for $\gamma$ and $\eta_3$ are obtained from analysis of the data for $\Gamma$ and $\sqrt{\Omega}$ in 230-240 nm 9CB and 8CB films (Figs. 4.9 and 4.10). In these cases, however, the solid line fits encompass a range of $q_x$ through the underdamped-overdamped dynamical crossover. Eq. (4.6) was used to fit the underdamped regime, while the slower branch of the overdamped modes, with relaxation rate $\Gamma - \sqrt{\Omega}$, evaluated from the expressions in

![Graph](image)

Fig. 4.9 Dispersion of the frequency and damping for the $n=0$ layer fluctuation modes of a 230 nm 9CB smectic-A film. Solid lines are a fit based on Eqs. (4.6).
Eq. (4.6), was used above the crossover. The model, including the quartic corrections, provides a very good description over the full range of the data. The fit parameters give $\gamma = 27$ erg/cm$^2$, $\eta_3 = 0.015$ g/cm-s for 230 nm 9CB and $\gamma = 31$ erg/cm$^2$, $\eta_3 = 0.015$ g/cm-s.

Fig. 4.10 Dispersion of the frequency and damping for the $n = 0$ layer fluctuation modes of a 240 nm 8CB smectic-A film. Solid lines are a fit based on Eqs. (4.6).
for 240 nm 8CB. The surface tension values are reasonably consistent in both cases with the numbers obtained in the thinner films, but the values for the layer sliding viscosity are more than 50% larger.

The coefficients of the quartic correction terms $\Gamma$ and $\Omega$ used in the fits in Figs. 4.7 – 4.10 are of order $10^{-11}$ cm$^4$/s and $10^{-3}$ cm$^4$/s$^2$, respectively. The standard hydrodynamic theory for smectic films discussed in Chapter 3 gives a possible mechanism for $\Gamma$, if one combines the full expression for the damping $\Gamma = \eta(\bar{q})q^2/2\rho$, where $\eta(\bar{q})q^2 = \eta_3\bar{q}^2 + \eta'\bar{q}_z^2\bar{q}_z^2/q^2$, with the result from the surface boundary conditions for $q_z^{(0)}$ ($n = 0$ layer modes) expanded to second order in $q_z$ as given in Eq. (3.68). One may then calculate a quartic correction in $q_z$ with coefficient $\Gamma = -\eta'\gamma^2/12\rho B^2$. Stability arguments$^8$ (positive $\Gamma$) imply $\eta' \geq -4\eta_3$ so that taking the most favorable case, $\Gamma = \eta_3\gamma^2/3\rho B^2$, which, using $\eta_3$ and $\gamma$ from our fits and $B = 10^8$ erg/cm$^3$, gives a value of 3 orders of magnitude lower than the fitted value. Moreover, the corresponding quartic correction to the coefficient $\Omega$ is strictly negative. Finally, although the layer curvature elasticity ($Kq_z^4$) does give a positive contribution to $\Omega_z$, it is insignificant even at large $q_z$. Using a typical value of $K = 10^{-6}$ erg/cm and $q_z = 50000$ cm$^{-1}$, we estimate a correction of less than 1%.

In terms of the standard hydrodynamic model for a smectic-A film and prior experiments on bulk smectics, we are thus confronted with two unusual results from our dispersion data: an anomalously low value of layer sliding viscosity $\eta_3$, and the presence of additional terms or corrections in the $q_z$ dependence of the complex frequency for the
lowest energy \((n = 0)\) layer fluctuation modes of the film. The most straightforward explanation for the low value of \(\eta_3\) detected by surface light scattering is to invoke a distinct surface viscosity. To discuss this possibility, we recall some results from the layer hydrodynamics considered in Chapter 3. Using \(v_z = \partial u / \partial t = i\omega u\) (recall \(v_z\) = component of the fluid velocity normal to the layers), we can express Eq. (3.61) as

\[
-\rho(i\omega)^2 u + i\omega\eta_3q_s^2 u + i\omega(\eta_3 + \eta') \frac{\partial^2}{\partial z^2} u + (B \frac{\partial^2}{\partial z^2} - Kq_s^4) u = 0
\]

(4.7)

Here we have left in the \(z\) derivatives, in order to transform to a discrete layer model where it is more convenient to incorporate viscoelastic parameters specifically associated with the surfaces.

The discrete model assumes a set of layer displacements, \(u_1, \ldots, u_N\), where \(N\) is the total number of layers in the film, and \(u_1, u_N\) are the two surface layers. The derivatives

\[
\frac{\partial^2 u}{\partial z^2} \quad \text{become} \quad \frac{u_n - u_{n-1}}{a^2}, \quad \text{where} \quad a \quad \text{is the interlayer spacing.}
\]

Eq. (4.7) is then replaced by a set of \(N\) coupled equations in \(\{u_1, \ldots, u_N\}\):

\[
\begin{align*}
-\rho(i\omega)^2 + i\omega\eta_3 q_s^2 - \frac{\gamma}{a} q_s^2 - Kq_s^4 \biggr) u_1 + \left[ \frac{B}{a^2} - \frac{i\omega(\eta_3 + \eta')}{a^2} \right] (u_2 - u_1) &= 0 \\
-\rho(i\omega)^2 + i\omega\eta_3 q_s^2 - Kq_s^4 \biggr) u_n + \left[ \frac{B}{a^2} - \frac{i\omega(\eta_3 + \eta')}{a^2} \right] [(u_{n+1} - u_n) + (u_{n-1} - u_n)] &= 0 \quad (n = 2, 3, \ldots, N - 1) \\
-\rho(i\omega)^2 + i\omega\eta_3 q_s^2 - \frac{\gamma}{a} q_s^2 - Kq_s^4 \biggr) u_N + \left[ \frac{B}{a^2} - \frac{i\omega(\eta_3 + \eta')}{a^2} \right] (u_N - u_{N-1}) &= 0
\end{align*}
\]

(4.8)

Note that a surface viscosity \(\eta_3^s\) has been introduced, as well as a surface value \(K^s\) for the layer bending modulus. There are \(2N\) solutions \(i\omega^{(n)}\) to Eqs. (4.8) that must be determined.
by matrix algebra. (This differs from the continuum model where there is no cutoff in wavevector corresponding to the interlayer spacing and consequently an infinite sequence of \( q_z^{(n)} \), giving an infinite number of eigenfrequencies.) The algebraic details are complicated, and have been carried out only for the case \( B \gg |\omega (\eta_3 + \eta')| \) and \( \eta_3' = \eta_3 \) (i.e., no distinct surface viscosity)\(^{10} \). We will limit our discussion here to a few general comments.

First, if one assumes thin films, where, for the lowest energy modes, the underlying layers essentially follow the surface (\( u_1 - u_i \approx 0 \) and \( u_N - u_{N-1} \approx 0 \) in particular), one immediately gets frequencies for the surface motion that have damping \( \Gamma = \eta_3 q_z^2 / 2 \rho \). In this case, the viscosity extracted in our surface light scattering experiments could be much smaller than the bulk value simply if \( \eta_3' \ll \eta_3 \). On the other hand, if one couples appreciably to the bulk compressional modes (thick films), the differences in displacements are significant while the surface distortion is relatively small (\( u_1, u_N \) small compared to interior displacements \( u_n \)). In sufficiently thick films, bulk modes (with wavevector \( q_z \sim \pi / d \)) have the lowest energy, and we expect the damping in the roots of Eq. (4.8) to be controlled by the bulk viscosities.

Our second comment concerns the coefficient of the interlayer coupling – namely the factor \( B - i \omega (\eta_3 + \eta') \). When \( i \omega (\eta_3 + \eta') \ll B \), the matrix inversion and calculation of the eigenfrequencies in the discrete model is very much simplified, since one can neglect the \( \omega \) dependence in the interlayer coupling. [In the framework of the continuum model, this corresponds to the parallel simplification of the boundary conditions we assumed]
after Eqs. (3.72) and (3.73).] As a consequence, one gets the standard $q_x$ dependence of the dynamical parameters, $\Gamma \sim q_x^2$ and $\sqrt{\Omega} \sim q_x$, for small $q_x$. However, if $i\omega(\eta_++\eta') \to B$, $\Gamma$ and $\sqrt{\Omega}$ will acquire higher order terms in $q_x$. This can be sketched conceptually if we consider a perturbation analysis in a small parameter $\varepsilon = |\omega(\eta_++\eta')|/B$. The lowest order solutions to Eq. (4.8) (assuming $\varepsilon = 0$) will give $i\omega_{\varepsilon=0} \sim O(q_x^2) + iO(q_x)$. The next order will include terms of $\varepsilon$ and yield corrections of order $\varepsilon \omega_{\varepsilon=0} = \frac{(\eta_++\eta')}{B} |\omega_{\varepsilon=0} | \omega_{\varepsilon=0}$, which in turn will contain terms of higher order in $q_x$ – e.g., $O(q_x^3) + iO(q_x^3)$.

The question now is: when will these higher order corrections be observed? The answer clearly is at high frequency where $\varepsilon \to 1$. Taking $B = 10^8 \text{erg/cm}^3$, bulk values of $\eta_3,\eta' \sim 0.1-1 \text{g/cm-s}$ from the literature$^{11-13}$, and maximum $|\omega| \sim 10^8 \text{s}^{-1}$ from our data in Fig. 4.7-4.10, we get $\varepsilon \sim 0.1-1$, which is certainly significant. Thus at moderate – high values of $q_x$ used in our experiments and in thin films where $|\omega|$ is intrinsically large, we could indeed expect the higher order corrections to the dispersion of $\Gamma$ and $\sqrt{\Omega}$ encountered in the data analysis in Figs. 4.7-4.10.

The discrete model of smectic layer dynamics defined by Eqs. (4.8) and including a distinct surface viscosity $\eta'_s$ can therefore account for the main “anomalous” features we detected in “thin” films. It will clearly be useful for the future to perform a detailed (perhaps numerical) calculation of the eigenfrequencies based on this model.
The large difference between $\eta_3^t$ associated with nearly pure undulatory motion of a “thin” film and the previously reported bulk value $\eta_3$, generally measured on thicker samples, implies that one should see significant increase in the effective $\eta_3$ with increasing film thickness. In fact, we already noted evidence of such a change in the comparison of our results between 90-100 nm and 230-240 nm films. The issue of why $\eta_3^t$ could be so low is clearly a microscopic one. Perhaps the level of chain interdigitation between the surface and subsurface layers is significantly reduced (this could be the case if the surface is flatter on molecular length scales), resulting in substantially reduced friction for surface layer sliding.

4.4 Origin of the additional, overdamped mode observed in the layer dynamics of “thin” films

We now turn to the question of the origin of the additional, overdamped mode observed in our thin film correlation data. As mentioned previously, this mode is not accounted for in the simple hydrodynamic model of smectic-A layer modes, which arise from coupling of layer displacement $u$ to components of the velocity normal to the layers ($v_z$) or parallel to the layer plane and along the in-plane component of the wavevector probed ($v_x$). The dispersion of the additional mode, obtained from the fits of the 230 nm 9CB correlation data in Fig. 4.5, is plotted in Fig. 4.11. Its relaxation rate ($\Gamma'$) shows the qualitative behavior of a hydrodynamic mode ($\Gamma'$ scales with $q_z$) at lower $q_z$, but begins to turn over and level off at larger $q_z$. 
We know of no simple model of a single overdamped mode that can explain this unusual behavior. Instead, we can suggest a dual nature. Consider first the hydrodynamic, overdamped shear wave associated with gradients in $v_y$, the component of the velocity parallel to the film but out of the scattering plane (i.e., $\perp$ to $\vec{q}$). As we discussed in Chapter 3, this mode, though present in the standard hydrodynamic model of a smectic-A, decouples from $u$, and is not expected to contribute to light scattering. However, if the surface of the film is more ordered than the bulk (specifically, more ordered than a smectic-A) – e.g., if the surface molecules are tilted (smectic-C) or if there is some other form of biaxial order on the surfaces – the structure of the viscous dissipation tensor $\sigma'_{ij}$ would be more complicated, and $v_y$ would not generally decouple. In fact, this has been shown in the hydrodynamic theory of a smectic-C. As expressed in Eq. (3.63), the dispersion of the $v_y$ mode has the same form as the damping of the standard $u-v$ layer modes – i.e., $i\omega_{xy} = \eta_B q^2 / \rho$. From the solid line in Fig. 4.11 at lower $q_x$, we can estimate $\eta_B \approx 0.014$ g/cm-s, which is of the same order as the viscosity $\eta_3$ obtained from the $u-v$ modes.

A second dynamical consequence of surface order would be a nonhydrodynamic (i.e., essentially $q$-independent) mode associated with fluctuations of the order parameter (e.g., average molecular tilt in the case of smectic-C order). In fact, the relaxation rate for biaxial order fluctuations such as molecular tilt in smectics is typically in the MHz range (far from the disordering transition). This is the same order that we measure in Fig. 4.11 at larger $q_x$. The nonhydrodynamic nature of an order parameter mode also matches up with the leveling off of the $q_x$ dependence seen in the figure.
Fig. 4.11 Dispersion of the additional, overdamped mode from fits of the correlation data in Fig. 4.5 for the 230 nm 9CB film. Solid lines indicate a “hybrid” origin for this mode, i.e., a combination of hydrodynamic and nonhydrodynamic modes, as discussed in the text. The data interpolates between these modes.

Based on these observations and comments, we propose that the additional, overdamped mode arises from surface order and has a hybrid identity: At low $q_x$, it is
associated with transverse shear of the surface layer (a hydrodynamic mode), while at large $q_x$ (where scattering from hydrodynamic modes is weaker), the additional mode crosses over to a nonhydrodynamic, surface order parameter mode. A more ordered surface relative to the bulk is a common feature of freestanding smectic films\textsuperscript{15} and, as we have argued, provides a single source explanation for the different low and high $q_x$ dispersion of the additional mode observed in our experiment.

In case the additional surface order is associated with higher orientational order (e.g., surface tilt or biaxiality), one might also expect hydrodynamic optic axis (director) fluctuations to be detectable. The cross-section for these vanishes in our polarized (VV) light scattering geometry. We did, however, check for such fluctuations in a depolarized (VH) geometry, but detected no signal at the low laser powers typically used in our studies. This is consistent with the additional order being confined to the two surface layers, and with the order parameter being relatively small.

However, we attempted to test explicitly the proposition of surface order as the source of the additional mode in a different way: We devised a method of altering surface properties of the film without changing film thickness or significantly impacting bulk structure or bulk viscoelastic properties. Though somewhat tentative at present, we believe it could provide an interesting future avenue for research on films. The method involves varying the concentration of a polar solvent in the air atmosphere surrounding the film. We selected 1-propanol as the solvent, and used a 95 nm 8CB film at 25.5C in the smectic-A phase. In our preliminary study, the concentration was varied rather crudely. The solvent was filled into a standard glass vial placed outside, but fixed to the
outer cover, of the hot stage that contained the film. The open top end of the vial was exposed to the film through a 90° aluminum coupling that opened into the hot stage ~30 mm below the center of the film. The vial was heated controllably by a small resistance heater strip, wrapped around the vial and completely external to the hot stage. The temperature of the solvent was independently monitored. Thus, heating the vial provided a means of increasing the propanol vapor pressure surrounding the film. (The boiling point of 1-propanol at atmospheric pressure is 97.5°C.)

The concept is that the solvent will partially wet or perhaps enter the surface layers of the film at low concentration, before dissolving into the bulk and causing layer thinning and film collapse (the molecular structure of propanol is similar to the hydrocarbon tail of the liquid crystal). Such a collapse was in fact observed when we heated the vial to 50°C; film thinning was sudden and catastrophic. With the vial held below 50°C, the film thickness was found to be completely stable (and the same as in untreated air) for periods of several hours over which it was monitored.
Fig. 4.12 Measured correlation functions for the 8CB 95nm film exposed to Propanol at different temperatures. Solid lines are the fit to the hydrodynamic theory discussed in Eq. (4.5)
Fig. 4.13 Dispersion of relaxation mode, amplitude of relaxation mode, surface tension and layer sliding viscosity of 95 nm 8CB film exposed to propanol at different temperatures.
Fig. 4.12 shows correlation functions obtained for $q_x = 25641 \text{ cm}^{-1}$ on the 95 nm 8CB film in air, and in partial propanol atmosphere for vial temperatures of 22, 30, and 40ºC. Note that the second generation, picosecond correlator was used in these measurements; the data clearly confirm the performance of this instrument down to 125 picosec time resolution. The solid lines are fits to Eq. (4.5) (i.e., the same functions used in the analysis of the correlation data in section 4.1). Parameters from these fits are displayed in Fig. 4.13. We note that increasing the propanol concentration in the atmosphere has a dramatic effect primarily on the relaxation rate $\Gamma'$ of the additional, overdamped mode that we have suggested is associated with surface order. There is some decrease in the surface tension $\gamma$ and layer sliding viscosity $\eta_3$, parameters that are associated with the lowest energy ($n = 0$) $u-v$ layer modes, but this variation is modest compared to the ~4 fold increase in $\Gamma'$. 

For the value of $q_x = 25641 \text{ cm}^{-1}$ used, we are in the regime where we previously argued that nonhydrodynamic surface order parameter fluctuations are the dominant contributor to $\Gamma'$. In that case, we can suggest either a reduction in the viscosity associated with these fluctuations due to the propanol-rich atmosphere, or a stiffening of the corresponding surface elastic constant. Whatever the actual mechanism, our preliminary results suggest a strong correlation between surface layer composition / structure and the characteristics of the additional, overdamped mode detected in our light scattering experiments. Our “solvent vapor” studies certainly seem worthy of follow-up.
4.5 Surface light scattering measurements on a “thick” smectic-A film of 9CB

The results of the previous sections have revealed that in “thin” films, where scattering from the lowest energy, nearly pure undulation mode of the film dominates, distinct properties of the surface – layer sliding viscosity, dynamical effects of surface order – are apparently revealed, and that these properties require some fundamental reconsideration of the standard hydrodynamic models for smectic-A films. What happens in the opposite limit of a “thick” film – i.e., a film in which bulk modes (modes involving significant layer compression) are strongly excited and contribute to the polarized light scattering? We should expect the surface fluctuations in this case to be strongly coupled to the bulk modes; the question we wish to address in this section is what mix of bulk / surface parameters are needed to accurately describe these fluctuations.

We produced a 110 \( \mu \)m thick film of the smectic-A liquid crystal 9CB by surrounding the hole in the stainless steel film holder with a thick layer of sample and passing a wiper blade slowly through the sample and across the hole in a horizontal plane, with the temperature held constant about ~0.1 C below the nematic-smectic transition. The sample was then cooled to temperature approximately 2.5 C below the nematic-smectic transition, and the hot stage carefully rotated to a vertical position. The temperature was then held constant throughout the light scattering experiment. As described in Chapter 2, the film thickness was measured by comparing the spacing of interference fringes in light reflected from the film to those produced in reflection from the hot stage outer window (of 1 mm thickness), using a slightly focused laser beam incident at 300 to the film and window normals.
To observe scattering from bulk layer compression modes, the sample thickness \( d \) and/or the scattering vector \( q_x \) must be sufficiently large so that compression costs comparable (or less) energy than surface layer stretching. From our discussion in Chapter 3 (and section 4.1) this will occur when \( q_x^2 \gamma B / d \to 1 \). On the other hand, we would like to keep \( q_x^2 \gamma B / d < 1 \) so that there is still a detectable contribution from the surface modes, and Eq. (4.1) may still be used to lowest order for the appropriate \( q_x^{(n)} \). If we restrict \( q_x \) between 5000 and 20000 cm\(^{-1}\), we estimate that \( q_x^2 \gamma B / d \) ranges between 0.05 and 0.8 for \( \gamma = 29 \) erg/cm\(^2\), \( d = 110 \) µm, and \( B = 10^8 \) erg/cm\(^3\). In this range, we can expect to probe both surface and bulk layer modes. According to the continuum model, the complex frequencies of these modes will be

\[
i\omega_x^{(0)} = \frac{\eta_s q_x^2}{2\rho} \pm i \sqrt{\frac{2\gamma}{\rho d} q_x^2 - \left(\frac{\eta_s q_x^2}{2\rho}\right)^2 (\text{large } d) \frac{2\gamma}{\eta_s d} \frac{\eta_s q_x^2}{\rho}}
\]

\[
i\omega_x^{(n)} = \frac{\eta_s q_x^2}{2\rho} \pm i \sqrt{B \left(\frac{n\pi}{d}\right)^2 - \left(\frac{\eta_s q_x^2}{2\rho}\right)^2 (\text{large } d) \frac{B(n\pi / d)^2}{\eta_s q_x^2} \frac{\eta_s q_x^2}{\rho}}
\]

(4.9)

where we have taken \( q_x^{(n)} \) according to Eq. (4.1), although there should in principle be significant corrections to this equation at the largest \( q_x \) (20000 cm\(^{-1}\)) used in our experiment. We have also ignored the contribution of the layer bending elasticity \( Kq_x^4 \). This should be valid since, for our largest \( q_x \), we estimate \( 2\gamma / d \sim 7000 \) erg/cm\(^3\), \( B(\pi / d)^2 / q_x^2 \sim 30000 \) erg/cm\(^3\), and \( Kq_x^4 \sim 400 \) erg/cm\(^3\).

From Eq. (4.9) and for large thickness \( d \), the lowest energy (small \( n \)) modes should be overdamped, and the slower viscoelastic modes ("-“ roots) will completely
dominate. (In fact, no evidence of the fast inertial modes – the “+” roots, \( \eta q_z^2 / \rho \), in Eq. (4.9) – is observed in our measurements.) The time correlation function for polarized surface scattering from our thick film is then expected to be,

\[
\frac{\langle I_{yy}(0)I_{yy}(\tau) \rangle}{\langle I_{yy}^2 \rangle} \approx \left[ C_0 \exp(-\Gamma_0 \tau) + C_{\text{even}} \sum_{n=2,4,\ldots} \frac{\exp(-\Gamma n^2 \tau)}{\Gamma n^2} + C_{\text{odd}} \sum_{n=3,5,\ldots} \frac{\exp(-\Gamma n^2 \tau)}{\Gamma n^2} \right]^2 + 1 \tag{4.10}
\]

where \( C_0, C_{\text{odd}}, C_{\text{even}} \) are correlation amplitudes, the labels \( \text{odd}, \text{even} \) distinguish between optical factors \( |A_1|^2 \) and \( |A_2|^2 \) (see Eq. (3.42)), and

\[
\Gamma_0 = \frac{2\gamma}{\eta d}, \quad \Gamma_1 = \frac{B(\pi/d)^2}{\eta q_z^2}
\]

(The approximate sign in Eq. (4.10) refers to the assumptions made: neglect of curvature elasticity and use of Eq. (4.1) for the \( q_z^{(n)} \) even though the parameter \( q_z^2 \gamma B / d \) approaches 1 at the largest \( q_z \).) The sums in Eq. (4.10) do not extend out to infinity, because for sufficiently large \( n \) the modes will be underdamped. According to Eq. (4.9), this will occur when

\[
\frac{B}{\rho} \left( \frac{n\pi}{d} \right)^2 \geq \left( \frac{\eta q_z^2}{2\rho} \right)^2
\]

for the range of \( q_z \) used and \( d = 110 \, \mu\text{m} \), we estimate this corresponds to maximum \( n \) ranging from 4 to 70. These modes will be substantially reduced in amplitude, however.

Fig. 4.14 presents correlation data for our 110 \( \mu\text{m} \) 9CB film taken about 2.5\( ^\circ \)C below the SmA-nematic transition. The data are consistent with overdamped dynamics, as expected. The solid lines are fits to Eq. (4.10) with the sums restricted to the
appropriate range for overdamped modes at each $q$. Variable parameters included the three amplitudes $C_0$, $C_{\text{even}}$, and $C_{\text{odd}}$, plus the relaxation rates $\Gamma_0$ and $\Gamma_1$. We observe that the fits are quite good.

Fig. 4.14 Measured correlation data and fits for the 9CB 110$\mu$m thick films. The solid lines are the fit to Eq. (4.10) of the text.
Fig. 4.15 The relaxation rates $\Gamma_0$ and $\Gamma_1$ for the fitted correlation data of the thick films and the solid line shows the fits for $\Gamma_0 = \frac{2\gamma}{\eta s d}$ and $\Gamma_1 = \frac{B(\pi / d)^2}{\eta s q_i^2}$ respectively.
Fig. 4.16 Amplitudes of compression mode and pure undulation with the increasing $q_x$.

The dispersion of $\Gamma_0$ and $\Gamma_1$ is plotted in Fig. 4.15, and the solid lines are simple one parameter fits to Eq. (4.11), which represent the data well and give $2\gamma/\eta_3 d = 10755$ s$^{-1}$ and $B(\pi/d)^2/\eta_3 = 1.63 \times 10^{13}$ s$^{-1}$ cm$^{-2}$. Using $d = 110$ µm and $\gamma = 29$ erg/cm$^2$ (from our thin film data for 9CB discussed in sec. 4.2), we calculate $\eta_3 = 0.49$ g/cm-s and $B = 1.00 \times 10^8$ erg/cm$^3$. These values are in reasonable agreement with literature values.
reported on bulk samples of 9CB from other techniques\textsuperscript{11,16,17}. There is no evidence of anomalous $q_s$ dependence as we saw in the thin films and attributed to complications in the dynamical analysis when $|\omega|\eta_3 = B$. This concern should not apply to our thick film data where $\Gamma_0\eta_3, \Gamma_1\eta_3 \ll B$. Finally, Fig. 4.16 shows the effect of increasing $q_s$ on the amplitudes of the compression modes ($C_{\text{even}} + C_{\text{odd}}$) relative to the nearly pure undulation mode ($C_0$). As expected, the former exhibit a relative increase in amplitude, since the compression modes are weighted by $k_B T / B(\pi / d)^2$, while the undulation mode is weighted by $k_B T / (2\gamma q_s^2 / d)$, which decrease with increasing $q_s$.

It is interesting that in the “thick” film results the viscosity $\eta_3$ calculated from the relaxation rate of the surface mode ($\Gamma_0$) agrees with commonly reported bulk values, and differs from the much lower value extracted from the analysis of our “thin” film data (where the surface mode is underdamped and corresponds to nearly pure undulation). Clearly, a more complete analysis of the crossover from thin to thick film dynamics (as determined by the parameter $q_s^2 \gamma B / d$ in the hydrodynamic equations) is necessary. Such an analysis could be based either on the discrete layer model (Eq. 4.8 in section 4.2) or on a continuum model that incorporates a distinct surface viscosity in the boundary conditions.
4.6 References


CHAPTER 5

RESULTS ON LAYER DYNAMICS IN “THIN” SMECTIC-C AND HEXATIC-B FILMS

In order to explore further the hypothesis of Chapter 4 that the additional, overdamped mode detected in our light scattering experiments on thin smectic-A films is due to enhanced surface order, we performed a series of preliminary studies of layer fluctuations in smectic-C and hexatic-B films in the limit \( q_d / B \ll 1 \) (“thin” film limit).

5.1 Light scattering from layer fluctuations in a “thin” smectic-C film

In this section, we present results of surface light scattering measurements on the smectic-A and C phases of a 270 nm film of the liquid crystal \( \overline{8S5} \). The bulk phases of this material were summarized in Chapter 5, and the film preparation procedure was identical to that used for 9CB and 8CB films, as described in Chapter 2. The light scattering geometry, measuring the VV scattering from spatio-temporal modulations of the film reflectivity, was also the same as in the cyanobiphenyl measurements.

Figure 5.1 shows time correlation functions of the scattered intensity measured as a function of temperature for the 270 nm \( \overline{8S5} \) film using the picosecond correlator, and with in plane wavevector set at \( q_x = 6900 \text{ cm}^{-1} \). The smectic-A – C transition occurs at approximately 56.8°C on cooling. This was confirmed by examining the texture of the film in reflected, depolarized white light; the transition is revealed by enhanced depolarized light scattering and the development of a Schlieren texture. The correlation
data reveal underdamped layer dynamics; the solid lines are five parameter fits to Eq. (4.4), including the additional (overdamped) model we also observed in the thin cyanobiphenyl films discussed in Chapter 4. The fits are very good. Below the Smectic-\(A\) – \(C\) transition (e.g., at 52 and 48\(^\circ\)C), we note that the data oscillates below a nearly flat background, which slowly decays at the longer times (off the edge of the figure). We believe this reflects a weak contribution of tilt director modes, which can contribute in polarized scattering if the tilt directions are not aligned along the polarization axis (i.e., if the tilt direction is degenerate in the layer plane). Crossing the polarizers (VH scattering geometry) clearly revealed dynamic scattering from fluctuations of the in-plane director. Above the transition, we observed no effect of pretransitional tilt fluctuations (i.e., smectic-C order parameter fluctuations) in our VV-polarized back scattering geometry. This could be due to the fact that in backscattering from the bulk, the \(q_z\) probed is very large, and there will be a large elastic energy (and consequently weak scattering) associated with tilt, even close to the transition. It would be useful in the future to make complimentary measurements in a forward scattering geometry, at low scattering angles.

The temperature dependences of the frequency and relaxation rate of the underdamped \(u\)-\(v\) layer modes, and of the additional overdamped mode, obtained from fitting the correlation data in Fig. 5.1 are displayed in Fig. 5.2. The frequency of the underdamped mode is essentially flat as a function of temperature through the \(A\)-\(C\) transition; since for low \(q_x\), the frequency is basically \(\sqrt{2\gamma/\rho d} q_z\), we conclude that the film surface tension is essentially the same in the A and C phases, and we deduce its value is 27.6 erg/cm\(^2\), which is quite typical of thermotropic smectic films. The damping
Fig. 5.1 Intensity time correlation function measured on 270nm $8\bar{5}$ film at different temperatures at $q_x = 6900\text{cm}^{-1}$. The solid lines are the fit to undulation mode plus additional overdamped mode discussed in Eq.(4.5).
Fig. 5.2 Dispersion of the frequency and damping rate for the underdamped mode and additional overdamped mode with temperature at $q_x = 6900 \text{ cm}^{-1}$. 
of the underdamped mode, and also of the additional, overdamped mode, are comparable; the associated relaxation rates essentially double as the temperature is lowered through the transition across the full range of temperatures studied. Given that the relaxation rate of the underdamped mode should be proportional to the layer shear/sliding viscosity \( \eta_3 \), we conclude that \( \eta_3 \) actually decreases slightly as smectic-C order is established in the film.

We also performed a scan of \( q_x \) at a fixed temperature of 46ºC in the smectic-C phase. Fig. 5.3 shows the corresponding measured correlation functions and fits. The expected crossover from under to overdamped layer dynamics is observed at large \( q_x \). The dispersion of the dynamical parameters, plotted in Fig. 5.4, yields a value of \( \eta_3 = 0.045 \text{ g/cm-s} \), somewhat larger than in a similar thickness 8CB film (Chapter 4) but, as in the case of the 8CB film, at least an order of magnitude lower than literature values for the “bulk” shear viscosities. The dispersion of the additional mode (bottom panel of the Fig. 5.4) is clearly hydrodynamic (the fit is to a \( q_x^2 \) dependence). The curvature of this dispersion gives a viscosity coefficient of 0.015 g/cm-s, of the same order as \( \eta_3 \). This result strongly suggests that the identification, proposed in Chapter 4, of the additional mode at low \( q_x \) with the transverse shear wave associated with velocity component \( v_y \) (parallel to the layer plane but perpendicular to the scattering vector \( \vec{q} \)), is reasonable, especially since the broken orientational symmetry of the smectic-C implies that the \( v_y \) mode does not generally decouple from the layer displacement \( u^{1,2} \). (In Chapter 4, we could only speculate that the film surface was more highly ordered than a Smectic-A phase.)
Fig. 5.3 Intensity time correlation function measured on 270nm $8\overline{5}$ film. The solid lines are the fit to undulation mode plus additional overdamped mode discussed in Eq.(4.5).
Fig. 5.4 Top panel is dispersion of the frequency and damping rate for the underdamped mode. Fit gives $\eta = 0.045 \ \text{g cm}^{-1} \ \text{s}^{-1}$ and $\gamma = 28 \ \text{erg cm}^2$. Bottom panel shows damping rate for the additional overdamped mode. Fit gives $\eta = 0.015 \ \text{g cm}^{-1} \ \text{s}^{-1}$ at $T= 46.0 \ ^{\circ}\text{C}$ for a $8\overline{5}5$ film of thickness 270nm.
5.2 Light scattering from layer modes in a “thin” hexatic-B film

Films of the thermotropic liquid crystals 64COOBC were used to probe the effect of in-layer hexatic (or bond orientaitonal) order on the smectic layer dynamics. Here we focus on results from a “thin” 55 nm film. The smectic-A – hexatic-B transition occurs in 64COOBC films at ~56.7ºC. Fig. 5.5 shows correlation data (and fits to Eq. (4.4)) obtained in the smectic-A phase as a function of \( q_x \), while Fig. 5.6 shows the dispersion of the corresponding fit parameters. The surface tension is found to be 28 erg/cm\(^2\), and the viscosity \( \eta \) is 0.027 g/cm-s, again much lower than the typically reported for “bulk” smectics, but substantially higher than smectic-A films of comparable thicknesses for the cyanobiphenyl compounds studied in Chapter 4. The relaxation rate of the additional overdamped mode also reveals the hydrodynamic, low \( q_x \) dependence seen in the other smectic films. The effective shear viscosity obtained from a fit to a parabolic \( q_x \) dependence (solid line in Fig. 5.6) is 0.020 g/cm-s. Once again, it seems reasonable to associate the mode with transverse shear wave (velocity component \( v_y \)), although in the smectic-A phase of 64COOBC, the additional broken symmetry on the surface may be due to hexatic order. It would be useful to investigate whether the detailed form of the viscous dissipation tensor permits a coupling of \( v_y \) to the layer displacement \( u \) (hence allowing fluctuations in \( v_y \) to couple to light scattering from film surface fluctuations).
Fig. 5.5 Measured intensity time correlation function measured on a 55nm thin 64COOBC film at 64 °C. Solid line are the fit based on Eq.(4.4).
Fig. 5.6 Top panel is dispersion of the frequency and damping rate for the underdamped mode. Fit gives $\eta_2 = 0.027 \text{ g cm}^{-1} \text{ s}^{-1}$ and $\gamma = 28 \text{ erg cm}^2$. Bottom panel shows damping rate for the additional overdamped mode. Fit gives $\eta = 0.020 \text{ g cm}^{-1} \text{ s}^{-1}$ for 55nm thin 64COOBC film at 64 °C
We also performed a temperature scan of the correlation function across the *smectic-A – hexatic-B* transition at fixed $q_s = 7700$ cm$^{-1}$. The correlation data and fits are displayed in Fig. 5.7, and the temperature dependence of the dynamic parameters – frequency and relaxation rate of the underdamped layer mode (which is essentially due to film undulation) and the relaxation rate of the additional, overdamped mode – are presented in Fig. 5.8. The frequency – and related surface tension – shows basically no significant temperature dependence, as has been found by other experimental methods of measuring $\gamma$ in hexatics, while the two relaxation rates show only small jumps across the transition.
Fig. 5.7 Intensity time correlation function measured for 55nm thin 64COOBC film at a fixed wave vector $q_x = 7700 \, \text{cm}^{-1}$. Solid line are the fit based on Eq.(4.4).
Fig. 5.8 Temperature dependence of the frequency and damping rate for the overdamped mode and additional underdamped mode at a fixed wavevector \((q_z = 7700 \ cm^{-1})\).
We close this chapter with an interesting suggestion for a future experiment on a crystalline smectic film—e.g., the \textit{crystal-B} phase below the \textit{hexatic-B} in 64COOBC. The elastic free energy of a crystal B phase is\textsuperscript{1,6}

\begin{equation}
F = \frac{1}{2} B (\nabla \cdot u)^2 + \frac{1}{4} C_{44} |\nabla \times u|^2 + \frac{1}{2} K (\nabla^2 u)^2
\end{equation}

where $C_{44}$ is the layer shear elastic constant (and is not zero in a \textit{crystal-B} phase).

Analogously to the discussion in sec. 3.3 of Chapter 3 and sec. 4.4 of Chapter 4, and taking $\mathbf{q}_\perp = q_x$, the dynamical equation for the layer displacement in Fourier space (according to the continuum model) becomes

\begin{equation}
\rho \frac{\partial^2 u}{\partial t^2} + \eta q_x^2 \frac{\partial u}{\partial t} + \left[ B q_x^2 u + \frac{1}{4} C_{44} q_x^2 u + K q_x^4 u \right] = 0
\end{equation}

Solving this equation and imposing the simplified surface boundary conditions (as described after Eq. (3.66)), we find eigenfrequencies for the lowest energy layer modes in a thin film given by

\begin{equation}
\omega_z^{(0)} = \frac{\eta q_x^2}{2 \rho} \pm i \sqrt{\frac{2 \gamma'}{\rho d} q_x^2 - \left( \frac{\eta q_x^2}{2 \rho} \right)^2}
\end{equation}

where $\gamma' = \left( \gamma + \frac{1}{2} C_{44} d \right)$. This result reveals that in a light scattering measurement of a sufficiently thick \textit{crystal-B} film, the surface tension parameter should be enhanced by the bulk shear elastic constant. To see such an effect requires $d \sim 4\gamma / C_{44}$, or for typical $\gamma = 25$ \text{erg/cm}^2 and $C_{44} \sim 10^6$ \text{erg/cm}^3, $d \sim 0.5$ \text{\mu m}. This thickness is well within the practical range for a freestanding film, and, given the capabilities demonstrated in this dissertation, the experiment seems quite feasible.
5.3 Reference


CHAPTER 6

SUMMARY AND CONCLUSION

In this dissertation, we have described results of light scattering experiments on layer fluctuations in freestanding smectic liquid crystal films. Our experiments probe specifically the thermal motion of the film surfaces (which leads to spatio-temporal modulations of the film reflectivity) as a function of in-plane wavevector \( q_x \), in the regime where inertia, damping, and elasticity all make important contributions in the hydrodynamic description of the film motion. For accurate quantitative data, our work benefited crucially from our development of breakthrough instrumentation for photon correlation spectroscopy – namely, two generations of digital correlators whose operation is based on recording arrival times of photons down to nanosecond (and sub-nanosecond) time resolution, and software-processing this record into a short-time correlation function, while simultaneously performing a more standard, long-time correlation (from microseconds out to kiloseconds) in hardware. Thus, gapless correlation spectra of the scattered intensity in light scattering studies are now obtainable in real time starting from the sub-nanosecond regime and extending over 12-13 decades in time, within practical (~1 hr) integration periods at average minimum photon count rates \(~10^4 \text{ s}^{-1}\).

In thin films \( d \ll B / \gamma q_x^2 \), where \( B \) is the layer compression modulus and \( \gamma \) is the surface tension), we confirmed the underdamped nature of the dynamics of the lowest energy fluctuations (simple undulation mode) of the film for small \( q_x \) (in the optical
range), and the cross-over to overdamped dynamics at sufficiently large $q_x$, as predicted by the simple hydrodynamic model. This model corresponds to the limit of smectic hydrodynamics for an incompressible, isothermal film, where a simple balance of elastic restoring forces (surface tension and layer compression) represents the surface boundary condition. In particular, we found that our correlation data for the underdamped film undulation mode can be quantitatively described by the form calculated from the model.

However, we do observe several significant departures from the predictions of the simple model. First, the dispersion of the frequency and damping (relaxation rate) of the lowest energy layer fluctuations contain higher order terms in $q_x^2$ than expected from the model. Second, the effective layer sliding viscosity (the key damping parameter in the model), which is obtained from analysis of the experimental dispersion of the relaxation rate at low $q_x$, is ~50 times lower than the value previously measured by other techniques in bulk samples (thick films or samples contained between solid substrates). Third, we observe an additional overdamped fluctuation mode, which is not anticipated in the simple hydrodynamic description of a smectic-A film. The dispersion of the relaxation rate of this mode has a hybrid nature – hydrodynamic (relaxation rate $\Gamma \sim$ a power of $q_x$) for low $q_x$, and nonhydrodynamic ($\Gamma \sim$ independent of $q_x$) at sufficiently large $q_x$.

We propose that all three “complications” can be explained by two features: First, a more complete surface boundary condition – one that incorporates a distinct surface viscosity and treats, at least perturbatively, the high frequency limit ($i\omega \rightarrow B/\eta$, where $\eta$ is the effective layer viscosity). In this case, we suggest that a discrete layer model of the film hydrodynamics may provide the most useful analytical approach. The second feature
is to consider a higher degree of order on the film surfaces – e.g., biaxial order (surface molecular tilt being a possibility). In this case, one could explain the additional mode and its hybrid dispersion as a combination of (1) coupling of an overdamped, hydrodynamic shear wave, transverse to the scattering plane, to the film undulation at low $q_x$ (a shear mode that, in the simple hydrodynamic model of a pure smectic-A film, decouples from the detected undulations, but that could couple in the case of a smectic-C or similarly biaxial layer), and (2) the contribution of a nonhydrodynamic biaxial order parameter fluctuation that should dominate in scattering amplitude over mechanism (1) at sufficiently large $q_x$.

We performed preliminary experiments in which we specifically tried to alter the surface order on the film by introducing a polar solvent into the surrounding atmosphere – this was shown to primarily affect the parameters (relaxation rate and amplitude) of the additional, overdamped mode, as one might expect if this mode was indeed associated with higher order on the surfaces. These selective “solvent-containing atmosphere” experiments might be quite interesting to follow up on more extensively in the future.

We also investigated undulatory dynamics of smectic-C and hexatic thin films. Our results reveal that the surface tension and layer sliding viscosity vary only weakly with temperature across the smectic-A to smectic-C and smectic-A to hexatic-B transitions. They also support our proposal for the mechanism to generate coupling to an additional, overdamped mode (namely, the effect of higher order than a simple smectic-A, at least on the surfaces), which we observed in films with smectic-A structure in the bulk.
We can point out that two other possible proposals to explain the inadequacies of the simple hydrodynamic model applied to our experiments should be ruled out. First, one could consider a breakdown of the incompressibility assumption. The consequence would be coupling to mass density fluctuations (sound waves). But these modes should be quite fast (> GHz) and underdamped, not relatively slow and overdamped, as we observe for the additional mode in our experiments. Second, there is the so-called breakdown of linear hydrodynamics in smectics due to the higher order terms (required by rotational invariance) in the smectic free energy density – e.g.,

\[ B \left( \frac{\partial u}{\partial z} \right)^2 \rightarrow B \left[ \left( \frac{\partial u}{\partial z} \right)^2 - \frac{1}{2} (V_\perp u)^2 \right] \]

(where \( u \) is the layer displacement along average layer normal \( z \)). As reviewed in deGennes and Prost’s classic book on liquid crystal physics, the dynamical effect of such terms is to renormalize the elastic constant \( B \) and the smectic viscosities. But the correction to the layer sliding viscosity turns out to be only logarithmic in frequency (or in film thickness), and such a slow variation is not sufficient to account for the large discrepancy between the sliding viscosity we observe in “thin” films and that reported for bulk samples.

Interestingly, however, in our studies of thick smectic-\( A \) films (\( d \rightarrow B / \gamma q_x^2 \)), where “bulk” (i.e., layer compressional) modes contribute significantly to the light scattering and all detected modes are overdamped for the full accessible range of \( q_x \), we find rather reasonable agreement with typical bulk values of the hydrodynamic parameters – in particular, the compression elastic constant \( B \) and the effective layer sliding viscosity. This suggests that as the bulk modes get excited and contribute strongly

...
to the experiment, the viscoelastic properties cross over from being characterized by surface parameters to being determined by bulk parameters. Yet the theoretical details of this somewhat facile statement still do not seem to be worked out satisfactorily, and may, in fact, be fairly complicated.

Clearly ultrafast photon correlation spectroscopy combined with surface light scattering represents a promising new technique for the study of layer dynamics in freely suspended smectic films. One can imagine interesting extensions into supported films (i.e., one free surface, the near side of the supporting surface index matched to the sample, the far side antireflection-coated for the laser wavelength, the use of off-specular scattering geometries, etc); columnar liquid crystal films; ferroelectric films; and liquid crystal gel or elastomer films. Indeed the latter could provide a rather extreme test of fast time-domain correlation, since the finite shear modulus of gels and elastomers might raise the frequency of simple thin film undulations by an order of magnitude or more. However, the payoff could be substantial, since liquid crystal elastomers are predicted to exhibit rather spectacular elastic properties, and orientationally ordered gels are also emerging as systems of significant fundamental and practical interest.