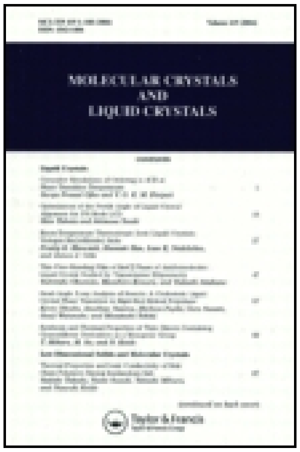

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# Noise Measurements and Anchoring in Liquid Crystals

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# NOISE MEASUREMENTS AND ANCHORING IN LIQUID CRYSTALS

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Abstract The wave-number spectrum of director orientational fluctuations in nematic liquid crystal with interface anchoring is found both for twist-bend and splay-bend deformations and homeotropic alignment. We show that the anchoring energy can be determined from the line broadening due to quasi-elastic Rayleigh scattering from these fluctuations. Our theoretical results are used to estimate the anchoring strength of 5 CB homeotropically aligned by DMOAP silane coated glass interface.

## INTRODUCTION

The preferred orientation of liquid crystal (LC) molecules which is specified by an unit vector $\underline{n}$ - the director - can take on any direction when there is no outside influence. Such a situation of course never occurs since there is always the interaction of LC with the surface of vessel walls. This interaction is usually anisotropic and the corresponding energy is minimum for some direction $\underline{n}_s$ which is called the easy axis. The part of the interfacial energy which defines the direction of $\underline{n}$ is known as the anchoring energy[1]. If the anchoring energy is homogeneous on the whole surface and there is a suitable surface geometry (e.g. two paralel plates with thin layer of LC in between) the LC director is forced to aligne along the easy axis on macroscopic scale. As it is well known, the director gives only the mean, statistically averaged molecular orientation and the local orientation may fluctuate around this equilibrium value.[2] Very strong light scattering is the result of thermal orientational fluctuations in nematic LC. The Orsay group have shown[3] that the fluctuations are overdamped and the noise spectrum of the scattered light is Lorentzian. Their results, have been obtained for an unlimited LC sample and thus any periodic harmonic deformation with any wave vector $\underline{q}$ corresponds to a proper mode of the system. In our opinion the term proper mode needs some clarification. Generally the director reorientation is connected with mass transfer and thus the director field fluctuations are locked with velocity field fluctuations. The rate of director's approach to its mean orientation therefore depends on both director and velocity deviation from equilibrium value. In infinite space with no constraints on director and velocity any periodic harmonic orientational deformation can always create a corresponding velocity distribution with the same wave vector. Both of these coupled fluctuations therefore relax exponentially[4] with the same relaxation time. Boundary conditions destroy the perfect matching. Consequently there are only certain wave vectors for which velocity and director fluctuations are matched. Our goal is to find this spectral law and to show that it can be used to determine the surface anchoring energy.

## FLUCTUATIONS IN NEMATIC WITH SURFACE ANCHORING

We have to proceed by solving the Ericksen-Leslie continuum equations[2] with boundary conditions. We require that the velocity be zero at the interfaces and the angle which the director makes with the easy axis should fulfill the condition

$$\frac{\partial \Theta}{\partial z} = \pm \frac{1}{L} \Theta \qquad (1)$$

on the boundaries z=-d z=+d of homeotropically aligned LC layer with no limits in the x and y directions. Thus the easy axis is paralel with the z axis. L is the extrapolation length[2] and in this case $L = K_3/W$, where W is the surface anchoring energy and $K_3$ is the bend elastic constant. We shall treat the twist-bend and the splay-bend deformations separately. In both cases we confine the fluctuations wave vector to zy plane. This implies that the director fluctuates in zx plane for twist-bend mode and in zy plane for splay-bend mode. Some simplifying assumptions had to be made in order to arrive at the solution.

a/ Since the LC is not limited in the y direction we assume that the proper mode may have any $q_y$ component of the wave vector $\underline{q}$.

b/ We assume to have an initial distribution of angles and velocities corresponding to the proper mode and thus all relaxing with the same relaxation time $\tau$. Therefore we can put

$$\Theta(y,z,t) = \Theta(z)\ \exp(-iq_y y)\ \exp(-t/\tau) \qquad (2)$$

c/ Following other authors[5] we neglect the inertia effects.

Twist-bend deformation

In this case only the $v_x = u$ component of velocity is not identically zero. Neglecting the products of perturbations we get from the continuum equations

$$K_3 \frac{\partial^2 \Theta}{\partial z^2} + K_2 \frac{\partial^2 \Theta}{\partial y^2} - \gamma \frac{\partial \Theta}{\partial t} - \mu_2 \frac{\partial u}{\partial z} = 0 \qquad (3)$$

$$\eta_c \frac{\partial^2 u}{\partial z^2} + \eta_a \frac{\partial^2 u}{\partial y^2} + \mu_2 \frac{\partial^2 \Theta}{\partial z\, \partial t} = 0 \qquad (4)$$

where $K_2$, $K_3$ are the twist and bend elastic constants, $\eta_a$, $\eta_b$, $\eta_c$ are the Miesowicz and $\mu_n$ (n = 1 to 6) are the Leslie viscosities[2]. After putting into Eqs. (3) and (4) the angle $\Theta$ given by Eq. (2) and similar expression for the velocity u we obtained after some manipulations the following differential equation

$$M_1 u^{(4)} + M_2 u^{(2)} + M_3 u = 0 \qquad (5)$$

The differentiations are taken with respect to a dimensionless variable $\xi = z/d$, where d is the semithickness of LC layer, and

$$M_1 = - \eta_c K_3 \tau$$

$$M_2 = d^2(\mu_2^2 - \eta_c \gamma + q_y^2 \tau (K_3 \eta_a + K_2 \eta_c))$$

$$M_3 = \eta_a q_y^2 d^4 ( \gamma - q_y^2 K_2 \tau) .$$

The general solution of this equation is

$$u(\xi) = a_1 \exp(k_1 \xi) + a_2 \exp(-k_1 \xi) + a_3 \exp(k_2 \xi) + + a_4 \exp(-k_2 \xi) \qquad (6)$$

It is easy to show that one of the dimensionless z components of the fluctuations wave vector $\underline{q}$ (let it be $k_1 = k$) is real and the other (let it be $k_2 = iP$) is imaginary. They are coupled by the relation between the roots of quadratic equation

$$k^2 - P^2 = -M_2/M_1 \qquad (7) .$$

The solution for the angle $\Theta$ can be expressed through the velocity u as

$$\Theta(\xi) = \tau((\mu_2^2 d^2 + \eta_a q_y^2 d^2 K_3 \tau) u^{(1)} - \eta_c K_3 \tau u^{(3)})/(\gamma d^2 -$$

$$- q_y^2 d^2 K_2 \tau) \quad (8).$$

We can apply the boundary conditions to these solutions and after some tedious but straightforward algebra we arrive at the selection rules for the dimensionless "wave-number" P (and also for k)

$$\mathrm{cotg}(P) = \frac{F + G(k)\mathrm{cotgh}(k)}{-iG(iP)} \quad (9)$$

for even modes and

$$\mathrm{tg}(P) = \frac{F + G(k)\mathrm{tgh}(k)}{iG(iP)} \quad (10)$$

for odd modes. We have used the abbreviations

$$F = L\,\eta_c d(k^2 + P^2)(\gamma - q_y^2 K_2 \tau) \quad (11)$$

$$G(m) = m\,(\mu_2^2 d^2 + \eta_a q_y^2 d^2 K_3 \tau - \eta_c K_3 m^2 \tau) \quad (12)$$

and m stands either for k or iP. The relaxation time is given by

$$\frac{1}{\tau} = \frac{K_2 q_y^2 - K_3 m^2/d^2}{\gamma - m^2 \mu_2^2/(\eta_c m^2 - \eta_a q_y^2 d^2)} \quad (13).$$

If we put m=iP we arrive at the result of Orsay group[3] for twist-bend mode. The difference is that P can acquire only the values fulfilling the selection rules. Eqs. (7) and (13) can be used to express k and $\tau$ as functions of P. Putting them into Eqs. (9) and (10) we obtain transcedent equations which give for every $q_y$ an infinite but discrete series of possible P wave numbers.

It is interesting to have a look at the solutions for the angle $\Theta$. The even $\Theta(\xi)$ solution is

$$\Theta(\xi) = E_v \left( \frac{\cosh(k\xi)}{\cosh(k)} - \frac{\cos(P\xi)}{\cos(P)} \right) - E_s \frac{\cosh(k\xi)}{\cosh(k)} \tag{14}$$

and the $\Theta(\xi)$ odd solution is

$$\Theta(\xi) = O_v \left( \frac{\sinh(k\xi)}{\sinh(k)} - \frac{\sin(P\xi)}{\sin(P)} \right) + O_s \frac{\sinh(k\xi)}{\sinh(k)} \tag{15}$$

We call $E_v$ and $E_s$ (resp. $O_v$ and $O_s$) the volume and surface amplitude of even respectively odd mode. It is obvious that the angle on the interface is given by the surface amplitude. The surface part of the solutions resembles a surface angular wave which decays exponentially as one goes from the surface deep into the volume. But such a surface wave without the volume part does not fulfill the boundary conditions. The amplitudes are coupled and their ratios are

$$\frac{E_s}{E_v} = \frac{iF}{G(iP)} \operatorname{tg}(P) \qquad \frac{O_s}{O_v} = \frac{iF}{G(iP)} \operatorname{cotg}(P) \tag{16a,b}$$

and only one of them must be determined from the free energy.

Splay-bend deformations

We get from the continuum equations for this case

$$K_1 \frac{\partial^2 \Theta}{\partial y^2} + K_3 \frac{\partial^2 \Theta}{\partial z^2} - \gamma \frac{\partial \Theta}{\partial t} - \mu_3 \frac{\partial v_z}{\partial y} - \mu_2 \frac{\partial v_y}{\partial z} = 0 \tag{17}$$

$$\eta_c \frac{\partial^2 v_y}{\partial z^2} - (\eta_c - \mu_5) \frac{\partial^2 v_z}{\partial z \partial y} + \mu_2 \frac{\partial^2 \Theta}{\partial z \partial t} = 0 \tag{18}$$

$$\eta_b \frac{\partial^2 v_z}{\partial y^2} - (\mu_1 + \mu_5 + \eta_b) \frac{\partial^2 v_y}{\partial y \partial z} + \mu_3 \frac{\partial^2 \Theta}{\partial y \partial t} = 0 \tag{19}$$

$$\frac{\partial v_y}{\partial y} + \frac{\partial v_z}{\partial z} = 0 \tag{20}$$

where $K_1$ is the splay elastic constant. The solutions are substantially more complex for this kind of deformations since there are two components of the velocity vector, $v_y$ and $v_z$ which are not zero. Therefore we shall give only the selection rules and relaxation time which are necessary to the analysis of the noise spectra. For even modes we obtained the selection rule

$$tg(P) = ( A(iP) - B(k_1) + C(k_1)R )/D \tag{21}$$

and for odd modes

$$cotg(P) = - ( A(iP) - B`(k_1) + C`(k_1)R`)/D` \tag{22}$$

with

$$A(m) = m^2(K_3 m^2 \eta_c \tau - (\eta_c + \eta_b + \mu_1)q_y^2 d^2 \tau - \mu_2^2 d^2)$$

$$B(m) = A(m)\ (1 + LC(m)/d)$$

$$C(m) = m\ tgh(m)\ .$$

In these equations m stands for $k_1$, $k_2$ and $k_3$=iP. C\` is obtained from C by changing tgh to cotgh. B\` is obtained from B by changing C to C\`. Further

$$R = ( B(k_2) - B(k_1) )/( C(k_2) - C(k_1) )$$

$$D = LPA(iP)/d - PR$$

and analogously for R\` and D\`. Any of the wave numbers $k_1$, $k_2$ or $k_3$=iP can be put into the equation for the relaxation time

$$\frac{1}{\tau} = \frac{K_1 q_y^2 - K_3 m^2/d^2}{\gamma - \dfrac{(\mu_3 q_y^2 d^2 + \mu_2 m^2)^2}{m^4 \eta_c - m^2 q_y^2 d^2 (\eta_c + \eta_b + \mu_1) + q_y^4 d^4 \eta_b}} \quad (23).$$

The wave numbers $k_1$, $k_2$ and $k_3$ are again not independent but are coupled by the relations for the roots of a cubic equation

$$k_1^2 k_2^2 k_3^2 = q_y^4 d^6 (\mu_3^2 - \eta_b \gamma + K_1 q_y^2 \eta_b \tau)/K_3\, \eta_c \tau \quad (24)$$

$$k_1^2 + k_2^2 + k_3^2 = d^2 (q_y^2 (K_3 (\eta_c + \eta_b + \mu_1) + K_1 \eta_c) + \mu_2^2 - \eta_c \gamma)/K_3\, \eta_c \tau \quad (25).$$

The solutions for the angular deviations from the mean orientation are quite complex but again contain the periodic as well as exponential parts.

The selection rules give for every $q_y$ an infinite but discrete series of possible P wave numbers. The corresponding Eqs. (9), (10) or (21), (22) are transcedent and can be solved only numerically. In Fig. 1 we present the theoretical dependence of relative linewidth change of lorentzian line, $\Delta\Gamma/\Gamma_o$ ($\Gamma = 1/\tau$) with increasing extrapolation length L for the splay-bend fluctuations. We have used the elastic constants and viscosities of 5 CB at 25°C ( $K_1 = 7.5\ 10^{-7}$ erg/cm$^2$, $K_3 = 9\ 10^{-7}$ erg/cm$^2$, $\mu_2 = -0.86$ cP, $\mu_3 = -0.042$ cP, $\gamma = 0.82$ cP, $\eta_b = 0.24$cP, $\eta_c = 1.1$ cP taken from the paper of Skarp et al.[6]), the value of $K_2 = 3.1\ 10^{-7}$ erg/cm$^2$ was taken from the paper of Clark and Leslie[5] and the value $\eta_a = 0.36$ cP was deduced from the extrapolated isotropic viscosity given by Constant and Raynes[7].

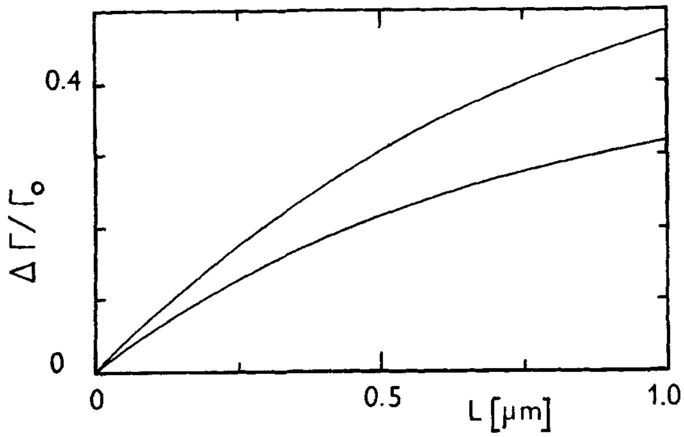


FIGURE 1. Theoretical dependence of relative linewidth change $\Delta\Gamma/\Gamma_o$ on extrapolation length L for 6.2 μm thick sample of 5 CB at 25°C. $q_y$ = 500 $cm^{-1}$, $\Gamma_o$ = 33.3 Hz (upper curve) and 1290 Hz (lower curve). These are the lowest and second lowest even modes. $W=9.10^{-7}/L$ $erg/cm^2$.

The viscosity $\mu_1$ was put equal to zero, but our calculations proved the results to be very insensitive to its actual value.

## EXPERIMENT AND RESULTS

We have used the photon correlation spectroscopy to measure the autocorrelation function of intensity fluctuations (Langley Ford 64 digital correlator) of the modes of a leaky wave-guide. The wave-guide has been formed by a thin layer (6.2 μm) of homeotropically aligned nematic LC 5 CB between two high index (n = 1.943) glass prisms. The surfaces of the prisms were treated with DMOAP silane. A number of leaky modes were excited due to the light scattering on director fluctuations when there was effective coupling of the incident laser beam (He-Ne laser, 5 mW) to one mode of the wave-guide. These modes radiated out of the wave-guide and formed a series of m-lines which could be observed on a screen. The twist-bend and splay-bend modes have been clearly spatially separated because of their different polarization. Having excited the n-th mode with laser beam incident at appropriate angle we measured the autocorrelation function of intensity fluctuations of $m=n\pm1$, $m=n\pm2$, etc. modes. The exciting beam was TM polarized and we have concentrated on TM polarized splay-bend modes which make accessible the small $q_y$ wave-numbers. Heterodyne technique had to be used in this region because of scattering from the prism surface and of the small geometrical factor. The thickness of the sample could be determined from the angular position of the radiating modes.[8] The electric field profile of the n-th mode across the leaky wave-guide is given by $\cos(k_z z)$ (even mode) or $\sin(k_z z)$ (odd mode) with $k_z = n\pi/2d$ (this holds for small n). The scattering of radiation from this mode gives rise to new modes of different m numbers. Their amplitudes are proportional to the integral of the product of the n and m modes' electric field profile and the director angular fluctuations. The LC director angular fluctuations can be decomposed into the proper modes. The selection rules for the $q_z$ wave-numbers of LC modes generally give $q_z$ different from the whole number multiple of $\pi/2d$ and thus all LC modes contribute to the excitation of any optical mode by scattering. This gives a multiexponential decay of autocorrelation function. Performing the integration we find that the amplitudes of modes excited by scattering are proportional to $1/((m\pm n)\pi/2d \pm q_z)$ (these terms come from $\Theta \approx \cos(q_z z)$ or $\Theta \approx \sin(q_z))$ and to $1/((m\pm n)^2 \pi^2/4d^2 + q_z^2)$ (these terms come from $\Theta = \sinh(q_z z)$ or $\Theta \approx \cosh(q_z z)$). Therefore in our preliminary analysis we have supposed that the contributions of all LC modes but the one with $q_z$ wave-number

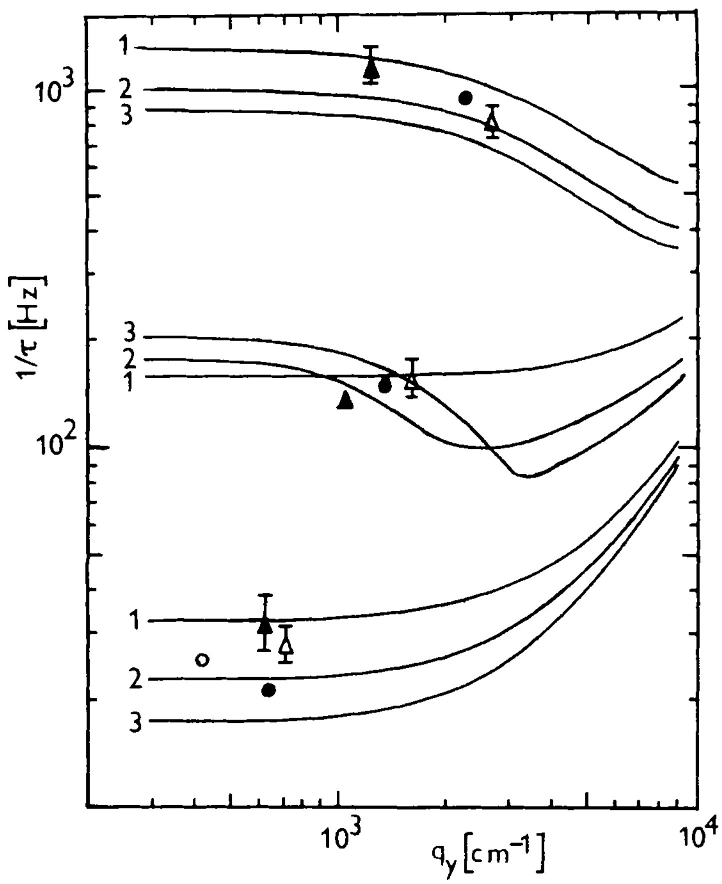


FIGURE 2. The dependence of $1/\tau$ on $q_y$. From bottom to top the series of curves correspond to lowest even, lowest odd and second lowest even modes of LC. Curves 1 are for L=0, curves 2 for L=0.5 μm and curves 3 for L=1 μm.

Δ : n=4 ; m=5, 6, 7 ▲: n=4 ; m=3, 2, 1

●: n=3 ; m=4, 5, 6 o : n=3 ; m=2

where n is the number of laser excited mode and m is the the number of scattering excited mode.

smallest and closest to $(m-n)\pi/2d$ were effectively suppressed.

We have analyzed the autocorrelation function as single-exponential for 1st, 2nd etc. LC mode, starting with the lowest even mode. The experimental results thus obtained as well as the theoretical dependence of $1/\tau$ on $q_y$ for 5 CB at 25°C are depicted on Fig.2. The rather high uncertainty of some experimental points may indicate that in these cases the assumption of single-exponential decay is not suitable. Comparing the experimental and theoretical results we may estimate the anchoring energy of silane treated surfaces to lie in the interval (1.8 - 3.6) $10^{-2}$ erg/cm$^2$. Similar values have been obtained on samples with different thicknesses.

In conclusion, we have shown that surface anchoring in nematic LCs can significantly modify the noise spectra of scattered light. It may lead to multiple correlation times for arbitrary scattering wave-vectors and increase the linewidth of Lorentzian lines. These effects should be taken into account also when light scattering is used to determine the viscosities and elastic constants of liquid crystals.

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