

**Dynamic Light Scattering
and
Optical Diffraction in
Cholesteric Liquid Crystals**

by

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Thesis submitted to the Jawaharlal Nehru University
for the award of the degree of
Doctor of Philosophy

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CERTIFICATE

This is to certify that the thesis entitled **Dynamic Light Scattering and Optical Diffraction in Cholesteric Liquid Crystals** submitted by M. S. Giridhar for the award of the degree of DOCTOR OF PHILOSOPHY of Jawaharlal Nehru University is his original work. This has not been published or submitted to any other university for any other degree or diploma.



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List of symbols frequently used in this thesis.

\mathbf{n}	Nematic director
S	Nematic order parameter
n_x, n_y, n_z	Cartesian components of director
P	Cholesteric pitch
q_0	Cholesteric wavevector
q'	Wavevector of non-uniform cholesteric
\mathbf{c}	Smectic c vector
\mathbf{i}	Polarization direction of incident light
\mathbf{f}	Polarization direction of the scattered light
i	Direction of incident light
\mathbf{k}_i	Wavevector of incident light
\mathbf{k}_s	Wavevector of scattered light
θ	Scattering angle
t	Time
T	Total integration time
τ	Delay time
j	Running discrete time index
δt	Discrete time interval Discrete time shift
τ_A	Relaxation time of process $A(t)$
E_s	Scattered electric field
I_s	Incident electric field
$g_1(\tau)$	Electric field autocorrelation function
$g_2(\tau)$	Intensity autocorrelation function
$G_2(\tau)$	Normalized intensity autocorrelation function
ω	Angular frequency of light
$\Delta\mathbf{k}$	Spread in wavevector
r, r'	Points on the detection plane
λ	Wavelength of light
Θ	Angle subtended at the detector by the source
β	DLS coherence factor
Ω	Solid angle subtended by the source at r
$G(\tau_r)$	Relaxation time distribution function
τ_r	Relaxation time
a, b, c	Fit parameters
A, B, C	Cumulant expansion coefficients

\mathbf{I}	Unit tensor
$\underline{\epsilon}$	Dielectric tensor
$\delta\underline{\epsilon}$	Dielectric tensor fluctuation
$\mathbf{D}_i, \mathbf{D}_s$	Incident and scattered displacement field vectors
$\mathbf{E}_i, \mathbf{E}_s$	Incident and scattered electric field vectors
Π	hertz vector
V	Scattering volume
\mathbf{q}	Scattering wavevector
K_1, K_2, K_3	Splay, twist and bend elastic constants
\mathbf{n}_o	Equilibrium orientation of the director
$\delta\mathbf{n}_o$	Fluctuation of the director
Ω_o	Volume element in the Fourier transform
θ_o	Polar angle made by director
ϕ	Director azimuth
$\mathbf{e}_1, \mathbf{e}_2$	Basis vectors in the frame with respect to \mathbf{q}
q_{\parallel}, q_{\perp}	Components of scattering wavevector
$\underline{\epsilon}_m$	Dielectric tensor in the molecular frame of reference
η_a, K_a	Viscosity coefficient and elastic constant of the mode a
τ_a	Relaxation time of mode a
G_1, G_2	DLS geometrical factors
k_B	Boltzmann constant
n_a	Director components in the $(\mathbf{e}_1, \mathbf{e}_2)$ basis
\mathbf{N}_o	Layer normal
V	Scattering volume
$\bar{\mu}$	Average refractive index
Ω	Volume element in Fourier transform
N	Total number of data points
χ^2	measure of goodness of fit
d	Sample thickness
L	Lateral sample size
$\Delta\mu$	Birefringence
μ_e	Extraordinary refractive index
μ_o	Ordinary refractive index
P	Pitch of cholesteric
ϵ_g	Gradient parameter
P_{def}	Deformation parameter
p	Smectic layer thickness, molecular dimensions
ψ	Direction of the diffracted wave

ψ_0	Tilt of the cholesteric sample with respect to scattering plane
θ_z	Director orientation at z in a uniform cholesteric
θ'	Director orientation at z in a non-uniform cholesteric

Preface

This thesis deals with dynamic light scattering (DLS) studies on thermotropic cholesteric liquid crystals, lyotropic nematic liquid crystals and theoretical studies on optical diffraction in non-uniform cholesteric liquid crystals in the phase grating geometry.

In chapter 1, we give an overview of liquid crystals and briefly review the theory of DLS from liquid crystals. The liquid crystal phase is characterized by the fact that it has a degree of molecular ordering that lies in between the short range order of isotropic liquids and the long range three dimensional positional order of crystals. For a material to have a liquid crystalline phase its molecules should be highly anisotropic in shape.

Depending on the type of ordering, liquid crystals themselves are further classified into various sub-phases. The average direction of the molecular orientation is denoted by an apolar unit vector n called the director.

The *nematic* phase is the simplest liquid crystalline phase where the molecules have only long range orientational order but no positional order. If the molecules happen to be chiral or if there are chiral dopants, the *cholesteric* phase occurs where the director uniformly rotates in space as one moves along a direction perpendicular to itself giving rise to a helical structure with a definite pitch. The local structure of the cholesteric phase is the same as that of the nematic. Another form of liquid crystal has a layered structure in addition to nematic like orientational order. Such layered phases are called the smectic phases. The layer spacing is of the order of the molecular length. In these phases, there is a one dimensional quasi-long range ordering along the layer normal and liquid like ordering within the layers. When the director is parallel to the layer normal the phase is called *smectic-A* and when it is tilted in a plane, with respect to the layer normal, the phase is called the *smectic-C* phase. If the molecules are chiral, the *smectic C** phase occurs where the director is not only tilted at a constant angle with respect to the normal in each layer but the azimuth of the tilt precesses uniformly about the layer normal resulting in a helical structure of definite pitch. Other than these commonly occurring liquid crystalline phases there are also

defect proliferated phases like the *twist grain boundary* (TGB) phases and the blue phases. Instead of rod like molecules one can have liquid crystalline ordering arising out of disk like molecules. Such liquid crystals are called *discotic* liquid crystals.

Liquid crystals can also be classified into the *thermotropic* and *lyotropic* types. In thermotropic liquid crystals, phase transitions are brought about by change of temperature. Lyotropic liquid crystals are made up of surfactant molecules dissolved in a solvent, generally water. When such molecules are introduced into a solvent, depending on the concentration, the molecules self-assemble into larger structures of various kinds. These structures arrange themselves with liquid crystalline ordering. Perhaps the most distinguishing factor between thermotropics and lyotropics is that phase changes in lyotropics can be brought about by changing the temperature or the concentration of the solvent relative to surfactant molecules.

The interaction between liquid crystal molecules is very weak. Therefore even at ambient temperatures long wavelength thermal fluctuations of the system are easily excited. These thermal excitations are strongly coupled to the fluctuations of the dielectric tensor of the medium and thus leads to intense scattering of light. Light scattering due to director fluctuations in nematics has been very well studied and it has been shown to be 10^6 times greater than scattering due to normal density fluctuations. We briefly review this theory in the first chapter since it serves as a good introduction to the DLS technique and provides the necessary background for some of the new studies reported in chapters 3, 4 and 6.

DLS is a powerful tool to study the slow dynamics occurring in soft condensed matter systems like polymer solutions, foams, colloidal suspensions, colloidal crystals and liquid crystals. In liquid crystals, the intensity of the scattered light is due to the incessant thermal fluctuations of the director. The intensity autocorrelation function carries information about the relaxation times of the thermally excited modes of director fluctuation in the liquid crystal sample. In general, the scattered light will contain contributions from various modes. By properly selecting the polarizations of the incident and scattered beams and the alignment of the director with respect

to the scattering plane it is possible in some cases to isolate a particular mode. In such cases the intensity autocorrelation function decays with a single exponential. Selecting the right scattering geometry can considerably simplify DLS data analysis. Chapter 2 deals with a part of the instrumentation required for performing DLS experiments. We describe in detail the design, construction and testing of certain electronic modules that were fabricated by us for amplifying the photomultiplier tube (PMT) pulses and for suppressing the noise using pulse height discrimination. This system was used in conjunction with a commercially obtained Malvern digital correlator. DLS involves detecting the rapid intensity fluctuations of the scattered light (on micro second to milli second time scales). These fluctuations are sensed by PMTs specially designed to perform photon counting. The output of the PMT is a rate modulated pulse train containing both signal and noise pulses. The pulse train is amplified by a *pre-amplifier* and passed on to a *discriminator*. The discriminator suppresses the noise and standardizes the signal pulses which are fed to a digital correlator for on-line autocorrelation.

In chapter 3 we describe DLS experiments undertaken to study the director dynamics and thereby determine the viscoelastic coefficients of the liquid crystal. The important area of application of liquid crystals is in the field of display technology. One of the main factors that determines the performance of liquid crystal displays is the viscoelastic coefficient of the material, which is closely related to switching speed of the display. DLS is a versatile method used to determine the viscoelastic coefficients of liquid crystals. Depending on the scattering geometry the different viscoelastic coefficients can be obtained. The experiments performed in this chapter are aimed at investigating the viscoelastic coefficients of cholesteric liquid crystals. These experiments are performed in the back scattering mode where the detector senses the reflected light from the sample. In cholesterics there exist two independent dynamic director modes with wavevectors parallel to the twist axis viz., the twist mode and the umbrella mode. The twist mode involves fluctuations of the director in a plane perpendicular to the helix axis resulting in pitch fluctuations, while the umbrella

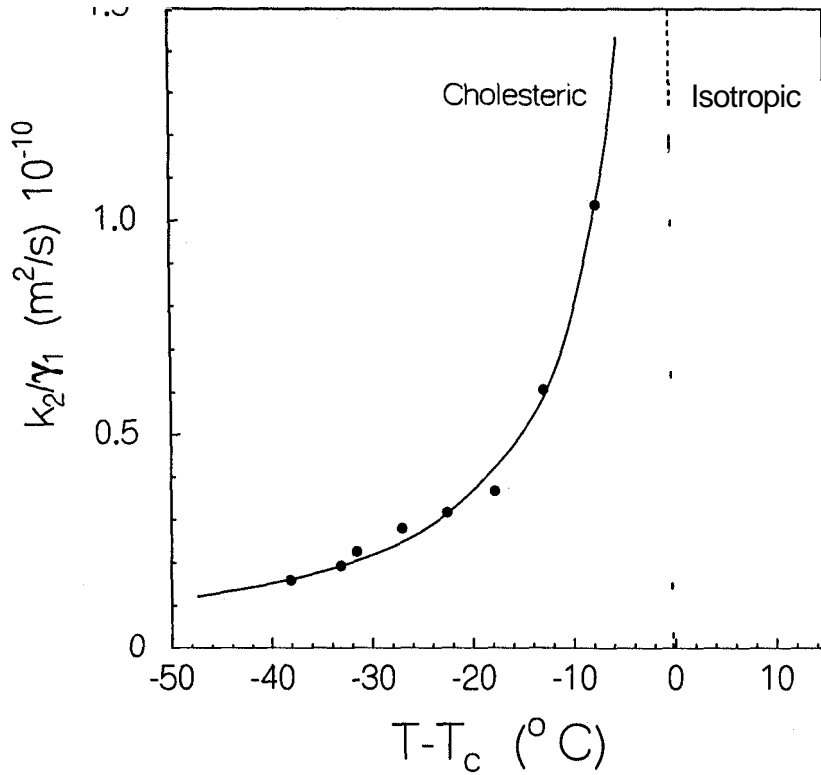


Figure 1: Variation of the viscoelastic coefficient K_2/γ_1 with temperature. The solid line is a guide to the eye. T_c is the cholesteric to isotropic transition temperature.

mode involves out of plane director fluctuations. We have investigated the twist mode fluctuations of cholesteric samples in a wave vector regime comparable to the equilibrium wave vector of the cholesteric. It has been theoretically shown that a twist mode fluctuation of wave vector q has a relaxation frequency

$$\frac{1}{\tau(q)} = \frac{K_2}{\gamma_1}(q - q_0)^2$$

Where $\tau(q)$ is the experimentally obtained relaxation time of the mode with wave vector q . K_2 is the twist elastic constant and γ_1 the twist viscosity coefficient.

By fitting a quadratic function of q to the above dispersion relation we can obtain the viscoelastic coefficient K_2/γ_1 and the equilibrium wave vector q_0 . As a cross check, we compared the values of the pitch obtained from the DLS experiments with those obtained from our experiments on selective reflection in the Bragg mode. The values of the pitch we get from these two methods agree very well. We have obtained the value

of the twist viscoelastic coefficient, K_2/γ_1 over a range of temperatures starting from well within the cholesteric phase to temperatures close to the cholesteric-isotropic' transition. We find the interesting result that K_2/γ_1 diverges as one approaches the transition point. The variation of K_2/γ_1 with temperature is shown in figure(1). Incidentally, these experiments were performed in the backscattering arrangement.

In chapter 4 we describe our DLS experiments on cholesterics where we probe thermal fluctuations with wave vectors perpendicular to the helix axis. Here the light scattering experiment is performed in the forward scattering arrangement unlike the back scattering arrangement as described in the previous chapter. In the forward scattering arrangement, light scattered in the forward direction is detected and analyzed. An analysis of the scattering geometry reveals that the scattered wave vector has components both along and perpendicular to the twist axis of the cholesteric. The intensity autocorrelation function obtained from these experiments were clearly multi exponential. We find the best fit to be a sum of two exponentials to the data and obtain two relaxation times which are fairly well separated. These correspond to a fast and a slow relaxation mode in the system. We observe that the strength of the fast mode decays rapidly with decreasing wavevector and the slow mode has a much weaker dependence of its strength on the scattering wavevector.

In chapter 5 we have studied the diffraction in the phase grating geometry of non-uniform cholesteric liquid crystals. In literature, the optical properties of cholesterics have been studied in two important geometries; the Bragg geometry and the phase grating geometry. In the Bragg geometry light propagates along, or at an angle θ ($0 \leq \theta < \pi/2$) with respect to the helix axis resulting in phenomenon such as selective Bragg reflection which is exploited in applications like thermography. On the other hand, in the phase grating geometry, the light propagates in a direction normal to the helix axis. If the direction of the electric vector of the incident light is perpendicular to the helix axis it senses a periodically varying refractive index and undergoes diffraction. Such diffractive elements find applications as beam couplers in optical signal transmission systems.

In recent times, there has been a lot of interest in non-uniform cholesterics. Sophisticated techniques have been developed using which cholesteric samples with uniform pitch gradients have been prepared. In the Bragg geometry non-uniform cholesterics exhibit wide reflection bands covering the entire visible spectrum. Non-uniform cholesterics have been used to build high efficiency reflective displays. In chapter 5, we study diffraction in the phase grating geometry in non-uniform cholesterics. The non-uniformity being a gradient in the pitch. The two special cases considered are (i) the pitch gradient is symmetric with respect to the center of the sample and (ii) the pitch gradient is asymmetric with respect to the sample center. Our studies show that in both cases, compared to the uniform cholesteric, the diffracted intensity decreases and the diffraction pattern becomes either symmetric or asymmetric depending on the type of non-uniformity. The important results of our investigations are shown in **figure(2)**. For a uniform input beam, each diffraction order becomes broad and in the first case the intensity profile of the order is irregular (**figure 2(c) and 2(d)**) while in the second case it is nearly flat (**figure 2(b)**).

These results for a Gaussian input beam, are shown in **figure(3)**. In the first case, the diffraction profile for each order is asymmetric (**figures 3(c) and 3(d)**). Also, the asymmetry in the profile clearly depends on the type of non-uniformity. In the second case, the profile of the diffraction order, just becomes broad (**figure 3(b)**). In these calculations we have assumed the Gaussian amplitude width to be half the sample size. Our results indicate that even a 5% gradient in the pitch can drastically alter the diffraction profiles. These results have important bearings on the transmission of optical signals employing phase gratings.

In addition, we have also considered two effects that **affect** the profiles of the diffraction orders, *viz.*, the effect of finite sample size and thermal fluctuations of the pitch. From our calculations of the widths of the diffraction orders for uniform cholesteric gratings of various sizes we find that broadening of the orders in samples having

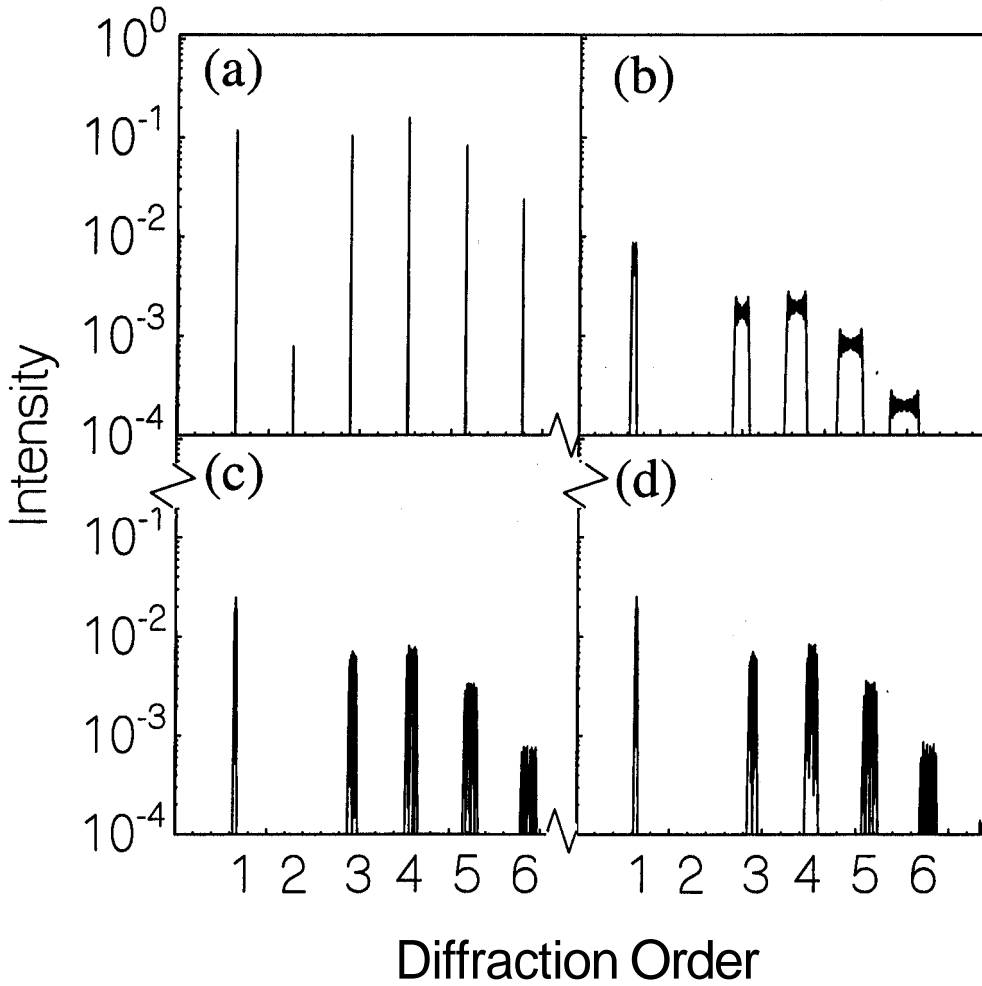


Figure 2: The profiles of the diffraction orders resulting from an input beam of uniform intensity. (a) The near delta function like orders from a uniform cholesteric of pitch $20 \mu\text{m}$. (b) From a cholesteric, where the pitch varies from $20 \mu\text{m}$ at one end of the sample to $22 \mu\text{m}$ at the other end. (c) From a cholesteric, where the pitch varies from $21 \mu\text{m}$ at the sample center to $20 \mu\text{m}$ at the sample ends. (d) From a cholesteric where the pitch varies from $20 \mu\text{m}$ at the sample center to $21 \mu\text{m}$ at the sample ends. In (c) and (d) the profiles of the corresponding diffraction orders are nearly indistinguishable. The values of the parameters used in these calculations are: birefringence, $\Delta\mu=0.07$; lateral sample size, $L = 100$ pitches; thickness, $d=15 \mu\text{m}$ and wavelength of light, $\lambda=0.633 \mu\text{m}$.

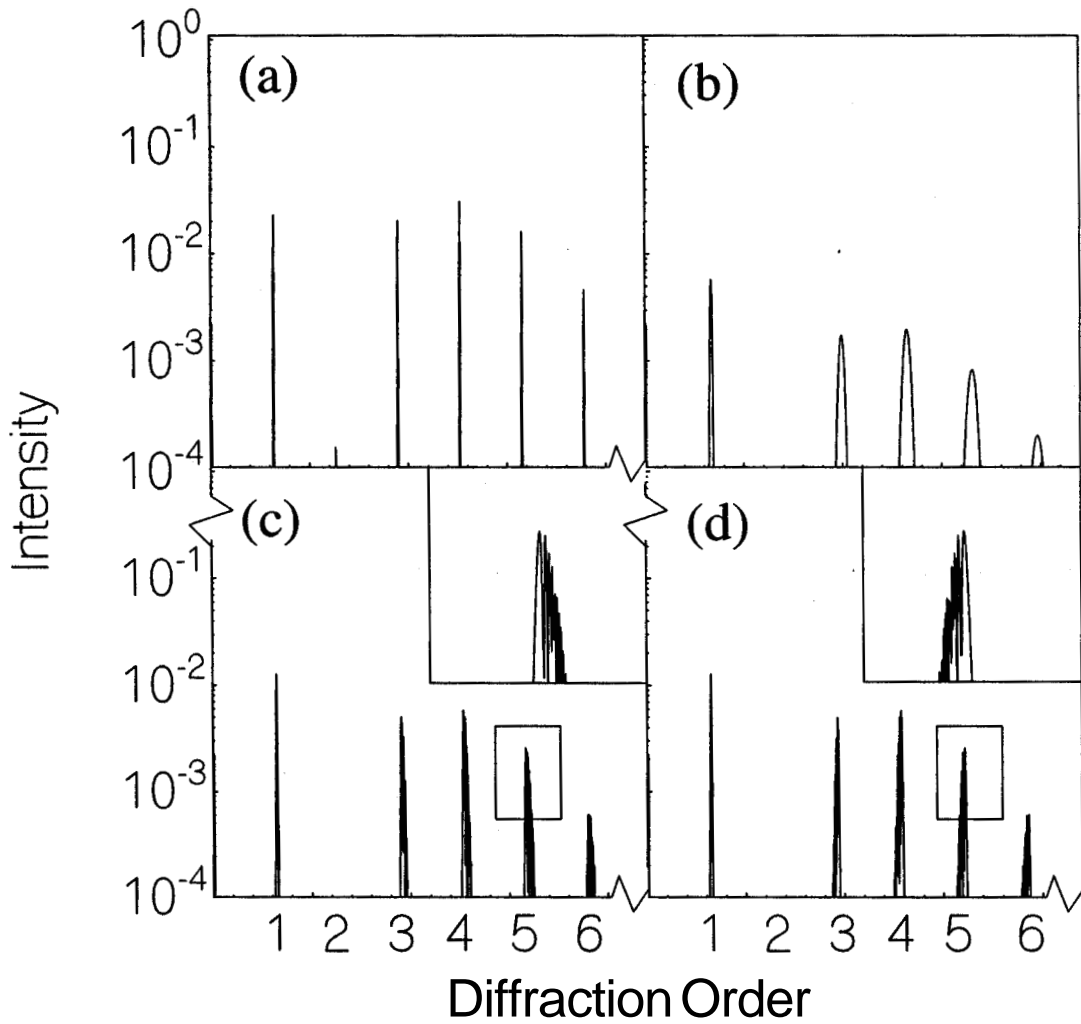


Figure 3: Diffraction orders from the very same structures (described figure(2)) but with a Gaussian input beam. The width of the input beam is a little less than half the sample size. In (c) and (d) the inset shows a magnified view of the fifth diffraction order to highlight the asymmetry in the intensity profiles.

more than 100 pitches is negligible. Hence, all our calculations are performed on samples with 100 pitches. It is well known that in x-ray diffraction from crystals, thermal fluctuations of the lattice give rise to diffuse background and broadening of the diffraction orders. In cholesterics, we have worked out the effect of thermal in-plane fluctuations of the director on the diffraction orders. We find that the effects are not very significant.

Many theoretical studies concerning the diffusion and dynamics of polymers and spherical particles in a oriented liquid crystal environment have been reported in literature. In chapter 6, we describe DLS experiments on the viscoelastic properties of a lyotropic liquid crystal doped with various concentrations of DNA. This has been carried out for DNA of different sizes. One of the experimental problems lies in preparing mixtures where the dopant DNA is homogeneously dispersed in the liquid crystalline medium. For our experiments we have chosen the M13 DNA (≈ 7 kbp) and λ DNA (≈ 48 kbp). The samples prepared with these types of DNA were inspected under a polarizing microscope and found to be homogeneous. The aim of the experiments in this chapter is to systematically study the effect of dispersing well characterized DNA on the viscoelastic modes in the liquid crystalline host. A lyotropic nematic liquid crystal was selected as the host material since it is naturally in an aqueous environment where the DNA can be dispersed homogeneously. The scattering geometry was taken such that the predominant contribution to intensity fluctuations was from the twist mode. We find a systematic dependence of the twist viscoelastic coefficient on the DNA concentration for the λ DNA but no such dependence of the viscoelastic coefficient on the M13 DNA. Our results are depicted in figure(4). In recent times there has been a lot of interest in the study of polymers dispersed in liquid crystalline environments. Such studies are of interest both from the fundamental physics and the applications point of view. The dynamics of polymers in anisotropic environments would lead to interesting effects like anisotropic diffusion. Polymer- surfactant mixtures are known to self assemble into a rich variety of structures. Many applications of such self assembly have been envisaged. Recently,

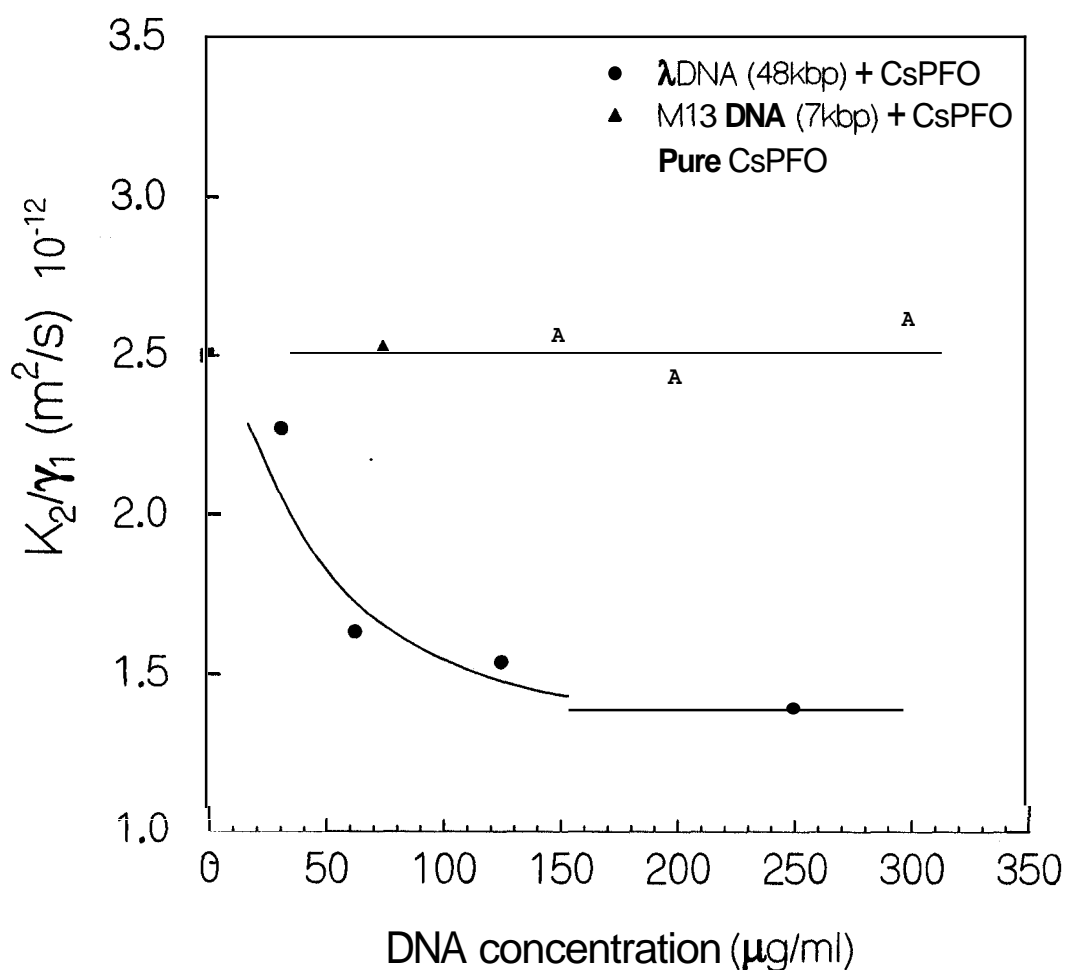


Figure 4: Illustrating the effect of various concentrations of λ DNA and M13 DNA on the twist viscoelastic coefficient of a lyotropic nematic liquid crystal. The solid lines are drawn as a cue to the eye.

attempts have been made to encapsulate biologically important polymers like DNA within such self assembled structures. There have been suggestions that such systems can be used for drug delivery and gene therapy. In this context, our experiments on lyotropic DNA mixtures are an attempt to understand the complex interactions and dynamics of such mixed systems.