Fluctuations of a cholesteric liquid crystal in a static magnetic field

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The normal modes of a cholesteric liquid crystal in the presence of a magnetic field are determined from the hydrodynamical equations. The damping constants of the orientation modes are found to be sensitive functions of the field and exhibit band gaps when their wave vector is an integral multiple of a reciprocal-lattice vector. The results disagree with those of an earlier calculation by Fan, Kramer, and Stephen and reduce to the correct result in the zero-field limit. The light scattered by the modes is discussed in the Born approximation.

I. INTRODUCTION

In the absence of magnetic fields and other perturbing forces, cholesteric liquid crystals have a helical structure.[1] The long axes of the molecules tend to be in planes and in any plane the ordering is like that in a nematic liquid crystal, i.e., the molecular axes tend to be parallel. In a direction perpendicular to these planes (the helical axis) the axes are rotated from point to point and trace out a helical path with a pitch of several thousand angstroms.

A static magnetic field $\vec{H}$ couples to the anisotropy of the magnetic susceptibility χ_a and tends to orient the molecules in the direction of the field (for $\chi_a > 0$).[2,3] If $\vec{H}$ is perpendicular to the helical axis the spiral structure tends to unwind and the crystal becomes nematic at a certain finite critical field.[4,5] When $\vec{H}$ is parallel to the helical axis an intermediate conical structure is stable if the elastic constants satisfy a certain inequality.[2]

In this paper we discuss how the fluctuations in orientation and the light scattering due to these fluctuations are modified when a static magnetic field distorts the crystal. The case when $\vec{H}$ is perpendicular to the helical axis has been discussed by Fan, Kramer, and Stephen[6] who found that the field produced band gaps in the damping constants of the director modes. Quantitatively their results are deficient, however, because they do not reduce to the correct limit when $\vec{H} = 0$. We derive expressions for the modes here which differ from those in Ref. 6 and which reduce to the correct limit when $\vec{H} = 0$.

In Sec. II we briefly review the effect of $\vec{H}$ on the static structure. In Sec. III the normal modes in the presence of $\vec{H}$ are discussed using the hydrodynamical equations. Finally in Sec. IV we consider the light scattering by these modes.

II. STATIC SOLUTIONS

First consider the distortion of the crystal when $\vec{H}$ lies perpendicular to the helical axis.[4] The Frank[7] free energy in the presence of the field can be written as

$$E_0 = \tfrac{1}{2} k_{11}(\nabla \cdot \vec{n})^2 + \tfrac{1}{2} k_{22}(\vec{n} \cdot \nabla \times \vec{n} + q_0)^2 + \tfrac{1}{2} k_{33}(\vec{n} \cdot \nabla \vec{n})^2 - \tfrac{1}{2}\chi_a(\vec{H} \cdot \vec{n})^2 , \tag{2.1}$$

where the k_{ii} are the Frank elastic constants and χ_a is the anisotropy of the magnetic susceptibility. We assume it to be positive and choose $\vec{H} = H\hat{e}_y$. The equilibrium configuration must satisfy the Euler-Lagrange equations[8]

$$\frac{\partial}{\partial x_j}\left(\frac{\partial E_0}{\partial n_{i,j}}\right) - \frac{\partial E_0}{\partial n_i} = 0 \tag{2.2}$$

with the constraint $\vec{n}^2 = 1$. The director $\vec{n}$ is defined in the usual way as a unit vector which lies along the direction of average molecular orientation at each point in space. It can easily be shown from (2.1) and (2.2) that $\vec{n}$ is given by

$$n_x^{(0)} = \cos\phi_0(z), \quad n_y^{(0)} = \sin\phi_0(z), \quad n_z^{(0)} = 0 , \tag{2.3}$$

where we choose the z axis to be the helical axis and where the pitch angle $\phi_0(z)$ is given by $\phi_0(z) = q_0 z$ when $H = 0$. The pitch in zero field is then $P_0 = \pi/q_0$. The magnetic field changes the pitch angle and it is given by

$$k_{22}\frac{d^2\phi_0}{dz^2} + \chi_a H^2 \sin\phi_0 \cos\phi_0 = 0 . \tag{2.4}$$

This has solution

$$\sin\phi_0(z) = \mathrm{sn}(z/\xi k, k) , \tag{2.5}$$

where $\mathrm{sn}(u, k)$ is a Jacobian elliptic function[9] of argument u and modulus k, and where $\xi^2 = k_{22}/\chi_a H^2$. The energy is minimized by choosing k such that

$$q_0\xi = 2E(k)/\pi k\,, \qquad (2.6)$$

and the pitch is given by

$$P(H) = P_0(2/\pi)^2 K(k) E(k) = 2\xi k K(k)\,, \qquad (2.7)$$

where $K(k)$ and $E(k)$ are the complete elliptic integrals of the first and second kinds, respectively. We see that $P(H) \to \infty$ logarithmically as $k \to 1$. From (2.6) this corresponds to a critical field

$$H_c = \tfrac{1}{2}\pi q_0 (k_{22}/\chi_a)^{1/2}\,. \qquad (2.8)$$

Typically $k_{22} \approx 10^{-6}$ dyn, $\chi_a \approx 10^{-6}$ cgs, $q_0 \approx 10^4$ cm^{-1} and this gives $H_c \approx 10^4$ G. At the critical field the helical structure has been completely unwound and we have the so-called magnetically induced cholesteric-nematic phase transition as first discussed by de Gennes.[4]

The effect of a static magnetic field parallel to the helical axis has been considered by Meyer.[2] If the helical axis stays parallel to H we would expect a conical configuration:

$$n_x^{(0)} = \cos\theta \cos q_H z, \quad n_y^{(0)} = \cos\theta \sin q_H z, \quad n_z^{(0)} = \sin\theta\,. \qquad (2.9)$$

According to Meyer such a configuration will be stable only when $k_{33} < k_{22}$ and the magnetic field lies in the range

$$(2/\pi)(k_{33}/k_{22})^{1/2} H_c \leq H \leq (2/\pi)(k_{22}/k_{33})^{1/2} H_c\,. \qquad (2.10)$$

In this range θ and q_H change continuously. Below it there is no perturbation ($\theta = 0$, $q_H = q_0$) and above it complete breakdown to the nematic state ($\theta = \frac{1}{2}\pi$). In the range given by (2.10) we have $q_H = (k_{22}/k_{33})(H/H_c) q_0$ so that the pitch decreases as H is increased.

III. NORMAL MODES

We assume the fluid to be incompressible. The effects of compressibility will be discussed briefly in Sec. IV. The director $\vec{n}$ can be decomposed into a static part $\vec{n}_0$ discussed above and a small time-dependent part $\vec{n}'(\vec{r}, t)$ which represents thermal fluctuations in the fluid. If we consider only those fluctuations which propagate parallel to the helical axis, the modes separate into a twist mode with a time-dependent pitch angle $\phi'(z, t)$ and a conical mode $n_z'(z, t)$. We consider each mode separately.

The equation of motion for the twist mode in the presence of the field is given by[6]

$$\frac{\partial^2 \phi'}{\partial u^2} - \frac{\gamma_1 \xi^2 k^2}{k_{22}} \frac{\partial \phi'}{\partial t} + k^2[1 - 2\,\mathrm{sn}^2(u, k)]\,\phi' = 0\,, \qquad (3.1)$$

where $u = z/\xi k \to q_0 z$ when $H = 0$. γ_1 is a Leslie[10] friction coefficient which has the units of a viscosity. Typically $\gamma_1 = 0.1$ P. We assume a Bloch expansion for $\phi'(z, t)$:

$$\phi'(z, t) = V^{-1/2} \sum_q \phi_q(z)\, e^{-\Gamma_{qH} t}\,; \qquad (3.2)$$

the volume V is included as a convenient normalization.

First consider the case of a small field. Then we can expand the equation to order k^2 where $k^2 = \chi_a H^2 / k_{22} q_0^2$. Inserting (3.2) into (3.1) gives a Mathieu equation in this limit:

$$\frac{d^2\phi_q}{du^2} + (a + k^2 \cos 2u)\,\phi_q = 0\,, \qquad (3.3)$$

with $a = \gamma_1 \Gamma_{qH}/k_{22} q_0^2$ and $u = q_0 z$. The solution of (3.3) to order k^2 [solutions of higher order are of no interest since (3.3) is only valid to order k^2] may be found by standard perturbation methods.[11] The requirement that the solution reduce to the previously known field-free result when $H = 0$ yields a relation between the damping constant Γ_{qH} and the field. The form of the solution depends on the value of the wave vector q and may be written as

(a) $q \ll q_0$ or $q \gg q_0$:

$$\phi_q(z) = e^{iqz} + \frac{k^2}{8}\left(\frac{\exp[i(q + 2q_0)z]}{q/q_0 + 1} - \frac{\exp[i(q - 2q_0)z]}{q/q_0 - 1}\right), \qquad (3.4)$$

$$\Gamma_{qH} \approx k_{22} q^2/\gamma_1 + O(k^4)\,; \qquad (3.5)$$

(b) $q \lesssim q_0$:

$$\phi_q(z) = \cos qz + (\tfrac{1}{4}k)^2 \cos(q + 2q_0)z\,, \qquad (3.6)$$

$$\Gamma_{qH} \approx k_{22} q^2/\gamma_1 - \tfrac{1}{2}(\chi_a H^2/\gamma_1)\,; \qquad (3.7)$$

(c) $q \gtrsim q_0$:

$$\phi_q(z) = \sin qz + (\tfrac{1}{4}k)^2 \sin(q + 2q_0)z\,, \qquad (3.8)$$

$$\Gamma_{qH} \approx k_{22} q^2/\gamma_1 + \tfrac{1}{2}(\chi_a H^2/\gamma_1)\,. \qquad (3.9)$$

There are two solutions and two different values of Γ_{qH} at the transition point $q = q_0$. This means Γ_{qH} has a gap

$$G_1 = \chi_a H^2/\gamma_1 \qquad (3.10)$$

at $q = q_0$ (see Fig. 1). When q is far from q_0 the perturbation is small and Γ_{qH} is essentially the field-free result $k_{22} q^2/\gamma_1$.

For fields comparable to H_c the approximation (3.3) is no longer valid and we must work with the exact equation (3.1). Using (3.2) we can write it in the form of a Lame's equation of order one[12]:

$$\frac{d^2\phi_q}{du^2} + [h - 2k^2 \mathrm{sn}^2(u, k)]\,\phi_q = 0\,, \qquad (3.11)$$

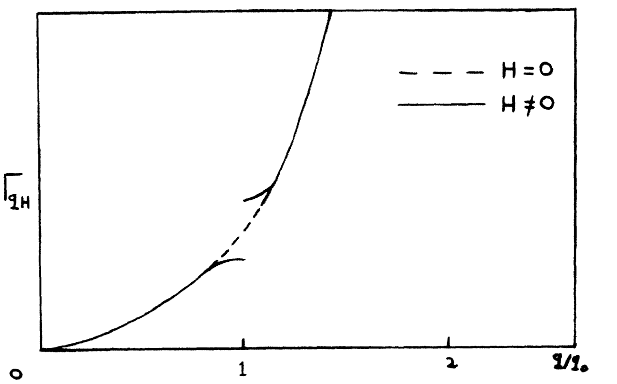

FIG. 1. Dispersion of the damping constant Γ_{qH} for the twisting mode in the presence of a magnetic field perpendicular to the helical axis.

where $h = k^2[(\xi^2\gamma_1\Gamma_{qH}/k_{22}) + 1]$. There exist three simple solutions to (3.11) for certain eigenvalues h. They are the ellipsoidal harmonics of the first order:

$$\begin{aligned}\phi_q(u) &= \mathrm{dn}(u,k), \quad h = k^2\\ &= \mathrm{cn}(u,k), \quad h = 1\\ &= \mathrm{sn}(u,k), \quad h = 1 + k^2 .\end{aligned} \tag{3.12}$$

By expanding the elliptic functions into Fourier series we find that the solutions and damping constants can be written as

(a) $q \ll q_H$:

$$\phi_q(z) = e^{iqz}\left(\frac{\pi}{2K} + \frac{2\pi}{K}\sum_{l=1}^{\infty}\frac{g^l}{1+g^{2l}}\cos 2lq_H z\right), \tag{3.13}$$

$$\Gamma_{qH} \approx 0 ; \tag{3.14}$$

(b) $q \lesssim q_H$:

$$\phi_q(z) = \frac{2\pi}{kK}\sum_{l=1}^{\infty}\frac{g^{l+1/2}}{1+g^{2l+1}}\cos(q+2lq_H)z , \tag{3.15}$$

$$\Gamma_{qH} \approx (1-k^2)(k_{22}/\gamma_1 k^2\xi^2) ; \tag{3.16}$$

(c) $q \gtrsim q_H$:

$$\phi_q(z) = \frac{2\pi}{kK}\sum_{l=1}^{\infty}\frac{g^{l+1/2}}{1-g^{2l+1}}\sin(q+2lq_H)z , \tag{3.17}$$

$$\Gamma_{qH} \approx k_{22}/\gamma_1 k^2\xi^2 . \tag{3.18}$$

In these equations g is the nome and is given by

$$g = e^{(-\pi K'/K)};\ K'(k) = K(k');\quad k^2 + k'^2 = 1 ; \tag{3.19}$$

and

$$q_H = \pi/P(H) = \pi/2Kk\xi . \tag{3.20}$$

The result (3.14) merely shows that the damping constant vanishes with wave vector even in a large field. This is to be expected since a transverse field produces no stabilizing effect on the director. This dispersion relation exhibits a gap but now the gap is shifted to $q = q_H$ corresponding to the increase in pitch. The magnitude of the gap is still given by (3.10) and it approaches the value $(\frac{1}{2}\pi)^2 \times (k_{22}q_0^2/\gamma_1)$ near the critical field. The solutions ϕ_q have the Bloch form associated with a periodic structure of period $P(H)$. The results for Γ_{qH} when expanded to order k^2 reduce to those obtained previously for small fields. They differ from the results for Γ_{qH} given in Ref. 6 which can easily be shown to diverge when $k, H \to 0$. The solutions ϕ_q reduce to the small-field results within a field-dependent normalization factor which may be fixed when correlation functions are computed, for example, and also differ from the results in Ref. 6.

The viscous splay modes discussed in Ref. 6 are also modified by the field. If $\gamma_1 + \gamma_2 \approx 0$ a "slow" conical mode n_z completely decouples from the "fast" viscous waves v_x, v_y. We shall assume this is the case. The Bloch expansion for n_z' is

$$n_z'(z,t) = V^{-1/2}\sum_q n_{qz}(z)\,e^{-\gamma_{qH}t} . \tag{3.21}$$

Using the hydrodynamical equations we can derive an equation for the amplitude n_{qz}:

$$\frac{d^2 n_{qz}}{du^2} + [h + (k_{33}/k_{11})k^2\,\mathrm{sn}^2(u,k)]\,n_{qz} = 0 , \tag{3.22}$$

where $h = (k^2\xi^2/k_{11})(\gamma_1\gamma_{qH} - k_{33}/k^2\xi^2)$. This is a generalized Lame's equation and closed-form solutions are only known when $(k_{33}/k_{11}) = -n(n+1)$ where n is an integer.[12] Such a condition will not, in general, be satisfied. For small fields we can expand (3.22) to order $k^2 = \chi_a H^2/k_{22}q_0^2$. It can then be put in the form of a Mathieu equation

$$\frac{d^2 n_{qz}}{du^2} + (a - b^2\cos 2u)\,n_{qz} = 0 , \tag{3.23}$$

where $a = (\gamma_1\gamma_{qH} - k_{33}q_0^2)/k_{11}q_0^2$, $b^2 = (k_{33}/2k_{11})k^2$, and $u = q_0 z$. The form of the solution again depends on the value of q:

(a) $q \ll q_0$ or $q \gg q_0$:

$$n_{qz} = e^{iqz} - \frac{k_{33}k^2}{16k_{11}}\left(\frac{\exp[i(q+2q_0)z]}{q/q_0+1} - \frac{\exp[i(q-2q_0)z]}{q/q_0-1}\right), \tag{3.24}$$

$$\gamma_{qH} \approx (k_{11}q^2 + k_{33}q_0^2)/\gamma_1 + O(k^4) ; \tag{3.25}$$

(b) $q \lesssim q_0$:

$$n_{qz} = \sin qz - \frac{k_{33}k^2}{16k_{11}}\sin(q+2q_0)z , \tag{3.26}$$

$$\gamma_{qH} \approx [(k_{11}q^2 + k_{33}q_0^2)/\gamma_1][1 - (k_{33}/4k_{11})k^2] ; \tag{3.27}$$

(c) $q \gtrsim q_0$:

$$n_{qz} = \cos qz - \frac{k_{33}k^2}{16k_{11}} \cos(q+2q_0)\,z\,, \qquad (3.28)$$

$$\gamma_{qH} \approx [(k_{11}q^2 + k_{33}q_0^2)/\gamma_1][1 + (k_{33}/4k_{11})k^2]\,. \qquad (3.29)$$

Again there is a gap in the dispersion relation of γ_{qH} at $q = q_0$. The size of the gap is

$$G_2 = \frac{k_{33}}{2k_{11}} \frac{\chi_a H^2}{k_{22}q_0^2} \frac{k_{11}+k_{33}}{\gamma_1} q_0^2 \qquad (3.30)$$

and it involves all three elastic constants. For $q \neq q_0$ γ_{qH} approaches the field-free result. It can be shown that a calculation valid to all orders of k^2 but only to first order in k_{33}/k_{11} gives for the gap size $G_2 = (8k_{33}q_H^2/\gamma_1)[g/(1-g^2)]$ where g is given by (3.19). For small k, $g \approx (\frac{1}{4}k)^2$ and this reduces to (3.30) to first order in k_{33}/k_{11}. As $H \to H_c$ we have $k^2 \to 1$ and G_2 approaches $2k_{33}q_0^2/\gamma_1$.

The effect of a magnetic field parallel to the helical axis can be discussed in the same way. If H is such that the conical configuration (2.9) is stable, the normal modes are the two independent components of $\vec{n}'$ which lie perpendicular to $\vec{n}_0$. They will be coupled together and also will be coupled to the viscous shear modes even when the fluctuations propagate parallel to the helical axis. If θ is small so that the structure is approximately helical the modes propagating along the helical axis will separate into a twist mode (ϕ') and a conical mode (n_z') as in the field-free case. The damping constants will be given by

$$\Gamma_{qH} \approx k_{22}q^2/\gamma_1, \quad \gamma_{qH} \approx (k_{11}q^2 + k_{33}q_0^2 - \chi_a H^2)/\gamma_1\,, \qquad (3.31)$$

where again we have taken $\gamma_1 + \gamma_2 \approx 0$. The damping of the conical mode decreases because the field has an unstabilizing effect on the director and softens the fluctuations. In contrast the twist mode is practically unaffected by the field when θ is small. The opposite case of $\theta \approx \frac{1}{2}\pi$ is easily discussed because then the structure is almost nematic and the normal modes will have approximately the same structure as in a nematic.[13]

IV. LIGHT SCATTERING

In the Born approximation the cross section for light scattering is related to the space-time Fourier transform of the autocorrelation function of the dielectric tensor ϵ_{ij}. Since in a cholesteric

$$\epsilon_{ij} = \epsilon_\perp \delta_{ij} + \epsilon_a n_i n_j\,, \qquad (4.1)$$

where $\epsilon_a = \epsilon_\parallel - \epsilon_\perp$ and $\epsilon_\parallel(\epsilon_\perp)$ is the dielectric constant parallel (perpendicular) to $\vec{n}_0$, fluctuations in $\vec{n}$ modulate the dielectric tensor and thus lead to strong light scattering. The light scattered by the normal modes when $\vec{H} = 0$ has been discussed in Ref. 6. The cross section is proportional to

$$\begin{aligned} I(\vec{q}, \omega) = (\tfrac{1}{2}\epsilon_a)^2 & [1 + \cos^2(\theta+\gamma)](1+\cos^2\theta) \\ & \times [S_1(\vec{q} + 2\vec{q}_0, \omega) + S_1(\vec{q} - 2\vec{q}_0, \omega)] \\ & + [\sin^2(\gamma + 2\theta) + \sin^2(\gamma+\theta)] \\ & \times [S_2(\vec{q} + \vec{q}_0, \omega) + S_2(\vec{q} - \vec{q}_0, \omega)]\,, \end{aligned} \qquad (4.2)$$

where $\vec{q}$ is the momentum transfer, ω is the frequency shift, θ is the angle between the incident ray and the helical axis, and γ is the scattering angle. $S_1(q, \omega)$ is the power spectrum of the twist mode

$$S_1(q, \omega) = \frac{2k_B T}{k_{22}q^2} \frac{\Gamma_q}{\omega^2 + \Gamma_q^2}\,, \qquad (4.3)$$

and $S_2(q, \omega)$ is the power spectrum of the conical mode

$$S_2(q, \omega) = \frac{2k_B T}{k_{11}q^2 + k_{33}q_0^2} \frac{\gamma_q}{\omega^2 + \gamma_q^2}\,. \qquad (4.4)$$

The evaluation of the cross section for arbitrary values of $\vec{H}$ when $\vec{H}$ is perpendicular to the helical axis is quite complicated and we will not discuss the general case here. However to order k^2 the cross section is unchanged from the field-free case (4.2) except that in (4.3) Γ_q is replaced with Γ_{qH} and in (4.4) γ_q is replaced with γ_{qH}. The magnetic field has little effect on the intensity of scattered light but significantly changes the width of the Rayleigh line and produces band gaps at $q = q_H$. Notice that the conical mode scatters light most strongly when $q = q_0$ whereas the twist mode scatters light most strongly when $q = 2q_0$. Also the two contributions have a different angular dependence. Thus the two modes should be separable experimentally.

A magnetic field parallel to the helical axis has the effect of softening fluctuations in the conical mode n_z' (provided that the static distortion is small). Therefore we should see an increase in the intensity scattered by this mode when the field is applied.

We have assumed throughout that the fluid is incompressible. In a compressible fluid there will be sound wave modes as well as the overdamped modes discussed here. It can be shown, because of the smallness of the orientational elastic constants that the sound wave approximately decouples from the director modes and is not affected by a static magnetic field. One can see this qualitatively by comparing the energy associated with a twist deformation ($k_{22}q_0^2$) and a magnetic deformation ($\chi_a H^2$) with the energy of the sound wave ($\rho_0 c^2$) where c is the sound velocity. Thus compressibility always plays a negligible role in the structure of the overdamped director modes.

In conclusion we have found that a static magnetic field applied perpendicular to the helical axis significantly changes the width of the Rayleigh lines due to the overdamped director modes. The most unique feature of the dispersion relation is the presence of band gaps in the damping constants when $q = q_H$. Our results differ from those given in an earlier calculation[6] and reduce to the correct limit when $H = 0$. When the field is parallel to the helical axis the damping constant of the conical mode decreases and the light scattered by it increases. There are no band gaps in this case.

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