
**Liquid Crystals**
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

# Field quenching of director fluctuations in thin films of nematic liquid crystals

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**To cite this Article** Dunmur, D. A. and Szumilin, K.(1989) 'Field quenching of director fluctuations in thin films of nematic liquid crystals', Liquid Crystals, 6: 4, 449 — 455
**To link to this Article: DOI:** 10.1080/02678298908034189
**URL:** http://dx.doi.org/10.1080/02678298908034189

LIQUID CRYSTALS, 1989, VOL. 6, No. 4, 449–455

# Field quenching of director fluctuations in thin films of nematic liquid crystals

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(*Received 3 March 1988; accepted 13 May 1989*)

The continuum theory of director fluctuations in nematic liquid crystals is extended to take account of finite sample size which more accurately describes experiments on thin films. The effect of external fields on director fluctuations is considered for two cell geometries: (i) the field parallel to the director for materials of positive susceptibility anisotropy, and (ii) the field perpendicular to the director for materials of negative susceptibility anisotropy. In the latter geometry, quenching of fluctuations leads to induced biaxiality. Comparison with experimental results shows that even allowing for the finite size of the sample, there is still a significant disagreement between theory and experiment, especially from thin samples.



## 1. Introduction

Liquid crystals are partially ordered fluids in which molecular orientations (nematics) or molecular positions and orientations (smectics) are correlated over distances equal to many molecular diameters. Restricting attention to molecular orientations, a local unique axis (the director) may be defined as the average (time or spatial) orientation for a molecular direction at some point in the fluid. Depending on external conditions, the director may itself be ordered to produce a monodomain sample of a liquid crystal. Thermal fluctuations in molecular orientations mean that the magnitude of local order will fluctuate as will the orientation of the director, and both effects will influence the macroscopic anisotropic properties of liquid crystal samples. For example the strong light scattering observed from liquid crystals is attributed to fluctuations of the director [1]. Fluctuations may also destroy the symmetry of a nematic phase, and biaxial fluctuation modes have recently been observed using light scattering [2].

The continuum theory of liquid crystals provides a description of their properties in terms of the local material anisotropy associated with the director. Fluctuations in the director are opposed by elastic, forces, and measurements of the mean square amplitude of director fluctuations from light scattering can be related to the Frank elastic constants [3]. The theory of director fluctuations assumes a continuum of fluctuation modes, for which the long and short wavelenth cut-offs are critically important. External fields will quench director fluctuations [13] and this effect has been observed and interpreted for both light scattering [4, 5] and refractive index measurements [6, 7]. Thermally excited director fluctuations will influence the macroscopic anisotropy, and the measured order parameter will be the local order parameter convoluted with director fluctuations [8]. Maier–Saupe theory provides an estimate of the order parameter which is fluctuation free, but it has been shown [9] that molecular field theories based on short range interactions can include director

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fluctuations. Here we consider the continuum approach to director fluctuations, and show that allowing for a finite sample size can affect the predicted physical response to external fields. The calculations are compared with our experimental observations [7, 14]. We also consider the case of fluctuations in a biaxial geometry for a field applied perpendicularly to the director for a material of negative susceptibility anisotropy: differential quenching of uniaxial fluctuations leads to field-induced biaxiality, which has recently been observed [10, 11].

## 2. Theoretical background

The simplest model of a nematic liquid crystal consists of rod-like molecules, the axes of which are partially aligned along the director $\mathbf{n}(\mathbf{r})$. We assume that the optic axis of the positive uniaxial phase is parallel to $\mathbf{n}(\mathbf{r})$ at the point $\mathbf{r}$ in the fluid. The order in the nematic phase can then be characterized by an ordering matrix $S_{\alpha\beta}$

$$S_{\alpha\beta}(\mathbf{r}) = \tfrac{1}{2}S(\mathbf{r})[3n_\alpha(\mathbf{r})n_\beta(\mathbf{r}) - \delta_{\alpha\beta}]. \tag{1}$$

The axes $\alpha$, $\beta$ are space fixed axes and $S(\mathbf{r})$ is the magnitude of the local order parameter, defined with respect to the local director orientation as

$$S(\mathbf{r}) = \langle P_2(i_\alpha n_\alpha(\mathbf{r}))\rangle_{V(\mathbf{r})}. \tag{2}$$

The average is taken over molecules (rod axis $i_\alpha$) within a volume $V(\mathbf{r})$ which is small in comparison with the fluctuations in $\mathbf{n}(\mathbf{r})$. If the magnitude of the local order is independent of position, then the macroscopic order parameter for a system of uniaxial symmetry is

$$S_{zz} = \tfrac{1}{2}S_0\langle(3n_z^2(\mathbf{r}) - 1)\rangle, \tag{3}$$

where the average is over fluctutions in the director orientation, while $S_0$ is the local order parameter defined by equation (2).

In continuum theory small static deformations of a nematic can be expressed in terms of the distortion free energy

$$\mathscr{F} = \frac{1}{2V}\int [k_{11}(\operatorname{div}\mathbf{n})^2 + k_{22}(\mathbf{n}\cdot\operatorname{curl}\mathbf{n})^2 + k_{33}(\mathbf{n}\times\operatorname{curl}\mathbf{n})^2 - \Delta\chi(\mathbf{n}\cdot\mathbf{F})^2]d\mathbf{r}. \tag{4}$$

Here $V$ is the sample volume, $\mathbf{F}$ is the applied field, $\Delta\chi$ is the susceptibility anisotropy, and $k_{11}$, $k_{22}$, $k_{33}$ are the Frank elastic constants for splay, twist and bend, respectively. It is convenient to express the spatial variation of $\mathbf{n}(\mathbf{r})$ in terms of its Fourier components $\mathbf{n}(\mathbf{q})$

$$\mathbf{n}(\mathbf{q}) = \frac{1}{V}\int v(\mathbf{r})\exp i\mathbf{q}\cdot\mathbf{r}\, d^3\mathbf{r} \tag{5}$$

and equation (4) then becomes

$$\begin{aligned}\mathscr{F} = \frac{1}{2V}\sum_q & [k_{11}q_x^2 + k_{22}q_y^2 + k_{33}q_z^2]n_x^2(q) \\ & + 2[(k_{11} - k_{22})q_xq_y]n_x(\mathbf{q})n_y(\mathbf{q}) \\ & + k_{11}q_y^2 + k_{22}q_x^2 + k_{33}q_z^2]n_y^2(\mathbf{q}) \\ & - \Delta\chi[n_x^2(\mathbf{q})F_x^2 + n_y^2(\mathbf{q})F_y^2(\mathbf{q})F_z^2].\end{aligned} \tag{6}$$

An applied field quenches the fluctuations giving rise to an increase in the optical anisotropy, which can be measured through a change in the birefringence. Assuming that fluctuations are small i.e. $n_x$ and $n_y \ll 1$, the experimentally measured quantities can be expressed in terms of the mean square amplitudes of the director fluctuations.

$$\langle n_z^2(\mathbf{r})\rangle = 1 - \langle n_x^2(\mathbf{r}) + n_y^2(\mathbf{r})\rangle = 1 - J \tag{7}$$

and

$$S_{zz} = S_0(1 - 3J/2). \tag{8}$$

The free energy in equation (6) can be diagonalized by an appropriate transformation $(n_x, n_y) \rightarrow (n_1, n_2)$, where $n_1$ and $n_2$ are decoupled modes representing mixtures of splay–bend and twist–bend deformations, respectively. The diagonalized form of the free energy becomes

$$\mathscr{F} + \tfrac{1}{2}\Delta\chi F_z^2 = \frac{1}{2}\sum_q \sum_{\alpha=1,2} n_\alpha^2(\mathbf{q})\lambda_\alpha(\mathbf{q}), \tag{9}$$

where $\lambda_1 = \lambda_+$ and $\lambda_2 = \lambda_-$,

$$\begin{aligned}\lambda_\pm = {} & [(k_{11} + k_{22}))(q_x^2 + q_y^2) + 2k_{33}q_z^2 + 2\Delta\chi F_z^2 - \Delta\chi(F_x^2 + F_y^2)] \\ & \pm [[(k_{11} - k_{22})(q_x^2 + q_y^2) - \Delta\chi(F_x^2 - F_y^2)]^2 \\ & - 4(k_{11} - k_{22})\Delta\chi(F_x^2 - F_y^2)q_y^2]]^{1/2}.\end{aligned} \tag{10}$$

Applying the equipartition theorem to the quadratic contributions to the free energy gives

$$\langle|n_\alpha(q)|^2\rangle = \frac{kT}{V}[\lambda_\alpha(\mathbf{q})]^{-1} \tag{11}$$

and

$$\begin{aligned}J_u(\mathbf{q}) &= \langle n_x^2(\mathbf{q}) + n_y^2(\mathbf{q})\rangle = \langle n_1^2(\mathbf{q}) + n_2^2(\mathbf{q})\rangle, \\ &= \frac{kT}{V}[\lambda_1^{-1}(\mathbf{q}) + \lambda_2^{-1}(\mathbf{q})].\end{aligned} \tag{12}$$

$J_u(\mathbf{q})$ is the contribution of mode $\mathbf{q}$ to the uniaxial director fluctuations; the total is obtained by integrating over all allowed $q$s

$$J = \frac{V}{(2\pi)^3}\int J_u(\mathbf{q})\,d\mathbf{q}. \tag{13}$$

For simplicity we shall only consider those configuratiaons of the field for which there is no macroscopic reorientation of the director, although it must be pointed out that fluctution quenching will also occur during a Freedericksz transition. For a material of positive $\Delta\chi$ a field applied along the $z$ axis will enhance the uniaxial anisotropy along this axis by quenching fluctuations in the $xy$ plane. If the material has a negative anisotropy, then applying a field along the $x$ or $y$ axes will quench the fluctuations in the $yz$ and $xz$ planes, increasing the uniaxial anisotropy along $z$, but also inducing biaxiality through differential quenching in the $xy$ plane.

*Positive $\Delta\chi$: F parallel to z.* This situation has been considered previously [6] with the result

$$J_u(\mathbf{q}) = kTV \sum_{\alpha=1,2} [k_{\alpha\alpha}(q_x^2 + q_y^2) + k_{33}q_z^2 + \Delta\chi F_z^2]^{-1}. \tag{14}$$

*Negative $\Delta\chi$: F perpendicular to z.* As we have explained for this configuration, quenching of director fluctuations increases the uniaxial anisotropy through $J_u(\mathbf{q})$

$$\begin{aligned} J_u^{\perp}(q) = {} & 2kT/V[[(k_{11} + k_{22})(q_x^2 + q_y^2) + 2k_{33}q_z^2 + |\Delta\chi|F_x^2 \\ & + [((k_{11} - k_{22})(q_x^2 + q_y^2) + |\Delta\chi|F_x^2)^2 + 4(k_{11} - k_{22})|\Delta\chi|F_x^2 q_y^2)]^{1/2}]^{-1} \\ & + [(k_{11} + k_{22})(q_x^2 + q_y^2) + 2k_{33}q_z^2 + |\Delta\chi|F_x^2 - [((k_{11} - k_{22})(q_x^2 + q_y^2) \\ & + |\Delta\chi|F_x^2)^2 + 4(k_{11} - k_{22})|\Delta\chi|F_x^2 q_y^2)]^{1/2}]^{-1}], \end{aligned} \tag{15}$$

where we have assumed that the field is along the $x$ axis. Additionally there is a field dependent biaxiality induced, whose magnitude may be related to

$$J_b^{\perp}(\mathbf{q}) = \langle n_x^2(\mathbf{q}) - n_y^2(\mathbf{q})\rangle. \tag{16}$$

In the general case of unequal elastic constants $\langle n_x^2(\mathbf{q}) - n_y^2(\mathbf{q})\rangle \neq \langle n_1^2(\mathbf{q}) - n_2^2(\mathbf{q})\rangle$ and the resulting expression for $J_b^{\perp}(\mathbf{q})$ is rather cumbersome. The evaluation of $J^{\perp}(\mathbf{q})$ for the special case of equal elastic constants will be considered subsequently.



## 3. Application to experiments

### 3.1. *Infinite sample*

Director fluctuations will contribute to measured components of the macroscopic order parameter as a sum over all modes $q$. For an infinite sample the sum may be replaced by an integral as in equation (13); the lower limit of integration is zero, while the upper limit $q_{\max}$ represents some limit to the applicability of the theory. For the two sample configurations considered previously we can obtain the following results for the contribution of director functuations to the measured order parameter.

*Positive $\Delta\chi$: F parallel to z*

$$S_{zz}'' = S_0\left[1 - \frac{3kT}{2\pi^2 k}\left\{q_{\max} - \frac{\pi}{2}\left(\frac{\Delta\chi F_z^2}{k}\right)^{1/2}\right\}\right]. \tag{17}$$

*Negative $\Delta\chi$: F perpendicular to z*

$$S_{zz}^{\perp} = S_0\left[1 - \frac{3kT}{2\pi^2 k}\left\{q_{\max} - \frac{\pi}{4}\left(\frac{\Delta\chi F_x^2}{k}\right)^{1/2}\right\}\right]. \tag{18}$$

For this configuration there is an induced biaxial order due to differential quenching of director fluctuations, given by:

$$S_{xx}^{\perp} - S_{yy}^{\perp} = \langle n_x^2(\mathbf{r}) - n_y^2(\mathbf{r})\rangle = -\frac{3S_0 kT}{8\pi k}\left(\frac{\Delta\chi F_x^2}{k}\right)^{1/2}. \tag{19}$$

In evaluating equations (17)–(19) we have assumed the one constant approximation ($k_{11} = k_{22} = k_{33} = k$). The cut-off $q_{\max}$ does not affect the field-dependent part of the order parameter, but will influence the field-free order parameter.

### 3.2. *Thin film*

Measurements of the effect of external fields on director fluctuations are made on thin films, and this should be accounted for in evaluating the sum over fluctuation modes. Accordingly equation (13) may be written as

$$J = \frac{V}{(2\pi^2)L} \sum_{qz} \int_0^{q_\perp} J_u(\mathbf{q}) d\mathbf{q}, \tag{20}$$

where $z$ is the direction of the shortest film dimension, and the integration is over $q_x$ and $q_y$, which are assumed to be unconstrained. The limit $q_\perp = q^2\max - q_z^2$, and $L$ is the sample thickness. For a field along the director axis of a material of positive susceptibility anisotropy we obtain the result

$$S_{zz} = S_0 \left[ 1 - \frac{3kT}{4\pi Lk} \sum_{q_z} \ln \left( \frac{1 + \zeta^2 q_{\max}^2 + \zeta^2 q_z^2}{1 + \zeta^2 q_z^2} \right) \right], \tag{21}$$

where $\zeta = (k/\Delta\chi F_z^2)^{1/2}$, and the sum in equation (21) can be evaluated for all $qz = n\pi/L$. The change in order parameter resulting from the application of a field becomes

$$\Delta S_F = \frac{S_{zz}(F) - S_{zz}(0)}{S_0} = \frac{3kT}{4\pi Lk} \sum_{q_z} \ln \left[ 1 + \left( \frac{\Delta\chi F^2}{kq_z} \right) \right]. \tag{22}$$

For small values of the field $\Delta S$ varies as the square of the field strength, as observed experimentally.



## 4. Results and discussion

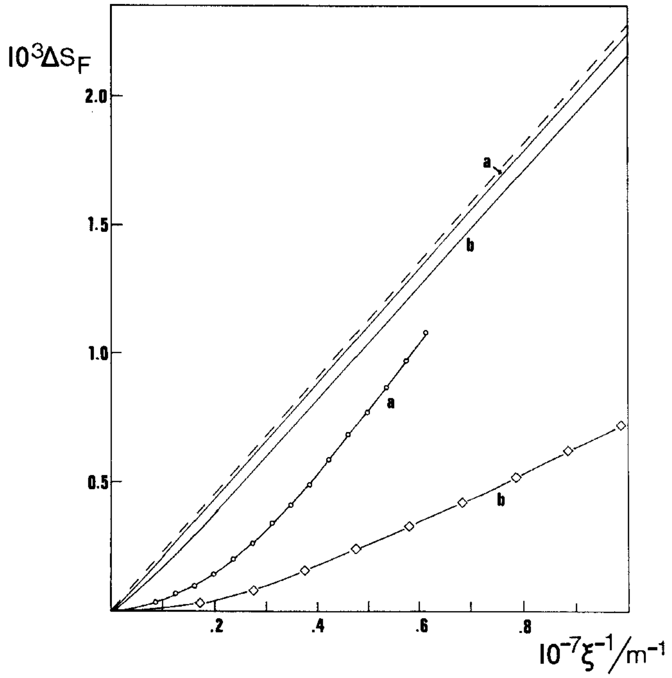
The first point to note is that even in the absence of an external field, director fluctuations contribute to the measured anisotropy, and this effect is dependent on sample dimensions. Our result for the biaxiality in director fluctuations given in equation (19) indicates that there is no field free biaxiality in nematic thin films. However, this result was obtained using the one constant approximation for the Frank elastic constants. If different values are assigned to $k_{11}$, $k_{22}$ and $k_{33}$, then the anisotropic boundary conditions of a thin film should result in induced biaxiality since the mean square amplitudes of director components $\langle n_x^2 \rangle$, $\langle n_y^2 \rangle$ and $\langle n_z^2 \rangle$ will all be different.

This paper is concerned with field effects on director fluctuations, and we have calculated $\Delta S_F$ for an infinite sample and for a thin film. Calculated values for $\Delta S_F$ are plotted in the figure for two nematic film thicknesses (11·8 $\mu$m and 69·3 $\mu$m): full lines are the results calculated using the sum over modes for thin films, while the short dashed lines were obtained using the result in equation (17) for an infinite sample. Experimental results for the two film thicknesses are also included, and it is clear than the observed fluctuation quenching is less than that predicted by theory.

The relationship between the order parameter, and the measured birefringence is

$$\left[ \frac{n_e^2 - n_o^2}{\bar{n}^2 - 1} \right] \propto S_{zz}, \tag{23}$$

where $n_e$ and $n_o$ are the extraodinary and ordinary refractive induces for an assumed uniaxial geometry. The experimental results included in this paper are for the nematic liquid crystal CB5 [15] for which the proportionality constant in equation (23) is




Experimental and theoretical results for field-induced quenching of director fluctuations in thin films of a nematic of positive susceptibility anisotropy. The ordinate is the relative change in order parameter $\Delta S_F$, and the abscissa is the reduced field strength $\zeta^{-1}$. Results are given for CB5 (4-n-pentyl-4′-cyanobiphenyl) at 28°C. (*a*) experimental (○) and calculated results for a film thickness of 69·3 μm. (*b*) experimental (◇) and calculated results for a film thickness of 11·8 μm. The broken line is the calculated result for an infinite sample.

about 0·5. Rearranging this equation gives the following expression for $\Delta s_F$ in terms of the field induced birefringence $\delta(n_e - n_o)F$

$$\Delta S_F = \frac{-2(n_e + n_o)\delta(n_e - n_o)F}{S_0(\bar{n}^2 - 1)}. \tag{24}$$

Here $S_0$ is the field free order parameter in the absence of director fluctuations, and $S/S_0 = (1 - 3kTq_{max}/2\pi^2 k)$ in the absence of a field. If $q_{max}$ is sufficiently small, then $S/S_0 = 1$ and equation (24) becomes

$$\Delta S_F = \frac{\delta(n_e - n_o)F}{(n_e - n_o)}. \tag{25}$$

Experimental results obtained from equation (25) are included in the figure and for both film thicknesses the experimental results are less than the calculated values; the difference is much greater for thin samples. For the thicker sample the experimental high-field slope of $\Delta S_F$ against reduced field strength $\zeta^{-1}$ is close to the theoretical result, bearing in mind that the latter depends on assumed values for the permittivity anisotropy ($\Delta\varepsilon = 11{\cdot}25$) and an average elastic constant of $4{\cdot}35 \times 10^{-12}$ N. There is still no complete explanation for our measurements on thin samples, where the quenching of director fluctuations by a field is much less than predicted. Our model has not included surface quenching of fluctuations, and this may·be important for thin films.

We are grateful to the University of Sheffield Academic Development Fund for a bursary to K. S. Valuable correspondence with Dr. M. Warner and Dr. T. E. Faber is also gratefully acknowledged.

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