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Publisher: Taylor & Francis

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## Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:

<http://www.tandfonline.com/loi/gmcl16>

### Fluctuations and Light Scattering in a Compressible Cholesteric Liquid Crystal

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Version of record first published: 21 Mar 2007.

To cite this article: J. D. Parsons & Charles F. Hayes (1975): Fluctuations and Light Scattering in a Compressible Cholesteric Liquid Crystal, *Molecular Crystals and Liquid Crystals*, 29:2, 295-309

To link to this article: <http://dx.doi.org/10.1080/15421407508083207>

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# Fluctuations and Light Scattering in a Compressible Cholesteric Liquid Crystal

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*(Received December 31, 1973; in final form April 5, 1974)*

The normal modes of a compressible cholesteric liquid crystal are determined from the hydrodynamical equations of Ericksen and Leslie for the case of the propagation vector parallel to the helical axis. Besides the overdamped twisting and viscous-splay modes present in the incompressible case we find a sound wave mode which couples to orientation and produces a propagating twist wave. The results are not restricted to wavelengths large compared to a pitch. The sound wave contributes six lines to the Brillouin spectrum at frequencies  $\pm cq$ ,  $\pm c(q \pm 2q_0)$ , where  $c$  is the sound velocity,  $q$  the momentum transfer and  $q_0 = \pi/P_0$  where  $P_0$  is the pitch. The twist wave contributes only to the latter four lines and its intensity dominates near the condition for Bragg scattering.

## I INTRODUCTION

Cholesteric liquid crystals are composed of long rodlike optically active molecules which tend to have a helical structure with a pitch  $P_0$  of several thousand ångströms.<sup>1,2</sup> In any plane perpendicular to the helical axis the ordering is nematic like, but the direction of orientation rotates as one translates along the helical axis. The periodic structure leads to strong Bragg scattering of light and several other remarkable optical properties.

If a beam of monochromatic light is passed through one of these materials there will be scattering due to fluctuations in pressure and entropy, just as in an ordinary fluid.<sup>3</sup> The fluctuations in pressure propagate at the speed of sound and lead to a Brillouin doublet. The width of these lines is related to dissipative processes like viscosity and thermal conduction which damp out the waves. The fluctuations in entropy are nonpropagating and lead to a Rayleigh line centered about the incident frequency. There will also be addi-

tional scattering due to fluctuations in orientation. For a nematic liquid crystal it has been shown<sup>4</sup> that the fluctuations in orientation dominate the Rayleigh spectrum at long wavelengths. Similarly in a cholesteric, orientation fluctuations will dominate the spectrum when the condition for Bragg scattering is fulfilled.<sup>5</sup> In this paper we evaluate the slowly relaxing modes of a compressible cholesteric and discuss the light scattering by them.

The normal modes and light scattering from an incompressible cholesteric liquid crystal have been discussed by Fan, Kramer, and Stephen.<sup>6</sup> They showed that there are two slowly relaxing overdamped modes which should be observable by Rayleigh scattering. One is a twisting and untwisting of the helical structure and the other is a mixed viscous splay mode.

The mode structure of a compressible cholesteric was discussed by Lubensky<sup>7</sup> for wavelengths large compared to the pitch. He found damped sound waves as well as the overdamped twisting mode found earlier.<sup>6</sup> Like nematics,<sup>8</sup> the damping constant was strongly anisotropic, but even with the Frank elastic theory the sound velocity turned out to be very slightly anisotropic. However the viscosity tensor used by Lubensky is characteristic of an arbitrary uniaxial system with the symmetry axis being simply the helical axis. This approximation is only valid when the wavelengths are large compared to the pitch. In this picture, the damping constant of the sound wave will not involve the local director at all, but only the helical axis, which is the direction of macroscopic symmetry breaking. When the wavelength of sound becomes comparable to the pitch this will no longer be true and the detailed nature of the order perpendicular to the helical axis becomes important.

We treat here a compressible cholesteric using the Ericksen-Leslie continuum approach which is not restricted to wavelengths large compared to a pitch. In this picture the viscosity tensor is *locally* uniaxial with the symmetry axis being the local director, just as in the nematic case. Of course this implies that the viscosity in the cholesteric is a periodic function of position along the helical axis since the local director is. If we are only interested in fluctuations whose wavelengths are much larger than the pitch then the two pictures are equivalent, since the periodicity averages out over several pitches. In addition our viscosity tensor reduces to the nematic case<sup>8,9</sup> when the pitch becomes large. This is a feature which must be present in any complete theory since a cholesteric is a twisted nematic. The hydrodynamical equations are solved for the normal modes. We find, besides the overdamped twisting and viscous splay modes present in the incompressible case,<sup>6</sup> a sound wave mode whose dispersion relation is similar to that in an ordinary fluid provided that it propagates along the helical axis. It couples to orientation and causes an orientation wave which is found to be a pure twist. Our methods are not rigorous in the sense that we cannot show rigorously that the line shapes of the modes are Lorentzian in the small  $q$  limit. However, any deviation from

Lorentzian shape for these modes is probably of order  $q_0 a$  ( $a$  = molecular length) which is always small in a real cholesteric.

The Brillouin scattering spectrum is discussed using the Born approximation and the Oseen<sup>11</sup>–deVries<sup>12</sup> optical model. We find six lines whose maxima lie at frequencies  $\omega = \pm cq, \pm c(q \pm 2q_0)$ , where  $q$  is the difference in wavevector between the incident and scattered light,  $\omega$  is the corresponding frequency shift,  $c$  is the sound velocity in the medium, and  $q_0 = \pi/P_0$ . The sound wave contributes to all six lines, whereas the twisting wave contributes only to the latter four, and dominates near the condition for Bragg scattering  $q = 2q_0$ . The viscous splay modes mentioned above are found to be completely uncoupled from the sound wave modes to first order when the fluctuations propagate parallel to the helical axis. Hence they give no contribution to the Brillouin spectrum.

In Sect. II, the Ericksen–Leslie continuum theory is modified slightly to apply to compressible cholesterics, and dispersion relations for the modes are derived. In Sect. III we discuss the damping due to thermal conductivity and derive a new term in the damping constant due to orientation fluctuations and absent in an ordinary fluid. A brief discussion of structural relaxation mechanisms important at low frequencies is also given. In Sect. IV, the relevant correlation functions are derived and these are applied in Sect. V to the calculation of the light scattering from these modes. Finally, in Sect. VI the spectrum is discussed in the light of experimental results and suggestions for future experiments are made.

## II HYDRODYNAMICS AND NORMAL MODES

Following Frank<sup>13</sup> we introduce at each point in space a unit vector  $\mathbf{n}$ , the director, which lies along the direction of average molecular orientation at that point. In an unperturbed nematic in equilibrium  $\mathbf{n}$  has constant direction, whereas in a cholesteric  $\mathbf{n}$  has spiral symmetry:

$$n_x^{(0)} = \cos q_0 z, n_y^{(0)} = \sin q_0 z, n_z^{(0)} = 0 \quad (2.1)$$

where the  $z$ -axis is taken to be the helical axis. The part of the free energy density depending on orientation is

$$E_0 = \frac{1}{2}k_{11}(\nabla \cdot \mathbf{n})^2 + \frac{1}{2}k_{22}(\mathbf{n} \cdot \nabla \mathbf{x} \mathbf{n} + q_0)^2 + \frac{1}{2}k_{33}(\mathbf{n} \cdot \nabla \mathbf{n})^2 \quad (2.2)$$

In a compressible cholesteric there may be additional terms in (2.2) due to the dependence of pitch on pressure and temperature, however they will be shown to be negligible in Sect. III. The equilibrium configuration must satisfy the Euler–Lagrange equations:<sup>14</sup>

$$\frac{\partial}{\partial x_j} \left( \frac{\partial E_0}{\partial n_{i,j}} \right) - \frac{\partial E_0}{\partial n_i} = 0 \quad (2.3)$$

with the constraint  $\mathbf{n}^2 = 1$ . We note that since the pitch is large on a molecular scale, the continuum expressions (2.2) and (2.3) can be used even when  $\mathbf{n}$  varies appreciably over a pitch. In equilibrium, and in the absence of external forces, (2.1) is readily shown to be a solution of (2.3), as expected.

To discuss dynamics, Ericksen<sup>15</sup> and Leslie<sup>16</sup> imagined a time dependent director  $\mathbf{n}(r, t)$  which in the static limit reduced to the Frank director  $\mathbf{n}(r)$ . In addition, there are the velocity, temperature, and pressure fields which appear in the hydrodynamics of an ordinary fluid. Omitting unnecessary nonlinear terms we have:

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{v}) = 0 \quad (2.4)$$

$$\frac{\partial}{\partial t} (\rho v_i) + (T_{ij} + t_{ij}), j = 0 \quad (2.5)$$

where  $\rho$  is the mass density and  $\mathbf{v}$  the fluid velocity. The reactive part of the stress tensor is given by

$$T_{ij} = p\delta_{ij} - \prod_{kj} n_{k,i} - E_0\delta_{ij} \quad (2.6)$$

where  $p$  is the pressure,  $E_0$  is given by (2.2) and

$$\prod_{ij} = -\frac{\partial E_0}{\partial n_{i,j}} \quad (2.7)$$

The dissipative part of the stress tensor is taken to be:

$$\begin{aligned} t_{ij} = & -\alpha_1 n_k n_p d_{kp} n_i n_j - \alpha_2 n_i \dot{n}_j^* - \alpha_3 n_j \dot{n}_i^* - \alpha_4 d_{ij} \\ & - \alpha_5 n_i n_k d_{kj} - \alpha_6 n_j n_k d_{ki} - \alpha_7 d_{kk} \delta_{ij} \\ & - \alpha_8 (n_k n_p d_{kp} \delta_{ij} + d_{kk} n_i n_j) - \alpha_9 e_{ipq} n_j n_p T_{,q} \\ & - \alpha_{10} e_{j pq} n_i n_p T_{,q} \end{aligned} \quad (2.8)$$

where

$$d_{ij} = \frac{1}{2}(v_{i,j} + v_{j,i}), \dot{n}_i^* = \dot{n}_i - \frac{1}{2}((\nabla \times \mathbf{v}) \times \mathbf{n})_i \quad (2.9)$$

The coefficients  $\alpha_i$  have the dimensions of a viscosity except for  $\alpha_9$  and  $\alpha_{10}$  which indicate that a temperature gradient gives rise to a torque on the molecules. These terms vanish in the nematic state. Parodi<sup>17</sup> has shown using the Onsager relations that  $\alpha_2 + \alpha_3 = \alpha_6 - \alpha_5$ .  $\alpha_4$  and  $\alpha_7$  are the only viscosities which remain in the isotropic phase.

Since the hydrodynamical equations contain the field  $\mathbf{n}(\mathbf{r}, t)$ , they must be supplemented with an independent equation which determines  $\mathbf{n}$ . We take this

equation to be<sup>18</sup>

$$\prod_{ij,j} + g_i + \gamma_1 \dot{n}_i^* + \gamma_2 n_j d_{ji} + \gamma_3 e_{ijk} n_j T_{,k} = 0 \quad (2.10)$$

where  $g_i = \partial E_0 / \partial n_i$ , and  $\gamma_1$  and  $\gamma_2$  are dissipative parameters which also have the units of viscosities.  $\gamma_3$  vanishes in the nematic state. It can be shown that conservation of angular momentum requires  $\gamma_1 = \alpha_2 - \alpha_3$ ,  $\gamma_2 = \alpha_5 - \alpha_6$ ,  $\gamma_3 = \alpha_{10} - \alpha_9$ . Note that the director equation reduces to the Frank theory (2.3) in the static limit. A microscopic justification of (2.10) in an incompressible nematic has been given by Lubensky.<sup>19</sup>

The normal mode solution to these equations follows the usual procedure.<sup>20</sup> One linearizes the equations in terms of the fluctuating parts of pressure  $p'$ , density  $\rho'$ , temperature  $T'$ , director  $\mathbf{n}'$ , and velocity  $\mathbf{v}$ . For a nematic, one adopts a cartesian coordinate system with the equilibrium director along the  $x$ -axis. The two independent components of  $\mathbf{n}'$  are then  $n'_y$  and  $n'_z$ . Similarly in a cholesteric we can adopt a helical coordinate system

$$\begin{aligned} \xi &= x \cos q_0 z + y \sin q_0 z \\ \eta &= y \cos q_0 z - x \sin q_0 z \end{aligned} \quad (2.11)$$

with the equilibrium director in the  $\xi$  direction. The two independent components of  $\mathbf{n}'$  are then  $n'_\eta$  and  $n'_z$ . Carrying through the linearization in these coordinates gives a relatively simple set of equations for the fluctuating modes:

$$k_{22} \frac{\partial^2 n'_\eta}{\partial z^2} - \gamma_1 \frac{\partial n'_\eta}{\partial t} - \gamma_1 q_0 v_z - A \frac{\partial v_z}{\partial z} = 0 \quad (2.12)$$

$$\rho_0 \frac{\partial v_z}{\partial t} + c_s^2 \frac{\partial \rho'}{\partial z} + k_{22} q_0 \frac{\partial^2 n'_\eta}{\partial z^2} - (\alpha_4 + \alpha_7) \frac{\partial^2 v_z}{\partial z^2} = 0 \quad (2.13)$$

$$\frac{\partial \rho'}{\partial t} + \rho_0 \frac{\partial v_z}{\partial z} = 0 \quad (2.14)$$

where we have restricted our selves to fluctuations which propagate along the helical axis. In these equations  $c_s$  is the sound velocity and is given by

$$c_s^2 = (\partial p / \partial \rho)_s \quad (2.15)$$

where  $s$  is the entropy. The quantity  $A$  has units of a viscosity and is given by

$$A = \gamma_s c_s \beta T_0 / c_p \quad (2.16)$$

where  $\beta$  is the coefficient of thermal expansion and  $c_p$  is the specific heat at constant pressure. In deriving these equations, we have used the small damping approximation and the relation<sup>20</sup>

$$T' = (c_s \beta T_0 / c_p) v_z \quad (2.17)$$

In the nematic limit  $q_0 = A = 0$ ,  $n'_\eta \rightarrow n'_y$  and the equations are completely uncoupled as is well known when the propagation vector is perpendicular to  $\mathbf{n}^{(0)}$ .

To solve these equations we assume expansions of the form:

$$\rho'(z, t) = \frac{1}{\sqrt{V}} \sum_q \rho_q e^{iqz} e^{i\omega_q t}; p_q^* = \rho_{-q} \quad (2.18)$$

with similar expansions for  $v_z$  and  $n'_\eta$ .  $V$  is the volume of the crystal and is put in as a convenient normalization. Putting (2.18) into (2.12), (2.13), and (2.14), and setting the determinant of the coefficients of  $p_q$ ,  $n_{q\eta}$ , and  $v_{qz}$  equal to zero, we derive the dispersion equation in the standard way:

$$(k_{22}q_0^2 + i\gamma_1\omega)[\omega(i\omega\rho_0 + \bar{\alpha}q^2) - i\rho_0q^2c_s^2] + (\gamma_1q_0 + iqA)k_{22}q_0q^2\omega = 0 \quad (2.19)$$

where  $\bar{\alpha} \equiv \alpha_4 + \alpha_7$ . Approximate roots of (2.19) are readily found to be:

$$\omega_q^{(\pm)} = \pm cq + i\Gamma_q \quad (2.20)$$

$$\omega_q^{(2)} = i(k_{22}q^2/\gamma_1) \quad (2.21)$$

where

$$c^2 = c_s^2 + k_{22}q_0^2/\rho_0; \Gamma_q = (\alpha_4 + \alpha_7)q^2/2\rho_0 + (A/\gamma_1)(k_{22}q^2/2\rho_0c^2)cq_0 \quad (2.22)$$

We have ignored further terms in the damping constants involving the small quantity  $(k_{22}q_0^2/\rho_0c^2)$ .

The real part of (2.20) essentially agrees with Lubensky's result and indicates that the sound velocity is very slightly anisotropic with respect to the helical axis. It should be mentioned that we have ignored the dependence of the pitch (or equivalently  $q_0$ ) on temperature and pressure in deriving this result. This problem is discussed in Sect. III where it is shown that the sound velocity in (2.22) is a "high" frequency value which differs from the hydrodynamical sound velocity discussed by Lubensky. The damping constant in (2.22) reduces to the nematic case<sup>13</sup> when  $q_0 = 0$  and disagrees with Lubensky's result (which appears to us to be in error) even at low frequencies. Note that the dispersion relation for sound waves has no unusual behavior at  $q = q_0$  as we might at first expect, since the cholesteric state is periodic. This is because when  $\mathbf{q}$  lies along the helical axis, which is the case treated here,  $\mathbf{q} \cdot \mathbf{n}_0 = 0$  everywhere and the crystal appears uniform. It can be shown<sup>20a</sup> that when  $\mathbf{q}$  points in an off-axis direction the damping constant shows a gap structure because of the periodic structure of the viscosity tensor.

Equation (2.21) is just the overdamped twisting mode found by Fan, Kramer, and Stephen.<sup>6</sup> The effects of compressibility on this mode are small,



of order  $(k_{22}q_0^2/\rho_0c^2)$ . The sound wave mode couples to orientation and generates a driven twist wave:

$$n_{qn} = [(A/\gamma_1) + i(q_0/q)](\rho_q/\rho_0) \quad (2.23)$$

Using (2.4), (2.5), and (2.10) we can derive equations between the fluctuating quantities  $n'_z$ ,  $v'_x$ , and  $v'_y$ . However these are found to be completely uncoupled from the propagating quantities and therefore will not be considered further.

### III ADDITIONAL DAMPING PROCESSES

We have evaluated the damping of the sound waves by considering the viscosity only. As is well known, however there are other processes such as thermal conduction which lead to considerable damping even in ordinary fluids. In liquids with structure, such as cholesterics, there is always additional damping in certain frequency ranges produced by various structural relaxation mechanisms. In this section we take some of these processes into account.

#### A Thermal conduction

The damping due to thermal conduction can be evaluated by the following well known method<sup>20</sup> provided the damping is small. Let  $\dot{E}$  be the rate of energy dissipation in the sound wave due to thermal conductivity. Then

$$\dot{E} = - \frac{\partial E}{\partial S} \dot{S} = -T\dot{S} \quad (3.1)$$

where  $S$  is the entropy and  $T$  is the equilibrium temperature. To calculate  $\dot{S}$  we use the conservation of entropy equation for the fluid. Dropping all terms except those due to thermal conductivity, we have:

$$\dot{S} = \int_V \frac{\partial}{\partial t} (\rho s) dV = \int_V \frac{q_i T_{,i}}{T^2} dV \quad (3.2)$$

where  $q_i$  is the heat current which in a linear approximation is given by

$$q_i = -\beta_1 \nabla T - \beta_2 n_j T_{,j} n_i - \beta_3 e_{ijk} n_j \dot{n}_k^* \quad (3.3)$$

here the  $\beta_i$  are thermal conductivity coefficients and are assumed independent of temperature. The term in  $\beta_2$  describes the well known anisotropy of the thermal conductivity, while the last term, present only in cholesterics, indicates that a change in orientation can give rise to a flow of heat even in the absence of a temperature gradient. Thus  $\beta_3$ , if nonzero, would be a

measure of the coupling between internal translational and rotational motion

We linearize (3.3) and substitute it into (3.1) and (3.2). Taking a time average over an oscillation, we find the average rate of energy dissipation to be

$$\langle \dot{E} \rangle = -\frac{V}{2} \left[ \beta_1 \left( \frac{1}{c_v} - \frac{1}{c_p} \right) + \beta_3 \left( \frac{\beta c_s}{c_p} \right) \left( \frac{A}{\gamma_1} \right) \right] q^2 v_{qz}^2 \quad (3.4)$$

where  $c_v$  is the specific heat at constant volume, and other quantities are as defined above. Now the total energy in the sound wave is:

$$E = \frac{1}{2}(\rho_0 v_z^2)V$$

The damping constant due to thermal conduction is then:

$$\Gamma_{\text{Th}} \equiv \frac{\langle \dot{E} \rangle}{2\langle E \rangle} = \left[ \beta_1 \left( \frac{1}{c_v} - \frac{1}{c_p} \right) + \beta_3 \left( \frac{\beta c_s}{c_p} \right) \left( \frac{A}{\gamma_1} \right) \right] \frac{q^2}{2\rho_0} \quad (3.6)$$

If either  $\beta_3$  or  $A$  vanish, (3.6) reduces to what one would get for an ordinary fluid. As is well known<sup>21</sup> in the case of small damping at small frequencies, the damping constants due to viscosity and thermal conduction are additive, and we will often write  $\Gamma_q$  to mean the sum.

## B Structural relaxation

Papoular<sup>22</sup> has suggested that there may be large damping and dispersion of low frequency sound waves in cholesterics due to a structural relaxation mechanism involving the helical structure. Since the pitch is dependent on the applied pressure and temperature it will be driven at the frequency of the wave. This means there is an additional coupling between the sound wave and the elastic restoring forces that determine the pitch. Since  $q_0 = \pi/P_0$ ,  $q_0 = q_0(p, T)$ . Expanding to first order in small quantities

$$q_0(p, T) = q_0(p_0, T_0) + \left. \frac{\partial q_0}{\partial p} \right|_0 p' + \left. \frac{\partial q_0}{\partial T} \right|_0 T' \quad (3.7)$$

Inserting this into (2.2) leads to additional terms in the equation of motion (2.13). However, because there is a finite relaxation time  $\tau_p$  for the distorted pitch to return to its equilibrium value, the oscillations in pitch will lag in phase relative to the pressure oscillations causing energy dissipation. If  $\omega\tau_p \ll 1$  then  $q_0$  is approximately in equilibrium and  $(\partial q_0/\partial p)_0$  and  $(\partial q_0/\partial T)_0$  can be approximated by the values one would obtain by a direct static measurement of pitch with  $p$  or  $T$  in the laboratory. For higher values of  $\omega$

this is no longer true and we have<sup>20</sup>

$$\frac{\partial q_0}{\partial p} = \frac{1}{1 + i\omega\tau_p} \left( \frac{\partial q_0}{\partial p} \right)^{(e)} \quad (3.8)$$

where  $q_0^{(e)}$  is the value of  $q_0$  in equilibrium. For these frequencies the speed of sound (2.15) becomes complex and there is large dissipation and dispersion as discussed in Ref. 22. The effect will be maximum when  $\omega\tau_p \approx 1$ . However, an order of magnitude estimate for  $\tau_p$  is<sup>22</sup>

$$\tau_p \approx (\eta/k_{22}q_0^2) \quad (3.9)$$

where  $\eta$  is a typical viscosity. Hence the sound waves observable by light scattering will normally have frequencies which satisfy  $\omega\tau_p \gg 1$ . For these large frequencies the pitch cannot respond to the driving pressure and (3.8) shows that the coupling due to this process is small enough to ignore. Thus we assume  $\omega\tau_p \gg 1$  and this is the justification for ignoring terms like (3.7) in our equations. In the expression for the sound velocity, (2.15), the derivative is taken at constant  $q_0$ , as are all the other thermodynamic parameters in our equations.

Near the transition temperature there may be large dispersion and attenuation due to structural relaxation caused by hetrophase fluctuations.<sup>23</sup> This process is assumed to occur because an increase in pressure can convert the fluid to a more compact molecular arrangement (larger order parameter). The effect will be maximum near the phase transition since the equilibrium between phases is very sensitive to pressure. In Ref. 23 the relaxation time for this process is estimated to be  $\tau \approx 10^{-8}$  sec. Our results will show that this effect may be observable from the high frequency direction by Brillouin scattering near the Bragg condition  $q = 2q_0$ .

#### IV CORRELATION FUNCTIONS

In order to evaluate the light scattering in Sect. V we shall need the correlation functions between the fluctuating quantities.

First consider the correlation between density fluctuations. For the  $q$ th Fourier component we have

$$\rho_q(t) = \rho_q(\omega)e^{i\omega_q t} \quad (4.1)$$

where  $\omega_q$  is given by (2.20). The Fourier transform of this is

$$\rho_q(\omega) = 2 \int_0^\infty \rho_q(t)e^{-i\omega t} dt = \frac{2i\rho_q}{(cq - \omega) + i\Gamma_q} \quad (4.2)$$

and this leads to the energy spectrum:

$$E(\omega) = (1/2\pi) |\rho_q(\omega)|^2 = (2/\pi) \frac{1}{(\omega - cq)^2 + \Gamma_q^2} \quad (4.3)$$

We now assume that we observe an ensemble of such fluctuations created at a constant rate with random phases. Then a finite power spectrum will result which will be proportional to the energy spectrum of a single fluctuation. The proportionality constant, which has units of frequency is conveniently chosen to have the value  $(\pi/2)\Gamma_q$  to normalize the spectrum. Thus we obtain:

$$S_{11}(q, \omega) = \langle |\rho_q|^2 \rangle \frac{\Gamma_q}{(\omega - cq)^2 + \Gamma_q^2} \quad (4.4)$$

The angular brackets in (4.4) indicate an ensemble average which can be evaluated with the help of (3.5) for the energy associated with this mode. In terms of  $\rho_q$  this becomes:

$$E = \frac{1}{2}(c^2/\rho_0) \sum_q |\rho_q(t)|^2 \quad (4.5)$$

The equipartition theorem then gives

$$\langle |\rho_q(t)|^2 \rangle = \langle |\rho_q|^2 \rangle = (k_B T / \rho_0 c^2) \rho_0^2 \quad (4.6)$$

where  $k_B$  is the Boltzmann constant, and use has been made of the stationary property of the fluctuations. From (2.23) we see that the power spectrum of the propagating fluctuations in orientation is:

$$S_{22}(q, \omega) = \left[ \left( \frac{A}{\gamma_1^2} \right)^2 + \left( \frac{q_0}{q} \right)^2 \right] \frac{S_{11}(q, \omega)}{\rho_0^2} \quad (4.7)$$

Similarly the cross correlations between fluctuations in density and orientation will yield

$$S_{12}(q, \omega) = S_{21}^*(q, \omega) = \left( \frac{A}{\gamma_1} + \frac{iq_0}{q} \right) \frac{S_{11}(q, \omega)}{\rho_0} \quad (4.8)$$

The power spectrum of the overdamped twisting mode can be evaluated by the same general arguments. We find

$$S_R(q, \omega) = \langle |n_{q\eta}|^2 \rangle \frac{\Gamma_R}{\omega^2 + \Gamma_R^2} \quad (4.9)$$

where  $\Gamma_R = k_{22} q^2 / \gamma_1$ . Using (2.2) and the equipartition theorem we find that

$$\langle |n_{q\eta}|^2 \rangle = (k_B T / k_{22} q^2) \quad (4.10)$$

## V LIGHT SCATTERING

In order to discuss the light scattering we must first have an optical model of the medium which relates fluctuations in the dielectric tensor with the fluctuations in orientation and density which we have calculated. Following Oseen<sup>11</sup> and deVries,<sup>12</sup> we assume that at each point  $\mathbf{r}$  the medium is uniaxial with the axis along the local director at that point:

$$\varepsilon_{ij} = \varepsilon_{\perp} \delta_{ij} + (\varepsilon_{\parallel} - \varepsilon_{\perp}) n_i n_j \quad (5.1)$$

where  $\varepsilon_{\parallel}$  and  $\varepsilon_{\perp}$  are the dielectric constants parallel and perpendicular, respectively, to the molecular orientation at the point in question.

We assume the scattering takes place in the  $yz$ -plane. Light of wave-vector  $\mathbf{k}_0$  is incident at angle  $\theta$  to the helical axis and is scattered through angle  $\gamma$  with wavevector  $\mathbf{k}_1$ . The scattering cross section per unit volume is then given in the Born approximation by

$$\frac{d^2\sigma}{d\Omega d\omega} = \frac{\pi}{2} \lambda^{-4} I(q, \omega) \quad (5.2)$$

where

$$I(q, \omega) = V^{-1} \int d^3r_1 d^3r_2 \int d\tau e^{iq \cdot (\mathbf{r}_1 - \mathbf{r}_2) - i\omega\tau} \sum_{f,i} \langle \delta\varepsilon_{fi}(\mathbf{r}_1, t_1) \delta\varepsilon_{fi}(\mathbf{r}_2, t_2) \rangle \quad (5.3)$$

In Eq. (5.3),  $\tau = t_1 - t_2$ ,  $\mathbf{q}$  and  $\omega$  are the momentum and energy transfer, respectively and  $\delta\varepsilon_{fi} = \mathbf{f} \cdot \delta\boldsymbol{\varepsilon} \cdot \mathbf{i}$  where  $\delta\varepsilon_{ij}$  is the fluctuating part of the dielectric tensor. The unit vectors  $\mathbf{f}$  and  $\mathbf{i}$  give the final and initial polarization direction of the light which has a vacuum wavelength of  $\lambda$ . As is well known, the Born approximation replaces the actual incoming and outgoing states with plane waves. Thus the calculation is only valid to lowest order in  $\varepsilon_a \equiv \varepsilon_{\parallel} - \varepsilon_{\perp}$ . Also, since cholesterics are usually optically active, the approximation will not give valid polarization information, hence in (5.3) we sum over the two possible incident and final polarizations.

The most important fluctuations in  $\varepsilon_{ij}$  are due to fluctuations in the density and in the director  $\mathbf{n}$ . Since the fluctuations are small we may evaluate the two contributions separately.

### A Cross section for density fluctuations

The part of  $\delta\varepsilon_{ij}$  due to density fluctuations can be evaluated using (5.1) to zero order in  $\mathbf{n}'$ . Writing

$$\varepsilon_{\perp}(\rho) = \varepsilon_{\perp}(\rho_0) + \left. \frac{d\varepsilon_{\perp}}{d\rho} \right|_0 \rho' \quad (5.4)$$

and a similar relation for  $\varepsilon_a$ , and defining

$$b_{\perp} = \left. \frac{d\varepsilon_{\perp}}{d\rho} \right|_0 \rho_0, \quad b_a = \left. \frac{d\varepsilon_a}{d\rho} \right|_0 \rho_0 \quad (5.5)$$

we find

$$\delta\varepsilon_{ij}^{(\rho)} = (b_{\perp} \delta_{ij} + b_a n_i^{(0)} n_j^{(0)}) (\rho' / \rho_0) \quad (5.6)$$

Putting (5.6) into (5.3) and using (4.4) and (4.6) we find

$$\begin{aligned} I_{11}(q, \omega) = & [b_{AV}^2 + (b_{\perp} \cos \gamma - \frac{1}{2} b_a \cos(\gamma + \theta) \cos \theta)^2] S_{11}(q, \omega) \\ & + (b_a/4)^2 (1 + \cos^2 \theta) (1 + \cos^2(\gamma + \theta)) \\ & \times [S_{11}(q - 2q_0, \omega) + S_{11}(q + 2q_0, \omega)] \end{aligned} \quad (5.7)$$

where  $b_{AV} \equiv \frac{1}{2}(b_{\perp} + b_{11})$ .

## B Cross section for orientation fluctuations

The fluctuation in  $\varepsilon_{ij}$  due to the director to first order is

$$\delta\varepsilon_{ij}^{(n)} = \varepsilon_a(\rho_0)(n_i^{(0)} n'_j + n'_i n_j^{(0)}) \quad (5.8)$$

Substituting (5.8) into (5.3) and using (4.7), (4.9), and (4.10) we find

$$\begin{aligned} I_{22}(q, \omega) = & (\varepsilon_a/2)^2 (1 + \cos^2 \theta) (1 + \cos^2(\gamma + \theta)) \\ & \times [S_{22}(q - 2q_0, \omega) + S_{22}(q + 2q_0, \omega) \\ & + S_R(q - 2q_0, \omega) + S_R(q + 2q_0, \omega)] \end{aligned} \quad (5.9)$$

The cross section will also contain cross terms involving  $\langle \delta\varepsilon_{ji}^{(\rho)} \delta\varepsilon_{ji}^{(n)} \rangle$ .

Using (4.8) we obtain

$$\begin{aligned} I_{12} + I_{21} = & (\varepsilon_a b_a/4) \operatorname{Im} [S_{12}(q - 2q_0, \omega) - S_{12}(q + 2q_0, \omega)] \\ & \times (1 + \cos^2 \theta) (1 + \cos^2(\gamma + \theta)) \end{aligned} \quad (5.10)$$

where  $\operatorname{Im}$  denotes the imaginary part. It is not difficult to see that the total cross section for each line is real and positive as it must be. For example, taking the line centered at  $c(q - 2q_0)$ :

$$\begin{aligned} I = & \left( \frac{k_B T}{\rho_0 c^2} \right) (1 + \cos^2 \theta) (1 + \cos^2(\gamma + \theta)) \left[ \left( \frac{b_a}{4} - \frac{\varepsilon_a}{4} \frac{q_0}{q - 2q_0} \right)^2 \right. \\ & \left. + \left( \frac{\varepsilon_a}{4} \right)^2 \left( \frac{A}{\gamma_1} \right)^2 \frac{\Gamma_{q-2q_0}}{(\omega - c(q - 2q_0))^2 + \Gamma_{q-2q_0}^2} \right] \end{aligned} \quad (5.11)$$

## VI SUMMARY AND CONCLUSIONS

We have extended the calculation of Fan, Kramer and Stephen to compressible cholesterics and have found a sound wave mode in addition to the overdamped orientation modes found by these authors. The sound wave couples to the director and produces a driven orientation wave which we predict should be a pure twist.

The mode structure of compressible cholesterics has been treated elsewhere<sup>7,24</sup> but these treatments are restricted to fluctuations whose wavelength is long compared to a pitch, and whose frequency is small compared to any inverse relaxation time. Although the treatment of the elastic properties by these authors could probably be extended to smaller wavelengths, their dissipative tensor is not correct when the wavelength becomes comparable to the pitch, since it does not take into account the local nematic ordering.

To summarize the difference between the above treatments of compressible cholesterics and ours, we may say that they have exploited the similarity between the macroscopic symmetry of the cholesteric and that of a smectic A liquid crystal, whereas we wish to emphasize the connection between the cholesteric and nematic phases. The nematic case can always be derived by setting  $q_0 = 0$  in our equations. There are several reasons why such a feature is desirable. As one looks at fluctuations with shorter and shorter wavelengths, the cholesteric behaves more and more like a nematic; thus the nematic case should be obtainable from the theory asymptotically as the pitch goes to infinity. There are many cholesteric-like systems which naturally have large pitches relative to the wavelength of visible light. For example, one can mix a nematic liquid crystal with optically active materials which impart a cholesteric-like pitch to the nematic.<sup>25</sup> The pitch of the resulting structure can be varied to very large values by varying the concentration of the optically active ingredient. The pitch of a cholesteric can be increased by applying a static magnetic field perpendicular to the helical axis,<sup>26</sup> until at a finite critical field, the structure completely unwinds and becomes nematic. One can also create a cholesteric-like twist of very long pitch in a nematic by applying suitable boundary conditions. All of these systems are most easily discussed in terms of a theory which regards a cholesteric as a twisted nematic and therefore is not restricted to variations slow in space relative to a pitch.

We have used the Born approximation to evaluate the Brillouin scattering produced by the propagating fluctuations. Unlike ordinary fluids, the density fluctuations give six lines whose maxima lie at frequencies  $\pm cq$ ,  $\pm c(q \pm 2q_0)$ . The appearance of the last four lines is due to the fact that the static structure is periodic (see Eq. 5.1) and is not due to any new modes in the crystal.

These lines can be thought of as due to scattering of light which has already been Bragg reflected by the static structure. Furthermore it should be noted that even if  $\varepsilon_a \ll \varepsilon_\perp$ , it is not necessarily true that  $b_a \ll b_\perp$ . Thus it is possible the intensity of all six lines will have roughly the same order of magnitude. The driven twist wave also contributes to the lines at  $\pm c(q \pm 2q_0)$  and from (5.11) one can see that it will dominate near the condition for Bragg scattering even if  $\alpha_a \ll b_a$ .

In recent experimental investigation,<sup>26</sup> only the principal lines at  $\omega = \pm cq$  were observed. However, an oriented crystal was not used although the domain sizes were large compared to a pitch. From (5.3) one can see that if the scattering volume contains several domains, each of which has a pitch vector that points in a distinct direction, there will be a set of shifted lines for each domain. Hence when there are many domains in the sample, the principal lines at  $\pm cq$  will dominate the Brillouin spectrum. Our results indicate that light scattering in a monodomain cholesteric at wavelengths comparable to a pitch will produce significant non-nematic behavior. The lines at  $\pm c(q \pm 2q_0)$  can be used near  $q = 2q_0$  to probe the low frequency behavior of the crystal.

Although our calculation is limited to modes which propagate along the helical axis, our methods are applicable to off axis directions, and in the helical coordinates (2.11) the problem is quite manageable. For example, we have evaluated the normal modes for the case where the propagation vector is perpendicular to the helical axis. These calculations will be published elsewhere.

## References and notes

1. I. G. Chistyakov, *Usp. Fiz. Nauk.*, **89**, 563 (1966) (*Soviet Phys. Usp.*, **9**, 551, (1966)).
2. Glenn H. Brown, J. W. Doane, and Vernon D. Neff, *A Review of the Structure and Properties of Liquid Crystals* (Chemical Rubber Co. Cleveland, 1971).
3. R. D. Mountain, *Rev. Mod. Phys.*, **38**, 205 (1966).
4. P. G. deGennes, *Mol. Cryst. Liq. Cryst.*, **7**, 325 (1969).
5. P. Pincus, *Compt. Rend.*, **267B**, 1290 (1969).
6. C. Fan, L. Kramer, and M. J. Stephen, *Phys. Rev.*, **A2**, 2482 (1970).
7. T. C. Lubensky, *Phys. Rev.*, **A6**, 452 (1972).
8. D. Forster, T. C. Lubensky, P. C. Martin, J. Swift, and P. S. Pershan, *Phys. Rev. Lett.*, **26**, 1016 (1971).
9. Group d'Etude des Cristaux Liquides (Orsay), *J. Chem. Phys.*, **51**, 816 (1969).
10. T. Lubensky, private communication.
11. C. W. Oseen, *Trans. Far. Soc.* **29**, 883 (1933).
12. Hl. deVries, *Acta Cryst.* **4**, 219 (1951).
13. F. C. Frank, *Disc. Far. Soc.* **25**, 19 (1958).
14. In this equation and those that follow, we use a Cartesian tensor notation where necessary.
15. J. L. Ericksen, *Arch. Ratl. Mech. Anal.* **4**, 231 (1960); **9**, 371 (1962), *Trans. Soc. Rheology*, **5**, 23 (1961).
16. F. M. Leslie, *Quart. J. Mech. Appl. Math.*, **19**, 357 (1966), *Proc. Roy. Soc. (London)* **A307**, 359 (1968). Also see M. J. Stephen, *Phys. Rev.* **A2**, 1558 (1970).



17. O. Parodi, *J. Phys.*, **31**, 581 (1970).
18. We have omitted an inertial term which is unimportant at low frequencies (see Ref. 9).
19. T. C. Lubensky, *Phys. Rev.*, **A2**, 2497 (1970).
20. See e.g. L. D. Landau and E. M. Lifshitz, *Fluid Mechanics* (Addison-Wesley Pub. Co., Reading, Mass., 1959).
- 20a. J. D. Parsons and C. F. Hayes, to be published.
21. See e.g. A. B. Bhatia, *Ultrasonic Absorption* (Oxford, London, 1967).
22. M. Papoular, *Phys. Lett.*, **A31**, 65 (1970).
23. W. A. Hoyer and A. W. Nolle, *J. Chem. Phys.*, **24**, 803 (1956).
24. P. C. Martin, O. Parodi, and P. S. Pershan, *Phys. Rev.* **A6**, 2401 (1972).
25. See e.g. D. W. Berreman and T. J. Scheffer, *Phys. Rev.* **25**, 577 (1970).
26. P. G. deGennes, *Sol. State Commun.*, **6**, 163 (1968), R. B. Meyer, *Appl. Phys. Lett.*, **14**, 208 (1969).
27. H. Rosen and Y. R. Shen, *Mol. Cryst. Liq. Cryst.*, **18**, 285 (1972).