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Hydrodynamics of Cholesteric Liquid Crystals

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The equations governing the linearized hydrodynamics of cholesteric liquid crystals are systematically deduced. They are valid for compressible as well as incompressible cholesterics and for arbitrary direction of mode propagation. The variables which contribute to the hydrodynamics are the conserved variables, mass density, energy density, and momentum density, and one additional broken-symmetry variable whose auto correlation function diverges at zero wave vector $\vec{k}$. This divergent auto correlation function is determined from the Frank free energy for cholesterics and is found to diverge as $(k_3^2 + ck_\perp^4)^{-1}$, where c is a constant, k_3 is the component of $\vec{k}$ parallel to the pitch axis, $\vec{p}^0$, and $k_\perp$ is the component perpendicular to $\vec{p}^0$. The form of this divergence implies that an infinite cholesteric is unstable with respect to fluctuations. The dephasing distance is, however, astronomical; and any finite sample is stabilized by its boundaries. The mode structure of the hydrodynamical equations is analyzed for an incompressible choleteric and for a compressible cholesteric for $\vec{k}$ along the two symmetry directions. The spectrum for $\vec{k}$ parallel to $\vec{p}^0$ includes a diffusive velocity and a diffusive director mode in agreement with the work of Fan, Kramer, and Stephen. The spectrum for $\vec{k}$ perpendicular to $\vec{p}^0$ has a similar structure. For $\vec{k}$ at an angle of 45° to $\vec{p}^0$, there is a propagating shear wave for sufficiently small k. The velocity of longitudinal sound is very slightly anisotropic. Hydrodynamical forms of dynamic response functions are derived, and flow of a cholesteric in a cylindrical capillary is discussed.

I. INTRODUCTION

Liquid crystals have recently become a subject of intensive study by chemists, physicists, mathematicians, and engineers. Several review articles[1-4] have already been written on the subject, and conferences dealing with liquid crystals are now held on a regular basis.[5-9] Liquid crystals are composed of long, usually organic molecules. In certain temperature ranges, these molecules become aligned collectively even though the substance as a whole can flow like a liquid. In 1922, Friedel distinguished three subclasses of the liquid crystalline state[8]; the nematic state [Fig. 1(a)] in which the long axes of the molecules are on the average aligned along one direction and the positions of their centers of mass fluctuate freely as in an isotropic fluid; the cholesteric state [Fig. 1(b)] in which free displacement of the centers of mass of the molecules is still allowed but in which their long axes are aligned in a helical pattern along a pitch axis with a characteristic pitch $\lambda_0 = 2\pi/q_0$; the smectic state [Fig. 1(c)] in which the long axes are aligned along one direction and in which the centers of mass are constrained to be in parallel equidistant planes with free displacement within any given plane.

The major aim of this paper is to determine the equations governing the hydrodynamics of the cholesteric state and to examine their consequences. Hydrodynamical equations determine the dynamics of a system in which all variables are in local thermodynamic equilibrium. Thermodynamic equi-

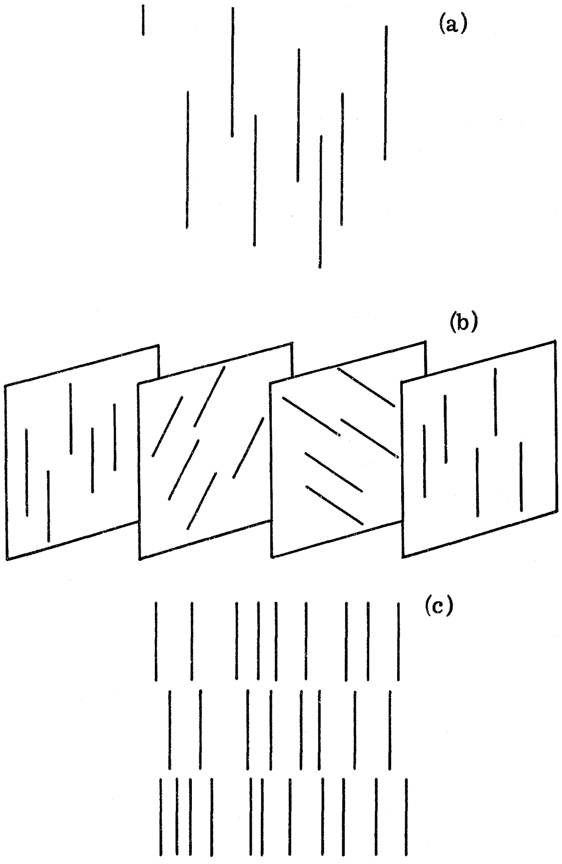

FIG. 1. (a) Schematic arrangement of molecules in a nematic liquid crystal, (b) in a cholesteric liquid crystal, and (c) in a smectic liquid crystal.

librium is produced and maintained by collisions between particles which occur on the average at time intervals τ. Hence, any disturbance which maintains local thermodynamic equilibrium must have temporal variations which are slow on a scale of τ, i.e., the frequency ω of disturbances described by the hydrodynamical equations must be such that $\omega\tau \ll 1$. Similar arguments apply to spatial variations. If λ is any characteristic "microscopic" length (usually a mean free path), the wave number k of any hydrodynamical disturbance must satisfy $k\lambda \ll 1$. In cholesterics, the latter condition imposes a particularly stringent boundary on the region of validity of hydrodynamics. The pitch λ_0 (usually the order of a few thousand angstroms) must be considered a "microscopic" length, and the wavelength of any hydrodynamical disturbance must be much greater than this. There may also be hydrodynamiclike behavior in cholesterics for wavelengths lying between λ_0 and the mean free path λ. We will not consider this regime.

The first problem we face is to determine which variables will enter into the hydrodynamical description of the cholesteric state; i.e., we must find those variables which will have variations which are slow in space and time. The most familiar hydrodynamical variables are densities of conserved quantities. The time development of these operators is controlled by a local conservation law relating their first time derivatives to gradients of local currents. After Fourier transformation, such local conservation laws imply that frequencies go to zero with wave number. Familiar examples of hydrodynamical equations resulting from local conservation laws are the spin diffusion equation in isotropic magnets and the Navier-Stokes equations in isotropic fluids. In a cholesteric liquid crystal (as in all nonrelativistic systems), mass, energy, and momentum are locally conserved; and mass density, energy density, and momentum density are hydrodynamical variables.

There is another class of hydrodynamical variables which occurs in systems in which a continuous symmetry has been broken. In such systems with free energy F, there is a variable (or variables) ϕ describing rotations in the space of broken symmetry. If $\delta F/\delta\phi$ tends to zero with wave number k, then the restoring force on ϕ tends to zero with k, and spatial and temporal variations in ϕ will be slow. ϕ will, therefore, be a hydrodynamical variable. An alternate, but equivalent, criterion for ϕ to be a hydrogynamical variable is for its autocorrelation function to diverge as k approaches zero. Systems which exhibit such broken symmetry hydrodynamics include superfluid helium,[9–11] ferromagnets,[12,13] antiferromagnets,[12] and nematic liquid crystals.[14–19]

We can determine which variables are hydrodynamical by considering a free energy which is an integral over volume of a local free-energy density. The free-energy density is expressed as a sum of a uniform part and a part which depends on gradients of variables and is zero in uniform systems. Usually, we can determine which variables have vanishing restoring forces by considering the invariances of the uniform part of the free-energy density. For example, the uniform free-energy density of a superfluid is invariant with respect to uniform translations of the superfluid phase, and this phase is a hydrodynamical variable. Similarly, the free-energy density of an antiferromagnet is invariant with respect to uniform angular displacements of the direction of staggered magnetization, and the two angles needed to describe these rotations are hydrodynamical variables. This type of argument does not work, however, unless the restoring forces at $k=0$ of the variables in question are identical to their zero k limit. For highly nonlocal modes, involving spatial rotations for example, the limits are not necessarily identical, and small changes in the local free-energy density do not necessarily imply small changes in the total free energy. In such cases, we must look at either the total free energy or at autocorrelation functions in order to determine which variables are hydrodynamical. In nematics, the local arguments do determine the variables with vanishing restoring forces even though the modes in question involve spatial rotations. This is the justification for the Frank local free-energy density for nematics.[20] In cholesterics, the situation is more complicated. In Sec. III of this paper, we will study the nature of the nonlocality which prevents the local-type arguments from working. We will then use the Frank free energy for cholesterics[20] to calculate autocorrelation functions. There is one divergent autocorrelation function which implies that one variable in addition to mass density, energy density, and momentum density is hydrodynamical.

The divergent autocorrelation function presents certain problems. It diverges not as k^{-2} as is usual but as $(k_3^2 + ck_\perp^4)^{-1}$, where c is a constant and k_3 and $k_\perp$ are, respectively, the components of $\vec{k}$ parallel and perpendicular to the pitch axis. This form of divergence implies that an infinite cholesteric is unstable with respect to fluctuations. The arguments used to show this are very similar to those developed by Landau and Peierls[21] to show that a three-dimensional body in which the density depends on only one coordinate must have a uniform density. A refinement of these arguments has been used by Mermin and Wagner[22] and by Hohenberg[23] to show that two-dimensional ferromagnets, superfluids, and superconductors cannot exist. In view of this instability, there are two attitudes one can adopt regarding the cholesteric state. The first is that an infinite cholesteric is in fact stable and the Frank free energy is unsuited for discussing fluctuations about the equilibrium state. The second is that the above considerations are correct, but that there are always boundaries which stabilize any real system. In this paper, we will adopt the latter attitude. Our methods can be applied to both cases, however, and we will point out whenever dynamical results for a stable system differ significantly from those for an unstable system. We will assume that the sole effect of the boundaries is to inhibit long-wavelength fluctuations which destroy the order. We will further assume that long-wavelength (but smaller than any sample dimension) and low-frequency fluctuations which occur within the bulk of the sample can be described by the hydrodynamical equations to be derived. This is a reasonable assumption since hydrodynamical equations describe fluctuations in which local equilibrium is preserved. In the bulk of a finite sample, the cholesteric state is the local equilibrium state.

Having determined which variables are hydrodynamical, we can use any of a number of methods to determine the actual form of the hydrodynamical equations.[12,13,24] We will employ the method developed by Halperin and Hohenberg to discuss hydrodynamics in magnetic systems.[12] A "conservation" law and a local current are introduced for the broken symmetry variable. The standard techniques[25] used to derive the Navier-Stokes equations can then be used to determine the constitutive relations for the currents of all of the conserved variables. This analysis is carried out in Secs. IV and V of this paper.

It should be mentioned that the methods employed in this paper are not the same as those of continuum mechanics. The continuum mechanics of liquid crystals is not restricted to hydrodynamical modes. In particule Fan, Kramer, and Stephen[26] have found finite-frequency modes in cholesterics using the techniques developed for nematics by Leslie[15] and Ericksen.[14] We will make no attempt to determine the nature of these modes though we will assume that for sufficiently long wavelengths, their frequencies are large compared to the frequencies of the hydrodynamical modes. Leslie[27] has derived the continuum equations for cholesterics and used them to discuss flow of a cholesteric between two infinite parallel plates. Using these equations, Brochard[28] has also discussed acoustical impedance of a quartz-cholesteric interface.

This paper is divided into eight parts. Section II discusses the symmetry of the cholesteric state. Section III derives the divergent correlation function for the Frank free energy and discusses its significance. Section IV discusses in some detail the thermodynamics of the hydrodynamical variables of cholesterics. This is necessary since the additional hydrodynamical variable in cholesterics has thermodynamic derivatives with respect to density and temperature as well as with respect to its conjugate field. Section V introduces the dissipative coefficients and produces the complete hydrodynamical equations. These equations are then analyzed for their mode structure. Particular attention is given to the structure along the symmetry directions. The orientational hydrodynamical mode for $\vec{k}$ along the pitch axis has the same form as predicted by Fan, Kramer, and Stephen with a slightly different definition of the elastic constant of interest. Starting with the microscopic definition of the partition function, Sec. VI justifies the entropy relation used in previous sections and proceeds to discuss the dynamical response functions of the hydrodynamical variables in cholesterics. The techniques used are those developed by Kadanoff and Martin[29] to describe isotropic fluids and subsequently applied to superfluid helium by Hohenberg and Martin.[30] Section VII shows how the hydrodynamics of the previous sections satisfies all of the Goldstone theorems[31,32] for the cholesteric state. Finally, Sec. VIII applies the hydrodynamical equations of Sec. V to the capillary flow of a cholesteric in a cylindrical tube first discussed by Helfrich.[33]

II. CHOLESTERIC ORDER

Order in liquid crystals is determined by the alignment of long molecules. A convenient microscopic definition[34] of the liquid-crystalline order parameter is obtained by introducing for each molecule α a center-of-mass coordinate and a unit vector $\vec{\nu}^\alpha$ along the long axis of the molecule. The order parameter is then the symmetric traceless tensor[35]

$$(\rho/m)Q_{ij}(\vec{r}t)=\sum_\alpha(\nu_i^\alpha\nu_j^\alpha-\tfrac{1}{3}\delta_{ij})\delta(\vec{r}-\vec{r}^\alpha(t))$$
$$=\sum_\alpha Q_{ij}^\alpha\delta(\vec{r}-\vec{r}^\alpha)\ . \qquad (2.1)$$

ρ is the mass density and m is the mass of each molecule. As long as the frequencies of the internal molecular modes are large, this definition of the liquid-crystal order is equivalent to one in terms of the quadripolar term in the mass density.[16] In uniaxial liquid crystals, in equilibrium, $\langle Q_{ij}(\vec{r})\rangle$ assumes the form

$$\langle Q_{ij}(\vec{r})\rangle=S[n_i^0(\vec{r})n_j^0(\vec{r})-\tfrac{1}{3}\delta_{ij}]\ , \qquad (2.2)$$

where $n_i^0(\vec{r})$ is the equilibrium director[20,36,37] and S is a measure of the degree of order.[38] In nematics, $\vec{n}^0(\vec{r})$ is a constant in space. In cholesterics, $\vec{n}^0(\vec{r})$ has spiral symmetry

$$\vec{n}^0(\vec{r})=\vec{n}^0\cos\phi^0(\vec{r})+(\vec{p}^0\times\vec{n}^0)\sin\phi^0(\vec{r})\ , \qquad (2.3)$$

where $\vec{p}^0$ is a unit vector along the pitch axis of the spiral structure, $\vec{n}^0$ is a unit vector in the plane perpendicular to $\vec{p}^0$, $\psi^0(\vec{r}) = (2\pi/\lambda_0)\vec{p}^0 \cdot \vec{r} + \phi$, and λ_0 is the pitch of the helix. ϕ is an arbitrary phase which can be chosen so that $\vec{n}(\vec{r}=0) = \vec{n}^0$. It is customary to set $2\pi/\lambda_0 = q_0$. Note that

$$\vec{\nabla}\psi^0(\vec{r}) = q_0\vec{p}^0 \ . \tag{2.4}$$

Deviations from cholesteric equilibrium can be described by letting

$$\vec{n}(\vec{r}) = \vec{\epsilon}_1(\vec{r}) \cos\psi(\vec{r}) + \vec{\epsilon}_2(\vec{r}) \sin\psi(\vec{r}) \ , \tag{2.5}$$

where

$$\psi(\vec{r}) = \psi^0(\vec{r}) + \delta\psi(\vec{r}) \ , \quad \vec{\epsilon}_1(\vec{r}) = \vec{n}^0 + \delta\vec{\alpha}(\vec{r}) \times \vec{n}^0 \ ,$$
$$\vec{\epsilon}_2(\vec{r}) = \vec{p}^0 \times \vec{n}^0 + \delta\vec{\alpha}(\vec{r}) \times (\vec{p}^0 \times \vec{n}^0) \ ,$$
$$\delta\vec{\alpha}(\vec{r}) = \vec{p}^0 \times \delta\vec{p}(\vec{r}) \ .$$

Hence, changes of $\vec{n}(\vec{r})$ from equilibrium are described completely by the independent variables $\psi(\vec{r})$ and $\vec{p}(\vec{r}) = \vec{p}^0 + \delta\vec{p}(\vec{r})$, which are not related by Eq. (2.4). $\vec{p}(\vec{r})$ is always perpendicular to $\vec{n}(\vec{r})$, whereas $\vec{\nabla}\psi(\vec{r})$ can point in any direction. Linear changes in $\vec{n}(\vec{r})$ can be expressed in terms of $\delta\vec{p}(\vec{r})$ and $\delta\psi(\vec{r})$:

$$\delta\vec{n}(\vec{r}) = [\vec{p}^0 \times \vec{n}^0(\vec{r})]\, \delta\psi(\vec{r}) + \vec{p}^0[\vec{p}^0 \cdot \delta n(\vec{r})] \ . \tag{2.6}$$

But since

$$p(\vec{r}) \cdot n(\vec{r}) = 0 \ ,$$

we have

$$\delta\vec{n}(\vec{r}) = [\vec{p}^0 \times \vec{n}^0(\vec{r})]\, \delta\psi(\vec{r}) - \vec{p}^0\, [\delta\vec{p}(\vec{r}) \cdot n^0(\vec{r})] \ . \tag{2.7}$$

$\vec{p}(\vec{r})$ can be chosen to be either a vector or a pseudovector, but once its signature under parity is chosen, that of $\psi(\vec{r})$ is determined. Let R be the parity operator, take $\vec{n}(\vec{r})$ and $\vec{n}^0$ to be vectors, and let

$$R\vec{p}(\vec{r})R^{-1} = \epsilon_p \vec{p}(-\vec{r}) \ , \quad R\psi(\vec{r})R^{-1} = \epsilon_\psi \psi(-\vec{r}) \ , \tag{2.8}$$

where ϵ_p and ϵ_ψ are the signatures of p and ψ under space inversion. Then we have

$$\begin{aligned} R\vec{n}(-\vec{r})R^{-1} &= -\vec{n}(\vec{r}) \\ &= -\vec{n}^0 \cos\epsilon_\psi \psi(\vec{r}) - \epsilon_p [\vec{p}(\vec{r}) \times \vec{n}^0] \sin\epsilon_\psi \psi(\vec{r}) \ . \end{aligned} \tag{2.9}$$

In order to obtain equality between the first and second lines of Eq. (2.9), we must have

$$\epsilon_p \epsilon_\psi = 1 \ . \tag{2.10}$$

Hence, if $\vec{p}$ is a vector, ψ is a pseudoscalar; and if $\vec{p}$ is a pseudovector, ψ is a scalar. Any equations describing physically observable quantities must reflect this invariance. These considerations apply to the equilibrium configuration and imply that q_0 must be a pseudoscalar regardless of the transformation properties of $\vec{p}$ and ψ. Since $\vec{n}(\vec{r})$ appears quadratically in the order parameter $\langle Q_{ij}(\vec{r}) \rangle$, physical quantities must be insensitive to whether $\vec{n}(\vec{r})$ is a vector or a pseudovector. The relation between $\vec{p}$ and ψ does not change if we choose $\vec{n}(\vec{r})$ to be a pseudovector rather than a vector.

III. AUTOCORRELATION FUNCTIONS

The total free energy for a cholesteric is invariant with respect to uniform rotational displacements of the pitch axis $\vec{p}$ and uniform translational displacements of the helix phase ψ. It is tempting, therefore, to say that these three independent variables have vanishing restoring forces in the zero k limit and thereby justify an expansion of the free-energy density in terms of gradients of these variables. Distortions of ψ are local, and terms in the free-energy density proportional to $|\vec{\nabla}\psi|^2$ are possible (Fig. 2). $\vec{p}$, however, is a highly nonlocal variable, and we can easily see how small changes in the local direction of $\vec{p}(\vec{r})$ can lead to large changes in the total free energy. Let us divide the cholesteric up into a series of large cells and require $\vec{p}$ to be uniform within each cell but allow the direction of $\vec{p}$ to change slightly from cell to cell. The total free energy is then the sum over all cell boundaries of the surface energy between neighboring cells. Consider now the various distortions that $\vec{p}$ can undergo, remembering that the surfaces of constant pitch phase are always perpendicular to $\vec{p}$ in any given cell. $\vec{p}(\vec{r})$ can undergo the same types of distortions as $\vec{n}(\vec{r})$ can in a nematic: splay, bend, and twist. In a splay distortion, the surfaces of constant phase can be continuously joined over the entire cell boundary [Fig. 3(a)]. The surface free energy is thus proportional to the square of the angle between the pitch axes in the two cells. The

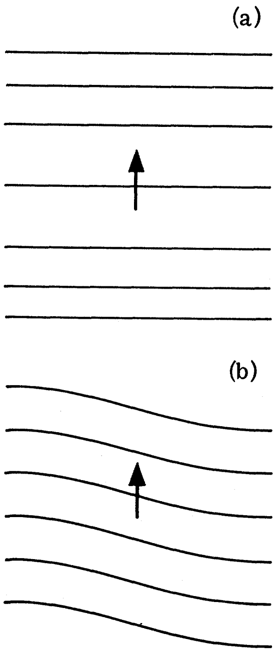

FIG. 2. Local distortion of the pitch phase. The curved lines represent planes of constant phase.

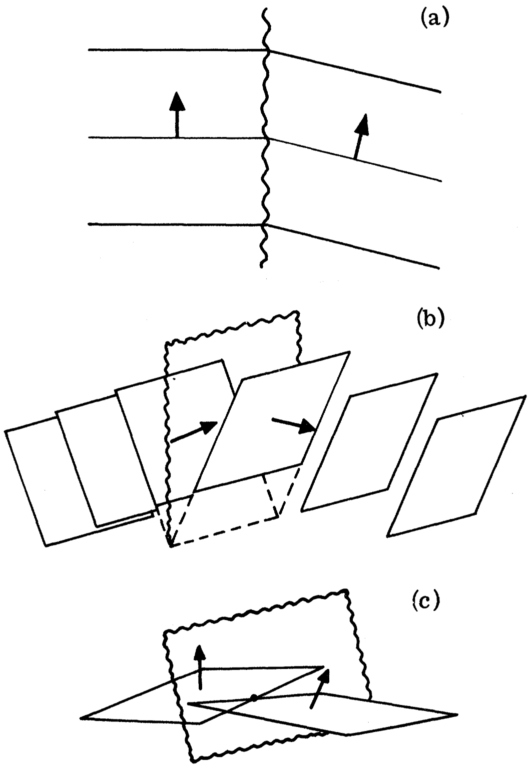

FIG. 3. (a) Splay distortion of the pitch director $\vec{p}(\vec{r})$. The arrows represent the direction of $\vec{p}(\vec{r})$ in each cell and the straight lines perpendicular to $\vec{p}(\vec{r})$ represent planes of constant phase. Note that the planes of constant phase of two adjacent cells can be joined continuously along the entire cell boundary. The energy of this distortion is proportional to the square of the angle between $\vec{p}(\vec{r})$ in adjacent cells. (b) Bend distortion of $\vec{p}(\vec{r})$. At one end of the cell boundary, the planes of constant phase are stretched apart, and the other end, they are compressed. The energy of this distortion is, therefore, proportional to the size of the cell and can be large for very small angles between $\vec{p}(\vec{r})$ in adjacent cells. (c) Twist distortion of $\vec{p}(\vec{r})$. It is not possible to match the planes of constant phase over the entire cell boundary. The amount of mismatch, and hence the energy of the twist distortion, is proportional to the size of the cell. The energies of bend and twist distortions do not go continuously to zero with wave number k.

restoring force for this type of distortion, therefore, goes to zero with k. In bend and twist distortions, it is impossible to match surfaces of constant phase over an entire cell boundary [Figs. 3(b) and 3(c)]. In fact, the amount of mismatch is proportional to the length of the cell. There is, hence, a finite energy associated with these distortions no matter how small the angle between the pitch axes of adjacent cells.[39]

This explains why a local free energy for cholesterics in terms of gradients of ψ and $\vec{p}$ would be meaningless. Fortunately, we do have a local free energy for cholesterics expressed in terms of $\vec{n}(\vec{r})$ rather than $\vec{p}(\vec{r})$ and $\psi(\vec{r})$. This is the free energy introduced by Frank[20] following work by Oseen[37] and Zocher.[36] We will use a slight modification of this free energy to calculate the director autocorrelation functions. The divergent component of this correlation function will tell us which variable is hydrodynamical.

We wish to calculate the equilibrium director autocorrelation function. This is directly proportional to the functional derivative of $\vec{n}(\vec{r})$ with respect to its conjugate field $\vec{h}_n(\vec{r})$ at constant chemical potential μ and temperature T. It is, therefore, most direct for us to calculate autocorrelation functions from a Gibbs free energy which is a function of μ, T, and $\vec{n}(\vec{r})$ rather than from the Frank free energy which is normally a function of density ρ, T, and $\vec{n}(\vec{r})$. The Gibbs free energy can be expressed as a sum of two parts,

$$G=\int d^3r\,\mathcal{G}_0(\mu, T, S, q_0)+\int d^3r\,\mathcal{G}_1(\mu, T, \vec{n}(\vec{r}))\,, \tag{3.1}$$

where

$$\mathcal{G}_1=\tfrac{1}{2}\overline{K}_1(\nabla\cdot\vec{n})^2+\tfrac{1}{2}\overline{K}_2[\vec{n}\cdot(\nabla\times\vec{n})+q_0]^2 +\tfrac{1}{2}\overline{K}_3[\vec{n}\times(\nabla\times\vec{n})]^2\,. \tag{3.2}$$

Bars have been placed over the elastic constants to distinguish them from the constants that appear in the Frank free energy. q_0 and S are determined as functions of μ and T by requiring

$$\left.\frac{\partial\mathcal{G}_0}{\partial q_0}\right|_{\mu,T,S}=0\,,\quad \left.\frac{\partial\mathcal{G}_0}{\partial S}\right|_{\mu,T,q_0}=0\,. \tag{3.3}$$

The total free energy is then minimized if $\nabla\cdot\vec{n}=0$, $\vec{n}\times(\vec{\nabla}\times\vec{n})=0$, and $\vec{n}\cdot(\vec{\nabla}\times\vec{n})=q_0(\mu, T)$. If there is an external field coupling to $\vec{n}$, the values of $\vec{n}\cdot(\vec{\nabla}\times\vec{n})$ can change. We will denote $\vec{n}\cdot(\vec{\nabla}\times\vec{n})$ by q_0, which is a function of an external field and any pair of longitudinal variables (μ and T or ρ and T, for example.

Director fluctuations are represented by the correlation function

$$I_{n_in_j}(\vec{r}\,\vec{r}\,')=\langle\delta n_i(\vec{r})\delta n_j(\vec{r}\,')\rangle\,, \tag{3.4}$$

where the brackets indicate an average over the equilibrium ensemble. $I_{n_in_j}$ is, of course, meant to be a shorthand for certain components of the correlation function of the microscopically defined operator $Q_{ij}(\vec{r}t)$. In nematics, there is translational invariance and $I_{n_in_j}(\vec{k})=\int d^3r\,e^{-i\vec{k}\cdot(\vec{r}-\vec{r}\,')}I_{n_in_j}(\vec{r}-\vec{r}\,')$ can be obtained from the equipartition theorem.[40] By the same technique,

$$I_{n_in_j}(k_3)=\int d^3r\,\exp[-ik_3\vec{p}^{\,0}\cdot(\vec{r}-\vec{r}\,')]\,I_{n_in_j}(\vec{r}\,\vec{r}\,')$$

can be obtained for cholesterics.[41] Because of the lack of translational invariance in cholesterics, $I_{n_in_j}\cdot(\vec{r}\,\vec{r}\,')$ for arbitrary $\vec{r}$ and $\vec{r}\,'$ is best determined by a calculation of

$$\chi_{n_i n_j}(\vec{\mathrm{r}}\,\vec{\mathrm{r}}\,') = \delta n_i(\vec{\mathrm{r}})/\delta h_{h_j}(\vec{\mathrm{r}}\,') ,$$

where $h_{n_j}(\vec{\mathrm{r}})$ is the field conjugate to $n_j(r)$.

By the fluctuation-dissipation theorem[42] for classical systems,

$$I_{n_i n_j}(\vec{\mathrm{r}}\,\vec{\mathrm{r}}\,') = k_B T \chi_{n_i n_j}(\vec{\mathrm{r}}\,\vec{\mathrm{r}}\,')$$

where k_B is the Boltzmann constant. It is convenient to express $I_{n_i n_j}(\vec{\mathrm{r}}\,\vec{\mathrm{r}}\,')$ in terms of the variables of Eq. (2.6),

$$\begin{aligned} I_{n_i n_j}(\vec{\mathrm{r}}\,\vec{\mathrm{r}}\,') = {} & [\vec{\mathrm{p}}^0 \times \vec{\mathrm{n}}^0(\vec{\mathrm{r}})]_i I_{11}(\vec{\mathrm{r}}\,\vec{\mathrm{r}}\,')[\vec{\mathrm{p}}^0 \times \vec{\mathrm{n}}^0(\vec{\mathrm{r}}\,')]_j \\ & + p_i^0 I_{22}(\vec{\mathrm{r}}\,\vec{\mathrm{r}}\,') p_j^0 + p_i^0 I_{21}(\vec{\mathrm{r}}\,\vec{\mathrm{r}}\,')[\vec{\mathrm{p}}^0 \times \vec{\mathrm{n}}^0(\vec{\mathrm{r}}\,')]_j \\ & + [\vec{\mathrm{p}}^0 \times \vec{\mathrm{n}}^0(\vec{\mathrm{r}})]_i I_{12}(\vec{\mathrm{r}}\,\vec{\mathrm{r}}\,') p_j^0 , \end{aligned} \tag{3.5}$$

where $I_{\alpha\beta}(\vec{\mathrm{r}}\,\vec{\mathrm{r}}\,') = I_{\psi_\alpha \psi_\beta}(\vec{\mathrm{r}}\,\vec{\mathrm{r}}\,')$ for α, $\beta = 1, 2$, and $\delta\psi_1(\vec{\mathrm{r}}) = \delta\psi(\vec{\mathrm{r}})$, and $\delta\psi_2(\vec{\mathrm{r}}) = \vec{\mathrm{p}}^0 \cdot \delta\vec{\mathrm{n}}(\vec{\mathrm{r}})$. The Gibbs free energy can readily be written in terms of the variables ψ_1 and ψ_2:

$$\begin{aligned} \delta G = \tfrac{1}{2} \int d^3 r \, (& \overline{K}_1 \{ \vec{\mathrm{p}}^0 \cdot \nabla\psi_2 + [\vec{\mathrm{p}}^0 \times \vec{\mathrm{n}}^0(\vec{\mathrm{r}})] \cdot \nabla\psi_1 \}^2 \\ & + \overline{K}_2 \{ [\vec{\mathrm{p}}^0 \times \vec{\mathrm{n}}^0(\vec{\mathrm{r}})] \cdot \nabla\psi_2 - \vec{\mathrm{p}}^0 \cdot \nabla\psi_1 \}^2 \\ & + \overline{K}_3 \{ [\vec{\mathrm{n}}^0(\vec{\mathrm{r}}) \cdot \nabla\psi_2]^2 + [\vec{\mathrm{n}}^0(\vec{\mathrm{r}}) \cdot \nabla\psi_1 + q_0 \delta\psi_2]^2 \}) . \end{aligned} \tag{3.6}$$

Let $h_\alpha(\vec{\mathrm{r}})$ be the field conjugate to $\psi_\alpha(r)$. Then

$$[\delta/\delta\psi_\alpha(r)] [G - \textstyle\int d^3 r \, h_\alpha(r) \psi_\alpha(r)] = 0 . \tag{3.7}$$

Equation (3.7) gives $h_\alpha(\vec{\mathrm{r}}) = \delta G/\delta\psi_\alpha(\vec{\mathrm{r}})$. In equilibrium $\delta\psi_\alpha(\vec{\mathrm{r}})$ is zero in the absence of external fields. G is quadratic in $\delta\psi_\alpha(\vec{\mathrm{r}})$; therefore, in equilibrium, $h_\alpha(r)$ is zero.

Differentiation of Eq. (3.7) with respect to $h_{\alpha'}(\vec{\mathrm{r}}\,')$ produces an equation for

$$\chi_{\alpha\alpha'}(\vec{\mathrm{r}}\,\vec{\mathrm{r}}\,') = \delta\psi_\alpha(r)/\delta h_{\alpha'}(r') .$$

$\chi_{\alpha\alpha'}(\vec{\mathrm{r}}\,\vec{\mathrm{r}}\,')$ is a function of $(\vec{\mathrm{r}} - \vec{\mathrm{r}}\,')_\perp$, z, and z', where z is the coordinate parallel to $\vec{\mathrm{p}}^0$ and $\vec{\mathrm{r}}_\perp$ is the coordinate perpendicular to $\vec{\mathrm{p}}^0$. Hence $\chi_{\alpha\alpha'}(\vec{\mathrm{r}}\,\vec{\mathrm{r}}\,')$ can be Fourier transformed:

$$\chi_{\alpha\alpha'}(\vec{\mathrm{r}}\,\vec{\mathrm{r}}\,') = \int \frac{d^2 k_\perp}{(2\pi)^2} e^{i \vec{\mathrm{k}}_\perp \cdot (\vec{\mathrm{r}} - \vec{\mathrm{r}}\,')_\perp} \chi_{\alpha\alpha'}(\vec{\mathrm{k}}_\perp, zz') . \tag{3.8}$$

Following the procedures outlined above, one obtains the following equation for $\chi_{\alpha\alpha'}(\vec{\mathrm{k}}_\perp zz')$:

$$H_{\alpha\overline{\alpha}}(\vec{\mathrm{k}}_\perp, z) \chi_{\overline{\alpha}\alpha'}(\vec{\mathrm{k}}_\perp, z, z') = \delta_{\alpha\alpha'} \delta(z - z') , \tag{3.9}$$

where summation over repeated indices is understood. For the case of equal elastic constants, we have

$$H(k_\perp z) = \overline{K} \begin{pmatrix} (d^2/dz^2) - k_\perp^2 & 2iq_0 \vec{\mathrm{k}} \cdot \vec{\mathrm{n}}^0(z) \\ -2iq_0 \vec{\mathrm{k}} \cdot \vec{\mathrm{n}}^0(z) & d^2/dz^2 - (k_\perp^2 + q_0^2) \end{pmatrix} , \tag{3.10}$$

where $\overline{K} = \overline{K}_1 = \overline{K}_2 = \overline{K}_3$. $H_{\alpha\overline{\alpha}}$ for the case of nonequal elastic constants is considerably more complicated. In this paper, we will quote the interesting results for the case of nonequal elastic constants but will not reproduce the calculation. The solution to Eq. (3.9) is

$$\chi_{\alpha\alpha'}(k_\perp zz') = -\sum_a \frac{\xi_\alpha(\vec{\mathrm{k}}_\perp za) \xi^*_{\alpha'}(\vec{\mathrm{k}}_\perp z'a)}{E_a} , \tag{3.11}$$

where $\xi_\alpha(\vec{\mathrm{k}}_\perp za)$ and E_a are the eigenfunctions and eigenvalues of $H_{\alpha\alpha'}$:

$$(E_a \delta_{\alpha\overline{\alpha}} - H_{\alpha\overline{\alpha}}) \xi_{\overline{\alpha}}(\vec{\mathrm{k}}_\perp za) = 0 . \tag{3.12}$$

Now, note the following symmetry property of H:

$$(\sigma_3 T_0)^N H (\sigma_3 T_0)^{-N} = H , \tag{3.13}$$

where N is an arbitrary integer, σ_3 is the Pauli matrix $\left(\begin{smallmatrix} 1 & 0 \\ 0 & -1 \end{smallmatrix}\right)$, and T_0 is the translation operator $e^{(\pi/q_0) d/dz}$. Hence if ξ_α is an eigenfunction of H with energy E_a, then so is $(\sigma_3 T_0)^N \xi_\alpha$; and a modified Floquet theorem[43] applies. The eigenfunctions of H can be expressed in the following form:

$$\xi(\vec{\mathrm{k}}_\perp z k_3) = e^{ik_3 z} \begin{pmatrix} \sum_m A_m(\vec{\mathrm{k}}_\perp) e^{2imq_0 z} \\ \sum_m B_m(\vec{\mathrm{k}}_\perp) e^{i(2m+1)q_0 z} \end{pmatrix} . \tag{3.14}$$

The eigenvalue equation is, from Eq. (3.10),

$$\{E - \overline{K}[k_\perp^2 + (k_3 + 2mq_0)^2]\} A_m - i\overline{K} q_0 (k_- B_{m-1} + k_+ B_m) = 0 , \tag{3.15a}$$

$$i\overline{K} q_0 (k_- A_m + k_+ A_{m+1}) + \{E - \overline{K}[(k_\perp^2 + q_0^2) + (k_3 + (2m+1)q_0)^2]\} B_m = 0 , \tag{3.15b}$$

where $k_\pm = k_{\perp 1} \pm ik_{\perp 2}$. If we use Eq. (3.15b) to determine B_{m-1} and B_m in terms of A_{m-1} and A_{m+1}, we obtain from Eq. (3.15a) a three-term recursion formula for the A_m's of the type encountered in the solution of the Mathieu equation[43]

$$\begin{aligned} 0 = {} & \left[E - \overline{K}[k_\perp^2 + (k_3 + 2mq_0)^2] - \overline{K}^2 k_\perp^2 q_0^2 \left(\frac{1}{E - \overline{K}\{(k_\perp^2 + q_0^2) + [k_3 + (2m+1)q_0]^2\}} + \frac{1}{E - \overline{K}\{(k_\perp^2 + q_0^2) + [k_3 + (2m-1)q_0]^2\}} \right) \right] A_m \\ & - \frac{\overline{K}^2 k_-^2 q_0^2}{E - \overline{K}\{(q_0^2 + k_\perp^2) + [k_3 + (2m-1)q_0]^2\}} A_{m-1} - \frac{\overline{K}^2 k_+^2 q_0^2}{E - \overline{K}\{(q_0^2 + k_\perp^2) + [k_3 + (2m+1)q_0]^2\}} A_{m+1} . \end{aligned} \tag{3.16}$$

A similar recursion formula can be obtained for the B_m's. We are only interested in values of k which are much less than q_0. A perturbation solution to Eq. (3.15) in powers of $k_\perp/q_0$ is straightforward. The three lowest eigenvalues and corresponding eigenfunctions are

$$E_0=\overline{K}\left(k_3{}^2+\frac{3}{8}\,\frac{k_\perp{}^2}{q_0^2}\right)\;,\quad E_1=E_{-1}=\overline{K}q_0^2+0(k^2)\;, \tag{3.17}$$

$$\xi_0(k_\perp k_3Z)=e^{ik_3z}\left(\frac{q_0^2}{q_0^2+\frac{1}{2}k^2}\right)^{1/2}\begin{pmatrix}1\\ i(\vec{k}_\perp/q_0)\cdot\vec{n}^0(z)\end{pmatrix}\;, \tag{3.18}$$

$$\xi_1=\begin{pmatrix}0\\ e^{i(k_3+q_0)z}\end{pmatrix}\;,\qquad \xi_{-1}=\begin{pmatrix}0\\ e^{i(k_3-q_0)z}\end{pmatrix}\;.$$

The eigenfunctions are normalized so that

$$\int_{-\infty}^{\infty}dz\,\xi_a(k_\perp k_3z)\,\xi^*_{a'}(k_\perp k_3{}'z)=\delta(k_3-k_3{}') \tag{3.19}$$

for k_3 and $k_3{}'$ in the first Brillouin zone {i.e., for k_3 and $k_3{}'$ in the interval $[-q_0,\,q_0]$}. Changes in $\vec{n}(\vec{r})$ along $\vec{p}^0$ are equivalent to changes in the pitch director along $\vec{n}^0(\vec{r})$. In fact, $\delta\vec{n}(\vec{r})\cdot\vec{p}^0=\delta\psi_2(\vec{r})=-\delta\vec{p}(\vec{r})\cdot\vec{n}^0(\vec{r})$. Hence, the response function $\chi_{\alpha\alpha'}(\vec{r}\,\vec{r}\,')$ can be expressed in terms of the correlation functions for $\delta\psi(\vec{r})$ and $\delta\vec{p}_t(\vec{r})$. The three lowest eigenstates of $\chi_{\alpha\alpha'}(\vec{r}\,\vec{r}\,')$ [Eq. (3.18)] correspond to first Brillouin zone (BZ) variations of these variables. Choosing the three-axis to be along $\vec{p}^0$ and spatial gradients to lie in the 1–3 plane, we obtain

$$\chi_{aa'}(\vec{k})=\begin{pmatrix}1/E(\vec{k}) & ik_\perp/q_0E(\vec{k}) & 0\\ -ik_\perp/q_0E(\vec{k}) & 1/2Kq_0^2+k_\perp{}^2/q_0E(\vec{k}) & 0\\ 0 & 0 & 1/2Kq_0{}^2\end{pmatrix}\;, \tag{3.20}$$

where $a,\ a'=\delta\psi,\ \delta p_1$, and δp_2 in that order,

$$\chi_{aa'}(\vec{k})=1/V\int d^3r\,d^3r'\,e^{-i\vec{k}\cdot(\vec{r}-\vec{r}\,')}\chi_{aa'}(\vec{r},\vec{r}\,')\;,$$

and

$$E(\vec{k})=\overline{K}k_3{}^2+\overline{K}_\perp(\vec{k})k_\perp{}^2\;, \tag{3.21a}$$

$$\overline{K}_\perp(\vec{k})=\overline{K}[\tfrac{1}{2}(k_3/q_0)^2+\tfrac{3}{8}(k_\perp/q_0)^2]\;. \tag{3.21b}$$

In a stable cholesteric, $\overline{K}_\perp(\vec{k})$ would have to be replaced by a constant proportional to $\overline{K}$. Equation (3.21) is only valid for $\vec{k}$ in the first BZ, but this is all we require for a determination of the hydrodynamical behavior of cholesterics. In the appropriate coordinate system, there is only one component of $\chi_{a,a'}$ which diverges in the zero $\vec{k}$ limit. The functions which diagonalize (3.20) are

$$\begin{aligned}\theta(\vec{r})&=\psi+(\nabla\cdot\delta\vec{p}/q_0)\;,\\ \theta_1(\vec{r})&=\nabla_\perp\psi+\delta p_1\;,\\ \theta_2(\vec{r})&=\delta p_2\;,\end{aligned} \tag{3.22}$$

where higher-order terms in ∇ have been neglected. We have

$$\begin{aligned}\chi_{\theta\theta}(\vec{k})&=\frac{1}{E(\vec{k})}\;,\\ \chi_{\theta_1\theta_1}(\vec{k})&=\chi_{\theta_2\theta_2}(\vec{k})=1/2Kq_0^2\;.\end{aligned} \tag{3.23}$$

$\theta(\vec{r})$ is, therefore, the only variable that has a divergent static correlation function. It is the variable which will appear in the discussion of hydrodynamics of cholesterics of Sec. IV. An analysis of the case of nonequal elastic constants shows that $\theta(\vec{r})$ is again the only variable with a divergent correlation function. It has the same form as Eq. (3.23), with

$$E(\vec{k})=\overline{K}_2k_3{}^2+\overline{K}_\perp(\vec{k})k_\perp{}^2\;, \tag{3.24a}$$

$$\overline{K}_\perp(\vec{k})=\left[\tfrac{1}{2}\overline{K}_2+\left(\frac{\overline{K}_1-\overline{K}_2}{\overline{K}_1+\overline{K}_3}\right)1\left(+\frac{\overline{K}_1+\overline{K}_2}{2\overline{K}}\right)\right]\left(\frac{k_3}{q_0}\right)^2+\left(\frac{\overline{K}_2+\overline{K}_3}{2(\overline{K}_1+\overline{K}_3)}\,\overline{K}-\tfrac{1}{8}\overline{K}_2\right)\left(\frac{k_\perp}{q_0}\right)^2 \tag{3.24b}$$

$$\equiv\overline{K}_\parallel\left(\frac{k_3}{q_0}\right)^2+\overline{K}_\perp\left(\frac{k_\perp}{q_0}\right)^2\;, \tag{3.24c}$$

where $\overline{K}=\frac{1}{3}(\overline{K}_1+\overline{K}_2+\overline{K}_3)$. Since $\delta\psi(\vec{r})$ and $\delta p_i(\vec{r})$ are the quantities which would be measured physically, it is of some interest to express their *divergent* parts in terms of $\theta(\vec{r})$:

$$\begin{aligned}\delta\psi(\vec{r})&=\theta(\vec{r})+O(\nabla^2)\;,\\ \delta p_i(\vec{r})&=(1/q_0)\nabla_{\perp i}\theta(\vec{r})+O(\nabla^2)\;.\end{aligned} \tag{3.25}$$

Note that the divergent variable contains contributions from local variations of the pitch phase and splay distortions of the pitch director. It does not contain contributions from the finite-energy pitch-bend and pitch-twist distortions.

Now, let us consider the divergent correlation function $\chi_{\theta\theta}(\vec{k})$ in more detail. It diverges as $k_3{}^2+ck_\perp{}^4$ (c is a constant) rather than as $k_3{}^2+c'k_\perp{}^2$ as is common for the transverse correlation function in most systems with broken symmetries. We can easily see from the form of the free energy of Eq. (3.6) that this form of divergence occurs because of the possibility of second Brillouin zone variations in one variable canceling the first Brillouin zone variations of another.[44] For example, suppose $\delta\psi_1=a_1\cos k_1x$, where k_1 is in the first BZ; then $(\vec{p}\times\vec{n}^0)\cdot\nabla\delta\psi_1=a_1k_1\sin q_0z\sin k_1x$. A variation in $\delta\psi_2$ of the form $\delta\psi_2=a_1k_1/q_0\cos q_0z\sin k_1x$ is such that $p^0\cdot\nabla\delta\psi_2+(p\times n^0)\cdot\nabla\delta\psi_1$ is zero, and the term following $\overline{K}_1$ in Eq. (3.6) does not contribute to this distortion. The absence of a $k_\perp^2$ term in $E(\vec{k})$ is a manifestation of all of the cancellations of this type that can occur.

The absence of a $k_\perp^2$ term in $E(\vec{k})$ implies that an infinite cholesteric described by the Frank free energy is unstable with respect to fluctuations and cannot exist. The argument is similar to that of Landau and Peierls[21] that there are no stable systems in which there is a density variation along one direction and Mermin and Wagner[22] and Hohenberg[23] that infinite two-dimensional ferromagnets and superfluids do not exist. The order-parameter correlation function $\langle Q_{ij}(\vec{r})Q_{kl}(\vec{r}\,')\rangle$ can be expressed in terms of $I_{\psi\psi}=k_BTS^2\chi_{\psi\psi}$ and $I_{p_ip_j}=k_BTS^2\chi_{p_ip_j}$:

$$\begin{aligned}\langle\delta Q_{ij}(\vec{r})\delta Q_{kl}(\vec{r}\,')\rangle={}&[n_i^0(\vec{r})p_j^0]_+n_s^0(\vec{r})I_{p_sp_t}(\vec{r}\,\vec{r}\,')n_t^0(\vec{r}\,')[n_k^0(\vec{r}\,')p_l^0]_+-[n_i^0(\vec{r})p_j^0]_+n_s^0(\vec{r})I_{p_s\psi}(\vec{r}\,\vec{r}\,')\{n_k^0(\vec{r}\,')[\vec{p}^0\times\vec{n}^0(\vec{r}\,')]_l\}_+\\&-\{n_i^0(\vec{r})[\vec{p}^0\times\vec{n}^0(\vec{r})]_j\}_+I_{\psi p_t}(\vec{r}\,\vec{r}\,')n_t^0(\vec{r}\,')[n_k^0(\vec{r}\,')p_l^0]_++\{n_i^0(\vec{r})[\vec{p}^0\times\vec{n}^0(\vec{r})]_j\}_+I_{\psi\psi}(\vec{r}\,\vec{r}\,')\{n_k^0(\vec{r}\,')[\vec{p}^0\times\vec{n}^0(\vec{r}\,')]_l\}_+,\end{aligned}\tag{3.26}$$

where $(n_i^0(\vec{r})p_j^0)_+=n_i^0(\vec{r})p_j^0+n_j^0(\vec{r})p_i^0$. If we let the 1 direction be along $\vec{n}^0(\vec{r})$ and the 2 direction be along $\vec{p}^0\times n^0(\vec{r})$, we find

$$\langle Q_{12}(\vec{r})Q_{12}(\vec{r}\,')\rangle=I_{\psi\psi}(\vec{r}\,\vec{r}\,')\ .\tag{3.27}$$

This is a measure of the fluctuations in the molecular direction which occur in the plane of perpendicular to the pitch axis. The first BZ component of Eq. (3.27) can easily be obtained, and the result integrated over $\vec{k}$:

$$\int\frac{d^3k}{(2\pi)^3}\langle Q_{12}(k)Q_{12}(-k)\rangle=\int\frac{d^3k}{(2\pi)^3}\frac{k_BTS^2}{\bar{K}_2k_3^{\,2}+(\bar{K}_{\parallel}/q_0^2)k_3^{\,2}k_\perp^{\,2}+(\bar{K}_\perp/q_0^2)k_\perp^{\,4}}\ ,\tag{3.28a}$$

$$\langle\sin^2\theta^\alpha\cos^2\theta^\alpha\rangle=\frac{k_BTS^2}{2}\int_{-\infty}^{\infty}\frac{dk_3}{(2\pi)}\int_0^\infty\frac{dx}{2\pi}\frac{1}{\bar{K}_2k_3^{\,2}+\bar{K}_{\parallel}/q_0^2k_3^{\,2}x+\bar{K}_\perp/q_0^2x^2}\ ,\tag{3.28b}$$

where θ^α is the angle particle α makes with the equilibrium director at the point where it is at any given instant of time. The integral or right-hand side of Eq. (3.27) is logarithmically divergent whereas the left-hand side is bounded by one. The only way that equality can hold is for S to be zero. In other words, cholesteric order cannot exist over an infinite sample.

On the other hand, the distance required to completely dephase the cholesteric order is astronomical. Let us calculate the quantity

$$B(\vec{r})=\langle|Q_{12}(\vec{r})-Q_{12}(0)|^2\rangle\tag{3.29}$$

for $\vec{r}=z\vec{p}^0$. This gives us a measure of how closely the molecules at $\vec{r}$ align along the preferred direction $\vec{n}^0(\vec{r})$ given that at $\vec{r}=0$, they are aligned along $\vec{n}^0(0)$. The corresponding quantity for nematics is $\langle|Q_{13}(\vec{r})-Q_{13}(0)|^2\rangle$ where the 3 axis is taken along $\vec{n}^0$. $B(\vec{r})$ is a monotonically decreasing function of the degree of order. If all of the molecules were rigidly fixed in the cholesteric structure, $B(\vec{r})$ would be zero for large $\vec{r}$. The maximum value of B is determined by its value in an isotropic system. [Remember $\langle Q_{12}(\vec{r})Q_{12}(0)\rangle$ tends rapidly to zero in an isotropic system.] We have

$$B_{\max}(\vec{r})=2\langle\cos^2\theta^\alpha\sin^2\theta^\alpha\rangle=\tfrac{8}{15}\ .\tag{3.30}$$

With $\vec{r}$ along $\vec{p}^0$, we obtain

$$B(z)=2k_BTS^2\int_{-q_0}^{q_0}\frac{dk_3}{(2\pi)}\int_0^\infty\frac{k_\perp dk_\perp}{(2\pi)}\frac{1-e^{ik_3z}}{E(k)}$$

$$\cong(1/4\pi)k_BTS^2(\bar{K}_2\bar{K}_\perp)^{-1/2}\ln q_0z\ .\tag{3.31}$$

But $(\bar{K}_2\bar{K}_\perp)^{-1/2}=k_BTS^2/a$, where a is a molecular length (~20 Å). Therefore z_c, the value of z beyond which memory of the orientation of the molecules at $z=0$ is lost, is determined approximately by

$$\ln q_0z_c\sim(1/q_0a)\tfrac{16}{15}\pi\sim\tfrac{1}{2}(\lambda_0/a)\ .\tag{3.32}$$

λ_0 is twice the wavelength of light that is Bragg reflected from a cholesteric which is typically 5000 Å. Hence we have

$$z_c\sim(1/q_0)e^{200}\sim10^{60}\,\text{km}\ .\tag{3.33}$$

This is an astronomical distance.

The cholesteric state does exist and has been observed in the laboratory. With this in mind, there are two attitudes that one can take toward the instability just discussed. The first is that the Frank free energy does not properly describe fluctuations in a cholesteric and that there really should be a $k_\perp^2$ term in the denominator of $\chi_{\theta\theta}(\vec{k})$. The second is that the Frank free energy does describe the cholesteric state but that boundaries stabilize any finite sample. Regarding the first possibility, addition of higher order terms in $\nabla_in_j(\vec{r})$ (i.e., cubic and quartic terms) which preserve the cholesteric structure for the minimum-energy state[45] to the Frank free energy does not alter the form of the static correlation functions of Eq. (3.20). Therefore, in order to obtain a $k_\perp^2$ term in the denominator of $\chi_{\theta\theta}(\vec{k})$, it is probably necessary to discard the concept of a local free energy density that can be expanded in powers of $\nabla_i n_j(\vec{r})$. In view of the success of the Frank free energy in explaining a wealth of static phenomena in both nematic and cholesteric liquid crystals, this is an unappealing proposition, but one which we will not discard completely. Consider now the second possibility. Most laboratory samples of cholesteric liquid crystals are no more than a centimeter in length, so that even if we misestimated the value of the exponent in Eq. (3.32) by as much as a factor of 10, there is no danger of complete dephasing of the cholesteric order in a laborabory size sample. The effect of the boundaries of any finite sample is to replace the integral over $\vec{k}$ in Eq. (3.30) by a discrete Fourier sum. $\chi_{\theta\theta}(\vec{k}=0)$ is nondivergent in a finite sample, but for higher (discrete) values of $\vec{k}$ the correlation functions in the finite sample are essentially the same as those for an infinite sample. In other words, boundaries can stabilize a structure that would be unstable in an infinite system without significantly altering the form of correlation functions in the interior of the sample. In the discussion of hydrodynamics of cholesterics in Sec. IV we will assume that the Frank form of $\chi_{\theta\theta}(\vec{k})$ is correct but will always note where and what kind of differences occur if a $k_\perp^2$ term were present.

IV. THERMODYNAMICS AND REACTIVE COEFFICIENTS

An understanding of the equilibrium properties and thermodynamics of any system is a prerequisite to an understanding of its hydrodynamics. The additional hydrodynamical variable $\theta(\vec{r}t)$ in cholesteric liquid crystals couples to the longitudinal variables of the system: pressure and temperature, for example. There are, therefore, a number of thermodynamic derivatives for cholesteric systems which are not present in isotropic fluids and which warrant discussion.

The calculation of the previous section determined $\delta\theta(\vec{r})$ in the first Brillouin zone as a function of its conjugate field $\delta h_\theta(\vec{r})$ at constant μ and T. If μ and T are allowed to vary, there can be long-range changes in $\theta(\vec{r})$, and it is judicious to use $\nabla_i\delta\theta(\vec{r})$ as our additional variable rather $\delta\theta(\vec{r})$. In analogy with superfluids, we will call $\nabla_i d\theta$, dv_{si}, although it should be noted that v_{si} in the present system is even under time reversal whereas v_{si} in superfluids is odd under time reversal. From Eqs. (3.21) and (2.3), we see that

$$dv_{si} = p_i^0\, dq_0 + dv'_{si} \,, \tag{4.1}$$

where

$$dv_{si} = \nabla_i\, d(\phi + \nabla\cdot\vec{p}/q_0) \,. \tag{4.2}$$

Equation (4.2) is only valid when dv_{si} does not vary in space. When there are spatial variations, we will take Eq. (4.1) to be the definition of dv_{si}. Note that dv_{si} is irrotational (i.e., the gradient of a scalar), but dv'_{si} need not be. ϕ is the phase variable discussed below Eq. (2.3).

The field $\vec{h}$ conjugate to $\vec{v}_s$ is related to h_θ via $h_\theta = -\vec{\nabla}\cdot\vec{h}$. Hence, by Eq. (3.22), changes in h_i at constant μ and T are given by

$$dh_3|_{\mu,T} = \bar{K}_2 dv_{s3}|_{\mu,T} \,, \tag{4.3a}$$

$$dh_1|_{\mu,T} = \bar{K}_\perp(\vec{k})dv_{s1}|_{\mu,T} \,, \tag{4.3b}$$

where, as always the three axis is along $\vec{p}^0$ and gradients lie in the 1-3 plane. Changes in q_0 do not affect v_{s1}, so that Eq. (4.3b) is valid even if μ and T change. Changes in q_0 are however reflected in changes of v_{s3}. Combining Eqs. (4.3a) and (4.1) and ignoring terms of order ∇_3, we have

$$dv_{s3} = \frac{1}{\bar{\bar{K}}_{22}}\, dh_3 + \left.\frac{\partial q_0}{\partial\mu}\right|_{T,h_3} d\mu + \left.\frac{\partial q_0}{\partial T}\right|_{\mu,h_3} dT \,. \tag{4.4}$$

Equations (4.3) and (4.4) express changes in v_{si} induced by changes in the independent variables h_i, μ, and T. As in isotropic liquids, this is not the most convenient set of variables to describe static experiments or hydrodynamics. In isotropic liquids, μ is usually eliminated in favor of the pressure P. In addition, the most convenient choice of densities of longitudinal extensive variables is the mass density $\rho(\vec{r}t)$, the enthalpy density $q(\vec{r}t)$ rather than $\rho(\vec{r}t)$ and the energy density $\epsilon(\vec{r}t)$. Changes in $q(\vec{r}t)$ are equivalent to T times changes in the entropy $\mathcal{S}$ divided by the volume V:

$$(T/V)d\mathcal{S} = dq \,. \tag{4.5}$$

In cholesterics, a similar but naturally more complicated choice of extensive and intensive variables is the most fruitful for the discussion of hydrodynamics.

Our starting point in the search for this new set of variables will be the intensive entropy relation

$$T ds = d\epsilon - \mu d\rho - \vec{v}\cdot d\vec{g} - \vec{h}\cdot d\vec{v}_s \,, \tag{4.6}$$

where $s = \mathcal{S}/V$, $\vec{g}$ is the momentum density and $\vec{v}$ an external velocity. We will justify this equation in Sec. VI. We can easily see that $q(\vec{r}t)$ defined by

$$q(\vec{r}t) = \epsilon(\vec{r}t) - [(Ts + \mu\rho)/\rho]\,\rho(\vec{r}t) - \vec{h}\cdot\vec{v}_s(\vec{r}t) \tag{4.7}$$

is the local density for cholesterics which satisfies Eq. (4.5). $q(\vec{r}t)$ is only meant to describe linear deviations from equilibrium. Hence, in the absence of external fields, the $\vec{h}\cdot\vec{v}_s(\vec{r}t)$ term can be ignored. Equation (4.7) should be regarded as an equation relating linear changes of q from equilibrium to linear changes in ϵ, ρ, and v_s from equilibrium. All variables not explicitly functions of $\vec{r}$ and t are evaluated in equilibrium. We can now express dh_3 in terms of the internal variables v_{s3}, q, and ρ:

$$dh_3 = K_2' dv_{s3} + \frac{\partial h_3}{\partial \rho}\bigg|_{v_{s3},s} d\rho + \frac{V}{T}\frac{\partial h_3}{\partial s}\bigg|_{v_{s3},\rho} dq\,, \tag{4.8}$$

where $K_2' = \partial h_3/\partial v_{s3})_{\rho,s}$. The derivatives of h_3 with respect to ρ and s can be expressed in terms of derivatives of q_0 with respect to ρ and s at constant h_3:

$$dh_3 = K_2'\left(dv_{s3} - \frac{\partial q_0}{\partial \rho}\bigg|_{h_3,s} d\rho - \frac{V}{T}\frac{\partial q_0}{\partial s}\bigg|_{h_3,\rho} dq\right). \tag{4.9}$$

Before introducing the equilibrium pressure, let us note

$$\frac{\partial T}{\partial v_{s3}}\bigg|_{\rho,s} = T\left(\frac{V}{T}\frac{\partial h_3}{\partial s}\right)_{\rho,v_s} = -K_2' T\left(\frac{V}{T}\frac{\partial q_0}{\partial s}\right)_{h_3,\rho} \tag{4.10}$$

$$\begin{aligned}\frac{\partial \mu}{\partial v_{s3}}\bigg|_{\rho,s} &= \frac{\partial h_3}{\partial \rho}\bigg|_{s,v_s} - \frac{Ts}{\rho}\frac{V}{T}\frac{\partial h_3}{\partial s}\bigg|_{\rho v_s} \\ &= -K_2'\frac{\partial q_0}{\partial \rho}\bigg|_{h_3,s} + K_2'\frac{Ts}{\rho}\frac{V}{T}\frac{\partial q_0}{\partial s}\bigg|_{h_3,\rho}.\end{aligned} \tag{4.11}$$

There are various ways of determining the stress tensor of a system. For us, the most direct way of determining the equilibrium stress tensor for a cholesteric is to determine $T\partial s/\partial t$ in terms of currents of the conserved quantities via Eq. (4.6) and to require that this quantity be zero in the absence of dissipation. The "conserved" quantities[12] are ϵ, ρ, $\vec{g}$, and $\vec{v}_s$. Their time derivatives are gradients of currents:

$$\begin{aligned}&\frac{\partial \epsilon}{\partial t} + \nabla\cdot\vec{j}^{\,\epsilon} = 0\,, \quad \frac{\partial g_i}{\partial t} + \nabla_j \sigma_{ij} = 0\,, \\ &\frac{\partial \rho}{\partial t} + \nabla\cdot\vec{g} = 0\,, \quad \frac{\partial v_{st}}{\partial t} + \nabla_i X = 0\,,\end{aligned} \tag{4.12}$$

where j_i^ϵ is the energy current, σ_{ij} is the stress tensor, and $X = -\partial\theta/\partial t$ is the current of the conserved variable v_{st}. There are reactive couplings of j_i^ϵ and X to v_i. By Galilean invariance, we know

$$j_i^\epsilon = (\epsilon\delta_{ij} + \sigma_{ji})v_j + j_i'^{\,\epsilon}\,, \tag{4.13}$$

where $j_i'^{\,\epsilon}$ is the dissipative part of the energy current. We can also determine the coefficient coupling X to v_i by Galilean and rotational invariance arguments. Consider a coordinate system moving with velocity $-\vec{v}$ relative to the lab frame. Call this the prime system. Then $\vec{r}' = \vec{r} + \vec{v}t$. Fields evaluated at the same point have the same value regardless of the coordinate system. Hence

$$\begin{aligned}&\psi(\vec{r}) = q_0\vec{p}^{\,0}\cdot\vec{r} + \phi = \psi'(\vec{r}') = q_0\vec{p}^{\,0}\cdot\vec{r}' + \phi'\,, \\ &\phi' = \phi - q_0\vec{p}^{\,0}\cdot\vec{v}t\,,\end{aligned} \tag{4.14a}$$

$$\frac{\partial\psi'(\vec{r})}{\partial t} = \frac{\partial\phi'}{\partial t} = -q_0\vec{p}^{\,0}\cdot\vec{v}\,. \tag{4.14b}$$

Similarly, by considering a rigid rotation about the 3-axis, we can derive

$$\frac{\partial\psi}{\partial t} = \frac{1}{2}\vec{p}^{\,0}\cdot\vec{\nabla}\times\vec{v}\,. \tag{4.15}$$

Therefore

$$X = q_0\vec{p}^{\,0}\cdot\vec{v} - \tfrac{1}{2}\vec{p}^{\,0}\vec{\nabla}\times\vec{v} + X'\,, \tag{4.16}$$

where X' is the dissipative part of X. There are additional reactive terms in X proportional to higher spatial derivatives of $\vec{V}$ which are of no real interest to us, though it is worth pointing out that the first contribution to X from the $\nabla\cdot\vec{p}/q_0$ part of ψ is $(1/2q_0)\vec{\nabla}\cdot\vec{p}\times(\vec{\nabla}\times\vec{v})$. Note that the reactive couplings to $\vec{v}$ are consistent with invariance under the parity transformation discussed in Sec. II.

We are now ready to return to the determination of the equilibrium stress tensor. Using Eqs. (4.6), (4.12), (4.13), and (4.16) and setting $g_i = \rho v_i$, we obtain by standard procedures[25] which are reproduced in Appendix A

$$\begin{aligned}T\left(\frac{\partial s}{\partial t} + \nabla\cdot\vec{v}s\right) = &-\nabla\vec{j}'^{\,\epsilon} + [(\mu\rho + Ts - \epsilon)\delta_{ij} - \sigma_{ji}]\nabla_i v_j \\ &+ q_0 p_j^0 h_i \nabla_i v_j + \tfrac{1}{2}p_k^0\epsilon_{kij}\vec{\nabla}\cdot\vec{h}\,\nabla_i v_j + \vec{h}\cdot\vec{\nabla}X'\,.\end{aligned} \tag{4.17}$$

Hence, the reactive part of the stress tensor is

$$\sigma_{ij}^R = P\delta_{ij} + q_0 p_i^0 h_j - \tfrac{1}{2}\epsilon_{ijk}p_k^0\vec{\nabla}\cdot\vec{h}\,, \tag{4.18}$$

where the pressure P is

$$P = \mu\rho + Ts - \epsilon\,. \tag{4.19}$$

σ_{ij} can be cast in a manifestly symmetric form by integration by parts if desired.[16]

The pressure differential satisfies

$$dP = \rho\, d\mu + s\,dT - \vec{h}\cdot d\vec{v}_s\,, \tag{4.20}$$

from which we obtain with the aid of Eqs. (4.10) and (4.11)

$$\frac{\partial P}{\partial v_{s3}}\bigg|_{\rho,s} = -K_2'\frac{\partial q_0}{\partial \rho}\bigg|_{h_3,s}\,. \tag{4.21}$$

The analysis of the mode structure for $\vec{k}$ in the three direction is simplified by the introduction of a special symbol for the 3-3 component of the stress tensor:

$$\Sigma \equiv \sigma_{33} = P + q_0 h_3\,. \tag{4.22}$$

The differential of Σ is expressible solely in terms of changes in external parameters:

$$d\Sigma = \rho\, d\mu + s\,dT + q_0\, dh_3\,. \tag{4.23}$$

The derivative of Σ with respect to v_{s3} at constant ρ and satisfies

$$\frac{\partial\Sigma}{\partial v_{s3}}\bigg|_{\rho,s} = K_2'\left(q_0 - \rho\frac{\partial q_0}{\partial\rho}\bigg|_{h_3,s}\right). \tag{4.24}$$

From the definition of $q(\vec{r}t)$, Eq. (4.7), and the expression for σ_{ij} just derived, we can see that the current for q is the dissipative part of the energy current

$$\frac{\partial q(\vec{r}t)}{\partial t}+\nabla\cdot\vec{j}'^{\epsilon}=0\ . \tag{4.25}$$

Furthermore, ignoring terms of order $\vec{h}$, q assumes the same form as in an isotopic fluid

$$q(\vec{r}t)=\epsilon(\vec{r}t)-[(\epsilon+P)/\rho]\rho(\vec{r}t)\ . \tag{4.26}$$

Before closing this section, let us emphasize that the elastic constant K_2 appearing in the Frank free energy is just the derivative of h_3 with respect to v_{s3} at constant density and temperature, $\partial h_3/\partial v_{s3}|_{\rho,T}$. We have introduced symbols for derivatives of h_3 with respect to v_{s3} with other variables held constant

$$K_2{}'=\frac{\partial h_3}{\partial v_{s3}}\bigg|_{\rho,S}\ ,\quad \overline{K}_2=\frac{\partial h_3}{\partial v_{s3}}\bigg|_{\mu,T}=\frac{\partial h_3}{\partial v_{s3}}\bigg|_{P,T}\ . \tag{4.27}$$

In the next Sec. V it will be useful to have a symbol for yet another derivative

$$\tilde{K}_2=\frac{\partial h_3}{\partial v_{s3}}\bigg|_{\Sigma,T}=\overline{K}_2\bigg/\left[1-q_0\Big/\rho\,\frac{\partial q_0}{\partial\rho}\bigg|_{P,T}\right]\ . \tag{4.28}$$

V. DISSIPATIVE COEFFICIENTS AND MODE STRUCTURE

The reactive parts of the various currents have been determined in the previous section. The dissipative parts are again determined with the aid of the linearized entropy production equation

$$T\,\frac{\partial s}{\partial t}+\nabla\cdot\left(\vec{v}s+\frac{1}{T}\vec{j}'^{\epsilon}\right)=-\sigma'_{ij}\nabla_i v_j-j_i'^{\epsilon}\,\frac{\nabla_i T}{T}-X'\nabla\cdot\vec{h}\ . \tag{5.1}$$

The constitutive relations for the dissipative currents are therefore

$$X'=-(1/\gamma)\nabla\cdot\vec{h}\ , \tag{5.2}$$

$$j_i'^{\epsilon}=-\kappa_{ij}\nabla_j T\ , \tag{5.3}$$

$$\sigma'_{ij}=-\nu_{ijkl}\,\nabla_l v_k\ , \tag{5.4}$$

where

$$\kappa_{ij}=\kappa_{\parallel}p_i^0p_j^0+\kappa_{\perp}\delta_{ij}^T \tag{5.5}$$

$$\begin{aligned}\nu_{ijkl}\nabla_k v_l={}&2\nu_2A_{ij}+2(\nu_3-\nu_2)\,[p_i^0p_k^0A_{kj}+p_j^0p_k^0A_{ki}]\\&+2(\nu_1+\nu_2-2\nu_3)p_i^0p_j^0(p_k^0A_{kl}\,p_l^0)+(\nu_4-\nu_2)\delta_{ij}A_{kk}\\&+(\nu_5-\nu_4+\nu_2)\,[\delta_{ij}p_k^0p_l^0A_{kl}+p_i^0p_j^0A_{kk}]\ ,\end{aligned} \tag{5.6}$$

where $\delta_{ij}^T=\delta_{ij}-p_i^0p_j^0$ and $A_{ij}=\frac{1}{2}(\nabla_i v_j+\nabla_j v_i)$. κ_{ij} is the thermal conductivity tensor and ν_{ijkl} the viscosity tensor. Positivity of entropy production implies

$$\begin{gathered}\kappa_{\parallel}>0\ ,\quad \kappa_{\perp}>0,\quad \gamma>0\ ,\quad \nu_4(2\nu_1+\nu_2)\geq(\nu_5-\nu_4)^2\ ,\\ \nu_2\geq0\ ,\quad \nu_3\geq0\ ,\quad \nu_4\geq0\ ,\quad 2(\nu_1+\nu_5)-\nu_4+\nu_2\geq0\ .\end{gathered} \tag{5.7}$$

There is no term in X' proportional to $q_0\vec{p}^0\cdot\nabla T$ because, if there were, $\partial\theta/\partial t$ would be nonzero in a constant temperature gradient. In other words, a cholesteric with a temperature gradient along its pitch axis would appear to rotate. This is a highly improbable behavior and to the author's knowledge has not been observed.

We are now in a position to write down the linearized hydrodynamical equations for all of the conserved variables:

$$\frac{\partial\rho}{\partial t}=-\rho\nabla\cdot\vec{v}\ , \tag{5.8a}$$

$$\frac{\partial g_i}{\partial t}=-\nabla_iP-q_0p_i^0\nabla\cdot\vec{h}+\tfrac{1}{2}\epsilon_{ijk}\nabla_j\nabla\cdot\vec{h}+\nu_{ijkl}\nabla_j\nabla_l v_k\ , \tag{5.8b}$$

$$\frac{\partial q}{\partial t}=\kappa_{ij}\nabla_i\nabla_jT\ , \tag{5.8c}$$

$$\frac{\partial v_{si}}{\partial t}=\nabla_i\left(-q_0\vec{p}^0\cdot\vec{v}+\tfrac{1}{2}\vec{p}^0\cdot(\nabla\times\vec{v})+\frac{1}{\gamma}\nabla\cdot\vec{h}\right). \tag{5.8d}$$

For some purposes, it is more convenient to eliminate a gradient from Eq. (5.8d):

$$\frac{\partial\theta}{\partial t}=-q_0\vec{p}^0\cdot v+\tfrac{1}{2}\vec{p}^0\cdot(\nabla\times\vec{v})-\frac{1}{\gamma}h_\theta\ , \tag{5.9}$$

where $h_\theta=-\vec{\nabla}\cdot\vec{h}$. The $\vec{p}^0\cdot(\vec{\nabla}\times\vec{v})$ and $\epsilon_{ijk}p_k^0\nabla_j\vec{\nabla}\cdot\vec{h}$ terms in Eqs. (5.8) will be neglected in this section because they contribute terms of higher order in k to the mode frequencies. To obtain the mode structure for cholesterics, we follow the standard procedure of taking the Laplace transform in time and Fourier transform in space of Eq. (5.8). Let $A(\vec{r}t)$ be any variable; then

$$A(\vec{k}\zeta)=\int d^3r\int_0^\infty dt\,e^{-ik\cdot\vec{r}+i\zeta t}A(\vec{r}t)\ . \tag{5.10}$$

ζ is assumed to have a small imaginary part to insure convergence. Also, we will set $A(\vec{k},\ t=0)=A(\vec{k})$. The most convenient set of variables for analyzing Eq. (5.8) is $\rho(\vec{k},\ \zeta)$, $q(\vec{k}\zeta)$, $g_2(k,\ \zeta)$, $g_{\perp}(k\zeta)$, $g_{\parallel}(k\zeta)$, and $\vec{v}_s(k\zeta)$. As usual, $\vec{k}$ lies in the 1-3 plane and

$$\begin{aligned}g_{\parallel}&=(1/k)(g_1k_1+g_3k_3)\ ,\\ g_{\perp}&=(1/k)(-g_3k_1+g_1k_3)\ .\end{aligned} \tag{5.11}$$

$g_{\parallel}(\vec{k},\ \zeta)$ is the longitudinal part of $\vec{g}$ and satisfies $\zeta\rho(\vec{k}\zeta)=kg_{\parallel}(\vec{k}\zeta)$. $\vec{g}_{\perp}(\vec{k}\zeta)$ is always perpendicular to $\vec{k}$ in the 1-3 plane.

For linear deviations from equilibrium any of the external variables P, Σ, T, and h_3 can be expressed in terms of the internal variables ρ, q, and v_{s3}. Let $B(\vec{k},\zeta)$ be one of the external variables; then

$$\begin{aligned}B(\vec{k}\zeta)={}&\frac{\partial B}{\partial\rho}\bigg|_{S,v_{s3}}\rho(\vec{k}\zeta)+\frac{V}{T}\,\frac{\partial B}{\partial S}\bigg|_{\rho,v_{s3}}q(\vec{k}\zeta)\\&+\frac{\partial B}{\partial v_{s3}}\bigg|_{\rho,S}v_{s3}(\vec{k}\zeta)\ .\end{aligned} \tag{5.12}$$

h_1 is not coupled to ρ and q to zero order in k so that it can be expressed simply in terms of $v_{s1}(\vec{k}\zeta)$:

$$h_1(\vec{k}\zeta)=\overline{K}_\perp(\vec{k})\,v_{s1}(\vec{k}\zeta)\ . \tag{5.13}$$

For variables characterizing initial conditions, it is convenient to use the external variables $P(\vec{k})$, $T(\vec{k})$, and $h(\vec{k})$:

$$\rho(\vec{k})=\frac{\partial\rho}{\partial P}\bigg|_{h,T}\delta P(\vec{k})+\frac{\partial\rho}{\partial T}\bigg|_{h,P}\delta T(\vec{k})+\frac{\partial\rho}{\partial h_3}\bigg|_{P,T}\delta h_3(\vec{k})\ , \tag{5.14a}$$

$$q(\vec{k})=\frac{T}{V}\frac{\partial\mathcal{S}}{\partial P}\bigg|_{h,T}\delta P(\vec{k})+\frac{T}{V}\frac{\partial\mathcal{S}}{\partial T}\bigg|_{h,T}\delta T(\vec{k})+\frac{T}{V}\frac{\partial\mathcal{S}}{\partial h_3}\bigg|_{P,T}\delta h_3(\vec{k})\ , \tag{5.14b}$$

$$v_{s3}(\vec{k})=\frac{\partial q_0}{\partial P}\bigg|_{h,T}\delta P(\vec{k})+\frac{\partial q_0}{\partial T}\bigg|_{h,P}\delta T(\vec{k})+\frac{1}{\overline{K}_2}\delta h_3(\vec{k})\ , \tag{5.14c}$$

$$v_{s1}(\vec{k})=\frac{1}{\overline{K}_\perp(\vec{k})}\delta h_1(\vec{k})\ . \tag{5.14d}$$

The momentum density is always linearly related to the velocity

$$\vec{g}(\vec{k}\zeta)=\rho\vec{v}(\vec{k}\zeta)\ , \tag{5.15a}$$

$$g(\vec{k})=\rho\vec{v}(\vec{k})\ . \tag{5.15b}$$

The dynamical equations (5.8) plus Eqs. (5.12), (5.13), and (5.15) relating internal to external variables completely define the hydrodynamical mode structure for cholesteric liquid crystals. There are five independent modes. The mode associated with g_2 decouples from all of the rest,

$$[-i\zeta+D_2(\vec{k})k^2]g_2(\vec{k},\zeta)=\rho v_2(k\vec{\zeta})\ , \tag{5.16}$$

where

$$D_2(\vec{k})=(1/\rho k^2)(\nu_2 k_1{}^2+\nu_3 k_3{}^2)\ . \tag{5.17}$$

The other four modes are all coupled together for general direction of propagation $\vec{k}$, making a determination of the eigenfrequencies extremely difficult. We will content ourselves with an examination of the mode structure in the absence of damping for general $\vec{k}$ and in the presence of damping for $\vec{k}$ along the 1 and 3 directions. The mode equations in the absence of damping are

$$\begin{pmatrix} \zeta^2-c_0^2k^2+K_2'\,q_0\,\dfrac{\partial q_0}{\partial\rho}\bigg|_{h,\mathcal{S}}k_3{}^2 & 0 & -iq_0k_3E'(k)+ik_3k^2K_2'\rho\,\dfrac{\partial q_0}{\partial\rho}\bigg|_{h,\mathcal{S}} \\ 0 & -i\zeta & q_0k_1/k \\ \zeta q_0k_3/\rho k^2 & -(k_1/k)\,q_0/\rho & -i\zeta \end{pmatrix}\begin{pmatrix}\rho(\vec{k}\zeta)\\ g_\perp(\vec{k}\zeta)\\ \theta(\vec{k}\zeta)\end{pmatrix}=\begin{pmatrix} i\zeta\,\delta\rho(\vec{k})\\ \rho v_\perp(\vec{k})\\ \delta\theta(\vec{k})+(iq_0k_3/\rho k^2)\,\delta\rho(\vec{k})\end{pmatrix}, \tag{5.18}$$

where

$$E'(k)=K_2'k_3^2+\overline{K}_\perp(k)\,k_1{}^2\ , \tag{5.19}$$

$$c_0^2=\frac{\partial P}{\partial\rho}\bigg|_{\mathcal{S},v_{s3}}\ , \tag{5.20}$$

and where we used

$$\frac{\partial h_3}{\partial\rho}\bigg|_{\mathcal{S},v_{s3}}=\frac{1}{\rho}\,\frac{\partial P}{\partial v_{s3}}\bigg|_{\rho,\mathcal{S}}=-K_2'\,\frac{\partial q_0}{\partial\rho}\bigg|_{h_3,\mathcal{S}}\ . \tag{5.21}$$

There are two propagating modes in Eq. (5.18): one longitudinal sound mode and one coupled θ-$g_\perp$ mode with velocities

$$c^2(k)=c_0^2+\frac{q_0^2E'(k)}{k}\,\frac{k_3{}^2}{k^4}-2K_2'\,q_0\,\frac{\partial q_0}{\partial\rho}\bigg|_{h_3,\mathcal{S}}\left(\frac{k_3}{k}\right)^2\ , \tag{5.22a}$$

$$c_\perp^2(k)\,k^2=\frac{q_0^2E'(k)}{\rho}\left(\frac{k_1}{k}\right)^2\ . \tag{5.22b}$$

Terms of higher order in $q_0^2E'/\rho c^2k^2\sim10^{-7}$ were neglected in these equations. Note that the velocity of longitudinal sound is anisotropic with the difference in velocity between the 3 and 1 directions being

$$K_2'\left[\left(\frac{q_0^2}{\rho}\right)-2q_0\,\frac{\partial q_0}{\partial\rho}\right]\ .$$

Since $\overline{K}_\perp(k)$ is proportional to k^2 for small k, the transverse mode is soundlike with $c_\perp^2k^2\sim k^2$ only for $k_1\sim k_3$ (i.e., for directions of propagation at 45° to the axes). For $k_3\cong0$, we have $c_\perp^2k^2\sim k_1{}^4$, and as we shall see later, the mode is dominated by damping. For $k_1=0$, we have $c_\perp^2k^2=0$ and the mode is purely diffusive. If $\overline{K}_\perp$ were proportional to a constant for small k, then the shear wave would propagate for $\vec{k}$ along the 1-axis.

When $k_3=0$, the ρ-q modes decouple from the $g_\perp$-v_{s1} modes (v_{s3} does not enter the mode structure along the 1-direction). We have

$$\begin{pmatrix} -i\zeta+\kappa\,\dfrac{V}{T}\,\dfrac{\partial T}{\partial\mathcal{S}}\bigg|_{\rho,v_s}k_1{}^2 & \kappa k_1{}^2\,\dfrac{\partial T}{\partial\rho}\bigg|_{v_s,\mathcal{S}} \\ -\dfrac{V}{T}\,\dfrac{\partial P}{\partial\mathcal{S}}\bigg|_{\rho,v_s} & \zeta^2-c_0^2k_1{}^2+iD_\parallel(k_1)\,k_1{}^2 \end{pmatrix}\begin{pmatrix} q(k_1\zeta)\\ \rho(k_1\zeta)\end{pmatrix}=\begin{pmatrix}\delta q(k_1)\\ (i\zeta-D_\parallel k_1{}^2)\,\delta\rho(k_1)\end{pmatrix}\ , \tag{5.23}$$

where $D_{\parallel}(k_1)=(\nu_2+\nu_4)/\rho$. This yields a damped longitudinal sound and thermal diffusion mode just as in an isotropic fluid with widths Γ_l and Γ_T of the two modes given by

$$\Gamma_l=(\kappa/c_{Pv_s})\,k_1^{\,2}\,, \tag{5.24a}$$

$$\Gamma_T=\frac{\nu_2+\nu_4}{\rho}\,k_1^{\,2}+\Gamma_l\left(\frac{c_{Pv_s}}{c_{\rho v_s}}-1\right), \tag{5.24b}$$

where c_{Pv_s} and $c_{\rho v_s}$ are, respectively, the specific heats per unit volume at constant (P, v_s) and (ρ, v_s).

The $g_\perp - v_{si}$ sub-block is

$$\begin{pmatrix} -i\zeta+(\nu_3/\rho)\,k_1^{\,2} & q_0\,(\overline{K}_\perp/q_0^2)\,k_1^{\,3} \\ -k_1\,q_0/\rho & -i\zeta+(\overline{K}_\perp/\gamma q_0^2)\,k_1^{\,4}\end{pmatrix}\begin{pmatrix} g_\perp(k_1,\zeta) \\ v_{s1}(k_1,\zeta)\end{pmatrix}=\begin{pmatrix}\rho\,v_\perp(k_1) \\ [1/\overline{K}_\perp(k_1)]\,h_1(k_1)\end{pmatrix}\,. \tag{5.25}$$

If we assume as usual that $\overline{K}_\perp\rho/\gamma^2\ll 1$, the two modes are readily found to be

$$\zeta_1=-i(\nu_3/\rho)k_1^{\,2}\quad, \tag{5.26a}$$

$$\zeta_2=-i\,\tfrac{1}{4}(\overline{K}_\perp/\nu_3)k_1^{\,2}\quad. \tag{5.26b}$$

Both of these modes are purely diffusive. Note the striking absence of the coefficient γ from these modes.

When $k_1=0$, the $g_\perp$ mode decouples from the others:

$$[-i\zeta+(\nu_3/\rho)k_3^{\,2}]g_\perp(k_3\zeta)=\rho\,v_\perp(k_3)\,. \tag{5.27}$$

The ρ, q, and v_{s3} modes are all coupled:

$$\begin{pmatrix} -i\zeta+\kappa k_3^{\,2}\,\dfrac{V}{T}\,\dfrac{\partial T}{\partial S} & \kappa k_3^{\,2}\,\dfrac{\partial T}{\partial\rho} & \kappa k_3^{\,2}\,\dfrac{\partial T}{\partial v_{s3}} \\ -\dfrac{V}{T}\,\dfrac{\partial\Sigma}{\partial S}\,k_3^{\,2} & \zeta^2-\dfrac{\partial\Sigma}{\partial\rho}\,k_3^{\,2}+i\zeta\,\dfrac{\nu_{\parallel}}{\rho}\,k_3^{\,2} & -\dfrac{\partial\Sigma}{\partial v_{s3}}\,k_3^{\,2} \\ \dfrac{1}{\gamma}\,\dfrac{V}{T}\,\dfrac{\partial h_3}{\partial S}\,k_3^{\,2} & \dfrac{1}{\gamma}\,\dfrac{\partial h_3}{\partial\rho}\,k_3^{\,2}+\dfrac{i\zeta q_0}{\rho} & -i\zeta+\dfrac{1}{\gamma}\,\dfrac{\partial h_3}{\partial v_{s3}}\,k_3^{\,2}\end{pmatrix}\begin{pmatrix} q(k_3\zeta) \\ \rho(k_3\zeta) \\ v_{s3}(k_3\zeta)\end{pmatrix}$$

$$=\begin{pmatrix}\delta q(k) \\ \left(i\zeta-\dfrac{\nu_{\parallel}}{\rho}\,k_3^{\,2}\right)\delta\rho(k_3) \\ \delta v_{s3}(k_3)-\dfrac{q_0}{\rho}\,\delta\rho(k_3)\end{pmatrix}, \tag{5.28}$$

where $\nu_{\parallel}=(2\nu_3-2\nu_1+\nu_4-\nu_2-\nu_5)$, and where all thermodynamic derivatives appearing in the matrix are taken with constant internal variables ρ, S, or v_{s3}. The determinant Δ of this matrix determines the mode structure and can be expressed in the following form:

$$\Delta=(i\zeta+D_q k_3^{\,2})(\zeta^2-c_3^{\,2}k_3^{\,2}+iD_l k_3^{\,2})(-i\zeta+D_{v_{s3}}k_3^{\,2})\,, \tag{5.29}$$

where c_3 is the sound velocity

$$c_3^2=\left.\frac{\partial\Sigma}{\partial\rho}\right|_{S,v_s}+\frac{K_2'\,q_0}{\rho}\left(q_0-\rho\left.\frac{\partial q_0}{\partial\rho}\right|_{h_3,}\right)$$

$$=c_0^2+\frac{K_2'\,q_0}{\rho}\left(q_0-2\rho\left.\frac{\partial q_0}{\partial\rho}\right|_{h_3,S}\right)\,. \tag{5.30}$$

A straightforward but tedious exercise in the manipulation of Jacobians shows

$$c_3^2\,D_q D_{v_{s3}}=\frac{\kappa}{\gamma}\,\frac{V}{T}\,\frac{\partial(T,\Sigma,h_3)}{\partial(S,\rho,v_{s3})}\,, \tag{5.31a}$$

$$D_q+D_{v_{s3}}=\kappa\,\frac{V}{T}\left.\frac{\partial T}{\partial S}\right|_{\Sigma v_s}\times\left(1-\frac{q_0}{\rho}\left.\frac{\partial\rho}{\partial v_{s3}}\right|_{\Sigma,T}\right)\left(1-\frac{q_0}{\rho}\left.\frac{\partial\rho}{\partial v_{s3}}\right|_{\Sigma,S}\right)^{-1}+\frac{1}{\gamma}\left.\frac{\partial h}{\partial v_{s3}}\right|_{\Sigma,S}\left(1-\frac{q_0}{\rho}\left.\frac{\partial\rho}{\partial v_{s3}}\right|_{S,\Sigma}\right)^{-1}, \tag{5.31b}$$

$$D_q+D_{v_{s3}}+D_l=\kappa\,\frac{V}{T}\left.\frac{\partial T}{\partial S}\right|_{\rho v_s}+\frac{1}{\gamma}\left.\frac{\partial h_3}{\partial v_{s3}}\right|+\frac{\nu_{\parallel}}{\rho}\,. \tag{5.31c}$$

Equations (5.31) can easily be solved for D_q, D_ρ, and $D_{v_{s3}}$. The solutions simplify greatly if $\kappa/c_{\Sigma v_{s3}}\gg K_2'/\gamma$, where $c_{\Sigma v_{s3}}$ is the specific heat per unit volume at constant Σ and v_{s3}. A typical value of κ is organic liquids is 3×10^{-4} cal/sm sec/K,[46] and the specific heat per unit volume of PAA is of order 2×10^4 erg/cm^3 °K,[47] yielding $\kappa/c_{\Sigma v_{s3}}$ $\sim6\times10^{-4}$ cm^2/sec. K_2 is of order 1.5×10^{-6} dyn

(Ref. 38) and γ or order 10^{-1} P (Ref. 17), yielding $K'_2/\gamma \sim 5\times10^{-6}$ cm^2/sec. It is therefore, reasonable to expect the above inequality to hold in cholesterics, in which case

$$D_{v_{s3}} = \frac{K'_2}{\gamma}\left[1 - \frac{q_0}{\rho}\, \frac{\partial\rho}{\partial v_{s2}}\bigg|_{\Sigma,T}\right]^{-1} , \tag{5.32a}$$

$$\begin{aligned} D_q = {} & \frac{\kappa}{c_{\Sigma v_{s3}}}\left(1 - \frac{q_0}{\rho}\,\frac{\partial\rho}{\partial v_{s3}}\bigg|_{\Sigma,T}\right)\bigg/\left(1 - \frac{q_0}{\rho}\,\frac{\partial\rho}{\partial v_{s3}}\bigg|_{\Sigma,\mathcal{S}}\right) \\ & + \frac{1}{\gamma}\left[\frac{\partial h_3}{\partial v_{s3}}\bigg|_{\Sigma,\mathcal{S}}\left(1 - \frac{q_0}{\rho}\,\frac{\partial\rho}{\partial v_{s3}}\bigg|_{\Sigma,\mathcal{S}}\right)^{-1}\right. \\ & \left. - \frac{\partial h_3}{\partial v_{s3}}\bigg|_{\Sigma,T}\left(1 - \frac{q_0}{\rho}\,\frac{\partial\rho}{\partial v_{s3}}\bigg|_{\Sigma,T}\right)^{-1}\right] . \end{aligned} \tag{5.32b}$$

VI. MICROSCOPIC VARIABLES AND CORRELATION FUNCTIONS

In previous sections, we have discussed cholesteric liquid crystals from a basically phenomenological point of view. We started from a phenomenological free energy expressed in terms of gradients of the director $\vec{n}$. This determined the additional variable which would appear in the macroscopic hydrodynamics discussed in Secs. IV and V. In this section, we will discuss cholesterics from a more microscopic point of view. We will derive the entropy relation [Eq. (4.6)] from a density matrix, and discuss what the hydrodynamical equations can tell us about the correlation functions of microscopic variables with particular emphasis on the liquid-crystal order parameter. We will not, however, attempt in any way to perform a first-principles calculation of the properties of the cholesteric state.

The equilibrium density matrix $\mathfrak{D}$ for a liquid crystal in an external field coupling to the order parameter is equal to

$$\exp\{-\beta[\mathcal{H} - \vec{P}\cdot\vec{v} - \mu m N - \textstyle\int d^3r\, Q_{ij}(\vec{r})H_{ij}]\} , \tag{6.1}$$

where β is the inverse temperature, $\mathcal{H}$ the Hamiltonian, $\vec{P}$ the total momentum operator $\int d^3r\, \vec{g}(\vec{r})$, N the number operator $(1/m)\int d^3r\, \rho(\vec{r})$, and H_{ij} the external field coupling to $Q_{ij}(\vec{r}t)$. H_{ij} is usually assumed to result from an external magnetic field coupling to the anistropic part of the polarizability of the liquid-crystal molecules. In this case $H_{ij} = \frac{1}{2}(\rho/m)\kappa_a H_i H_j = \frac{1}{2}\chi_a H_i H_j$, where H_i is the external magnetic field, κ_a the anistropic polarizability, and χ_a the susceptibility. Defining W to be $-\ln \mathrm{Tr}\, \mathfrak{D}$, we find

$$\begin{aligned} dW = {} & E\,d\beta - mNd(\beta\mu) - \textstyle\int d^3r\, \langle Q_{ij}(\vec{r})\rangle\, \delta(\beta H_{ij}(\vec{r})) \\ & - \vec{P}\cdot d(\beta\vec{v}) , \end{aligned} \tag{6.2}$$

where $E = \langle\mathcal{H}\rangle = \mathrm{Tr}\, \mathfrak{D}\mathcal{H}$ is the energy of the system. In Eq. (6.2), we have chosen not to make a notational distinction between the operators N and $\vec{P}$ and their equilibrium expectation values. The entropy is

$$\mathcal{S} = \beta[E - \mu m N - \vec{P}\cdot\vec{v} - \textstyle\int d^3r\, Q_{ij}(\vec{r})H_{ij}(\vec{r})] - W \tag{6.3}$$

and its differential satisfies

$$d\mathcal{S} = \beta[dE - \mu m\, dN - \vec{v}\cdot d\vec{P} - \textstyle\int d^3r\, H_{ij}(\vec{r})\,\delta\langle Q_{ij}(\vec{r})\rangle] . \tag{6.4}$$

The Gibbs energy used in Sec. III in terms of these variables is

$$G(\mu, T, \langle Q_{ij}\rangle) = TW + \textstyle\int d^3r\, \langle Q_{ij}(\vec{r})\rangle H_{ij}(\vec{r}) , \tag{6.5}$$

$$dG = -\mathcal{S}\, dT - mNd\mu + \textstyle\int d^3r\, H_{ij}(\vec{r})\,\delta\langle Q_{ij}(\vec{r})\rangle . \tag{6.6}$$

$\delta\langle Q_{ij}(\vec{r})\rangle$ contains in it variations of the five independent variables describing a symmetric traceless tensor. We have taken three of these variable to be the magnitude of the order parameter S and the two independent components of the unit director $\vec{n}(\vec{r})$. The two independent components associated with a possible biaxial term in $\langle Q_{ij}(\vec{r})\rangle$ are of no interest to us and will be ignored.[34] G can, therefore, be expressed as a functional of S and $\vec{n}(\vec{r})$, or alternatively as a functional of S, $\psi(\vec{r})$, and $\vec{p}(\vec{r})$:

$$\begin{aligned} dG = {} & -\mathcal{S}\, dT - mNd\mu + \textstyle\int d^3r\, h_s(\vec{r})\,\delta S(\vec{r}) + \int d^3r\, h_\psi(\vec{r})\,\delta\psi(\vec{r}) \\ & + \textstyle\int d^3r\, \vec{h}_p(\vec{r})\cdot \delta\vec{p}\cdot(\vec{r}) . \end{aligned} \tag{6.7}$$

The variations of $\psi(\vec{r})$ and $p_i(\vec{r})$ can be expressed in terms of the variables $\theta(\vec{r})$, $\theta_1(\vec{r})$, and $\theta_2(\vec{r})$ of Eq. (3.21). However, $\theta(\vec{r})$ is the only independent variable of the three. It is the only variable which exhibited a divergent autocorrelation function. We therefore argue that its fluctuations can persist for long times whereas the fluctuations in the other nonconserved variables die off in microscopic times. This is exactly analogous to the argument that fluctuations in the phase of a superfluid[36] or the transverse magnetization[12] in a ferromagnet persist for long times, whereas fluctuations in the condensate density n_0 or magnetization M_0 die off rapidly. In other words, if we wait for long enough times after shutting off external disturbances, M_0 in a magnet, n_0 in a superfluid, and S, θ_1, and θ_2 in a cholesteric will reach equilibrium values determined by the values of the conserved variables. These variables should not, therefore, be regarded as independent thermodynamic variables whereas those with fluctuations which persist for long times should. To eliminate S, θ_1, and θ_2 from our equations, we minimize Eq. (6.6) with respect to them, i.e., we set h_s, h_{θ_1}, and $h_{\theta_2} = 0$. As desired, the only variable from $\langle Q_{ij}(\vec{r})\rangle$ which remains is $\theta(\vec{r})$, which can be expressed in terms of $\vec{v}_s$ by integration by parts. The entropy equation then becomes

$$T\,d\mathcal{S} = d\epsilon - \mu\, d\rho - \vec{v}\cdot d\vec{g} - \vec{h}\cdot d\vec{v}_s , \tag{6.8}$$

which is just the equation introduced in Sec. IV.

Linear response functions have proven very useful in describing the interaction of systems with small external probes.[29,42] In classical system the causal response function of two variables A and B is

$$\tilde{\chi}_{AB}(\vec{r}\,\vec{r}, tt') = i\eta(t-t')\,\tilde{\chi}''_{AB}(\vec{r}\,\vec{r}, tt')\ , \qquad (6.9)$$

where $\eta(t-t')$ is the Heaviside unit step function and

$$\tilde{\chi}''_{AB}(\vec{r}\,\vec{r}', tt') = \tfrac{1}{2}i\,\langle [A(\vec{r}t), B(\vec{r}'t')]\rangle\ , \qquad (6.10)$$

where $[A, B]$ is the Poisson bracket of A with B. A and B are of course expressed in term of the dynamical variables of the system. We will be particularly interested in the frequency- and wave-number-dependent form on these response functions:

$$\chi''_{AB}(\vec{k}\omega) = (1/V)\int d^3r \int d^3r' \int_{-\infty}^{\infty} dt\, e^{-i\vec{k}\cdot(\vec{r}-\vec{r}')+i\omega(t-t')}\,\tilde{\chi}''_{AB}(\vec{r}\,\vec{r}', tt')\ , \qquad (6.11a)$$

$$\chi_{AB}(\vec{k}\zeta) = (1/V)\int d^3r\, d^3r' \int_{-\infty}^{\infty} d(t-t')\, e^{-i\vec{k}\cdot(\vec{r}-\vec{r}')+i\zeta(t-t')}\,\tilde{\chi}_{AB}(\vec{r}\,\vec{r}', tt') = \int \frac{d\omega}{\pi}\,\frac{\chi''_{AB}(\vec{k}\omega)}{\omega-\zeta}\ . \qquad (6.11b)$$

In translationally invariant systems, $\chi''_{AB}(\vec{k}\omega)$ determines $\tilde{\chi}''_{AB}(\vec{r}\,\vec{r}'tt')$ completely. In periodic systems such as cholesteric, off-diagonal matrix elements with different reciprocal lattice vectors are also needed for a complete specification of $\tilde{\chi}''_{AB}(\vec{r}\,\vec{r}'tt')$. However, the hydrodynamical behavior of variables in cholesterics is restricted to the first Brillouin zone. Fluctuations in off-diagonal components and higher Brillouin zones die off in microscopic times. Therefore, in the context of hydrodynamics, we may use $\chi''_{AB}(\vec{k}\omega)$ without ambiguity. $\chi''_{AB}(\vec{k}\omega)$ is related by the fluctuation-dissipation theorem to the correlation function

$$I_{AB}(\vec{k}\omega) = (1/V)\int d^3r\, d^3r' \int dt\, e^{-i\vec{k}\cdot(\vec{r}-\vec{r}')+i\omega(t-t')}\,\langle\{[A(\vec{r}t)-\langle A(rt)\rangle][B(\vec{r}'t')-\langle B(\vec{r}'t')\rangle]\}\rangle\ . \qquad (6.12)$$

In classical systems, this relation is written simply

$$I_{AB}(\vec{k}\omega) = (k_B T/\omega)\,\chi''_{AB}(\vec{k}\omega)\ , \qquad (6.13)$$

where k_B is the Boltzmann constant.

The variables A and B which are of interest to us are the "conserved" quantities $\rho(\vec{r}t)$, $\vec{g}(\vec{r}t)$, $q(\vec{r}t)$, and $\vec{v}_s(\vec{r}t)$. For linear deviations from equilibrium, $q(\vec{r}t)$ is given by Eq. (4.32) $\vec{v}_s(\vec{r}t)$ is $\vec{\nabla}[\psi(\vec{r}t)+\vec{\nabla}\cdot\vec{p}(\vec{r}t)/q_0] = \vec{\nabla}\theta(\vec{r}t)$, where for linear deviations from equilibrium

$$\psi(\vec{r}t) = (1/S)\,n_i^0(\vec{r})\,[\vec{p}^0\times\vec{n}^0(\vec{r})]_j\,Q_{ij}(\vec{r}t)\ , \qquad (6.14a)$$

$$p_i(\vec{r}t) = -(1/S)\,n_i^0(\vec{r})\,n_k^0(\vec{r})\,p_l^0\,Q_{kl}(\vec{r}t) - (1/S)\,[\vec{p}^0\times\vec{n}^0(\vec{r})]_i[\vec{p}^0\times\vec{n}^0(\vec{r})]_k\,p_l^0\tilde{Q}_{kl}(\vec{r}t)\ , \qquad (6.14b)$$

where $\tilde{Q}_{kl}(\vec{r}t) = \sum_\alpha(\vec{p}^0\times\vec{\nu}^\alpha)_k(\vec{p}^0\times\vec{\nu}^\alpha)_l\,\delta(\vec{r}-\vec{r}^\alpha(t))$. Both $\psi(\vec{r}t)$ and $p_i(\vec{r}t)$ are functions of the dynamical variables of the system as required. Since we will only use $\psi(\vec{r}t)$ and $p_i(\vec{r}t)$ in discussion of linear response functions, the presence of the equilibrium directors $\vec{n}^0(\vec{r})$ and $\vec{p}^0$ are in their definitions should cause no concern. In fact the equilibrium condensate wave function appears in a similar way in the definition of $\vec{v}_s$ in a superfluid.[30] Note that both $\langle\theta(\vec{r}t)\rangle$ and $\langle\vec{\nabla}\theta(\vec{r}t)\rangle$ are zero in equilibrium. This explains our reluctance to identify v_{s3} with q_0 in our treatment of hydrodynamics. However, small deviations of $\theta(\vec{r}t)$ from equilibrium do satisfy Eq. (4.1), i.e.,

$$dv_{si} = \nabla_i\, d\langle\theta\rangle = p_i^0\, dq_0 + \nabla_i\, d\phi'\ .$$

Hence, even though v_{si} is zero in equilibrium deviations of v_{s3} from equilibrium are equivalent to deviations of q_0 from equilibrium.

Following the procedure developed by Kadanoff and Martin,[29] we disturb the system in such a way that for all times less than zero, the system is in local thermodynamic equilibrium:

$$\begin{aligned}\delta\mathcal{H}(t) = -\int d^3r\,\{&[\delta T(\vec{r})/T][\epsilon(\vec{r}t)-\mu\rho(\vec{r}t)] \\ &+\delta\mu(\vec{r})\,\rho(\vec{r}t)+\delta\vec{v}(\vec{r})\cdot\vec{g}(\vec{r}t) \\ &+\delta\vec{h}(\vec{r})\cdot\vec{v}_s(\vec{r}t)\}\,e^{\epsilon t}\ , \quad t<0 \\ = 0\ , \quad t>0\ .\end{aligned} \qquad (6.15)$$

It is more convenient to express this disturbance in terms of P, T rather than T, μ:

$$\begin{aligned}\delta\mathcal{H}(t) = -\int d^3r\{&[\delta T(\vec{r})/T]\,q(\vec{r}t)+[\delta P(\vec{r})/\langle\rho\rangle]\rho(\vec{r}t) \\ &+\delta\vec{v}(\vec{r})\cdot\vec{g}(\vec{r}t)+\delta\vec{h}\cdot\vec{v}_s(\vec{r}t)\}\,e^{\epsilon t}\ , \quad t>0 \\ = 0\ , \quad t<0\ .\end{aligned} \qquad (6.16)$$

The change induced by $\delta\mathcal{H}(t)$ on any variable $A(\vec{r}t)$ for $t<0$ is

$$\delta\langle A(\vec{r}t)\rangle = \left.\frac{\partial\langle A\rangle}{\partial T}\right|_{P,\vec{n},\vec{v}}\delta T(\vec{r}) + \left.\frac{\partial\langle A\rangle}{\partial P}\right|_{T,\vec{n},\vec{v}}\delta P(\vec{r})$$

$$+\frac{\partial\langle A\rangle}{\partial\vec{v}}\bigg|_{T,P,\vec{h}}\cdot\delta\vec{v}(\vec{r})+\frac{\partial\langle A\rangle}{\partial\vec{h}(\vec{r})}\bigg|_{T,P,\vec{v}}\cdot\delta\vec{h}(\vec{r})\ , \tag{6.17}$$

and its Laplace transform is

$$A(\vec{k},\zeta)=L_{A\rho}\frac{\delta P(\vec{k})}{\rho}+L_{Ag}(\vec{k}\zeta)\frac{\delta T(\vec{k})}{T}$$

$$+L_{A\vec{g}}(\vec{k},\zeta)\cdot\delta\vec{v}(\vec{k})+L_{A\vec{v}_s}(\vec{k},\zeta)\cdot\delta\vec{h}(\vec{k})\ , \tag{6.18}$$

where the memory function $L_{AB}\,(\vec{k}\zeta)$ is

$$L_{AB}(\vec{k},\zeta)=\int\frac{d\omega}{\pi i}\ \frac{\chi''_{AB}(\vec{k}\omega)}{\omega(\omega-\zeta)}$$

$$=\frac{1}{i\zeta}\left[\chi_{AB}(\vec{k}\zeta)-\chi_{AB}(\vec{k})\right]. \tag{6.19}$$

The correlation function $I_{AB}\,(\vec{k}\omega)$ is easily obtained from $L_{AB}\,(\vec{k}\zeta)$:

$$I_{AB}(\vec{k},\omega)=\tfrac{1}{2}k_BT\left[L_{AB}(\vec{k},\omega+i\epsilon)+L_{AB}(\vec{k},\omega-i\epsilon)\right], \tag{6.20}$$

where ϵ is an infinitesimal.

Equations (6.18) (5.8), (5.12), (5.14), and (5.15) completely determine $L_{AB}(\vec{k}\zeta)$ and thus $I_{AB}(\vec{k}\omega)$ in the hydrodynamic limit for $A,\ B=\rho,\ q,\ \vec{g}$, or $\vec{v}_s$. $I_{g_2g_2}(\vec{k}\omega)$ has the same form as the transverse memory function in an isotropic fluid.[29] Similarly, $I_{\rho\rho}$, I_{qq}, and $I_{\rho q}$ for $\vec{k}$ along the 1-direction and $I_{g_\perp g_\perp}$ for $\vec{k}$ along the 3-direction have the same form as in an isotropic fluid. The other variables are mixed in a nontrivial manner. We will consider only $I_{v_{s1}v_{s1}}(k_1\omega)$ and $I_{v_{s3}v_{s3}}(k_3\omega)$, when $K_2'c_{\Sigma v_s}/\kappa\gamma \ll 1$. We have

$$I_{v_{s1}v_{s1}}(k_1\omega)=\frac{k_BTq_0^2}{\overline{K}_\perp k_1^2}\ \frac{(\overline{K}_\perp/4\nu_3)k_1^2}{\omega^2+[\overline{K}_\perp/4\nu_3)k_1^2]^2}\ , \tag{6.21}$$

$$I_{v_{s3}v_{s3}}(k_3\omega)=k_BT\left(\frac{1}{\overline{K}_2}-q_0\frac{\partial q_0}{\partial P}\bigg|_{h_3,T}\right)\left(1+\frac{\Delta\kappa}{\kappa}-\frac{\Delta c^2}{c_3^2}\right)\frac{D_{v_{s3}}k_3^2}{\omega^2+(D_{v_{s3}}k_3^2)^2}-\frac{\Delta\kappa}{\kappa}\ \frac{D_qk_3^2}{\omega^2+(D_qk_3^2)^2}$$

$$+k_BTq_0\frac{\partial q_0}{\partial P}\bigg|_{h_3,T}\left(1-\frac{\Delta c^2}{c_3^2}\right)\frac{\omega^2D_lk_3^2}{(\omega^2-c_3^2k_3^2)^2+(\omega D_lk_3^2)^2}\ , \tag{6.22}$$

$$\frac{\Delta\kappa}{\kappa}=\left[\left(1-\frac{q_0}{\rho}\frac{\partial\rho}{\partial v_{s3}}\bigg|_{\Sigma,T}\right)\bigg/\left(1-\frac{q_0}{\rho}\frac{\partial\rho}{\partial v_{s3}}\bigg|_{\Sigma,S}\right)-1\right]+\frac{c_{\Sigma v_{s3}}}{\kappa\gamma}\left[\frac{\partial h_3}{\partial v_{s3}}\bigg|_{\Sigma,S}\left(1-\frac{q_0}{\rho}\frac{\partial\rho}{\partial v_{s3}}\ {}_{\Sigma,S}\right)^{-1}\right.$$

$$\left.-\frac{\partial h_3}{\partial v_{s3}}\bigg|_{\Sigma,T}\left(1-\frac{q_0}{\rho}\frac{\partial\rho}{\partial v_{s3}}\bigg|_{\Sigma,T}\right)^{-1}\right]. \tag{6.23}$$

Antiresonant terms and terms of higher order in k^2 or $K_2'q_0^2/\rho c_0^2$ were neglected in Eqs. (6.22) and (6.23).

Having determined $I_{v_{s1}}$ and $I_{v_{s3}v_{s3}}$, we can evaluate

$$I_{p_1p_1}(\vec{k}\omega)=(1/q_0^2)\,I_{v_{s1}v_{s1}}(\vec{k}\omega)\ , \tag{6.24a}$$

$$I_{\psi\psi}(\vec{k}\omega)=(1/k^2)\left[I_{v_{s1}v_{s1}}(\vec{k}\omega)+I_{v_{s3}v_{s3}}(\vec{k}\omega)\right], \tag{6.24b}$$

$$I_{p_1\psi}=-(1/k^2)\,(ik_1I_{v_{s1}v_{s1}}+ik_3I_{v_{s1}v_{s3}})\ . \tag{6.24c}$$

Note that $I_{\psi\psi}$ includes contributions from the longitudinal sound and heat diffusion modes. The variable $p_2(rt)$ is not hydrodynamical; its static correlation function is finite at zero $\vec{k}$ and its fluctuations die off in microscopic times. The order-parameter correlation function can be expressed in terms of $I_{p_ip_j}$, $I_{\psi\psi}$, and $I_{p_i\psi}$:

$$(1/S^2)I_{Q_{ij}Q_{kl}}(\vec{r},\vec{r}',\omega)=[n_i^0(\vec{r})p_j^0]_+\,n_s^0(\vec{r})I_{p_sp_t}(\vec{r}\vec{r}'\omega)n_t^0(\vec{r}')\,[n_k^0(\vec{r}')p_l^0]_+$$

$$-[n_i^0(\vec{r})p_j^0]_+n_s^0(\vec{r})I_{p_s\psi}(\vec{r}\vec{r}'\omega)\{n_k^0(\vec{r}')[\vec{p}^0\times\vec{n}^0(\vec{r}')]_l\}_+-\{n_i^0(\vec{r})[\vec{p}^0\times\vec{n}^0(\vec{r})]_j\}_+I_{\psi p_s}(\vec{r}\vec{r}'\omega)n_s^0(\vec{r}')\,[n_k^0(\vec{r})p_l^0]_+$$

$$+\{n_i^0(\vec{r})\,[\vec{p}^0\times\vec{n}^0(\vec{r})_j\}_+I_{\psi\psi}(\vec{r}\vec{r}'\omega)\{n_k^0(\vec{r}')[\vec{p}^0\times\vec{n}^0(\vec{r}')]_l\}_+\ , \tag{6.25}$$

where $[n_i^0(\vec{r})p_j^0\,]_+=n_i^0(\vec{r})p_j^0+p_i^0n_j^0(\vec{r})$. In Eq. (6.25) we have left out contributions to $I_{Q_{ij}Q_{kl}}$ arising from fluctuations in the magnitude of the order parameter S and in biaxial components of Q_{ij} since they are not hydrodynamical. Note that $I_{Q_{ij}Q_{kl}}(\vec{k}\omega)$ calculated from Eq. (6.25) by assuming $I_{AB}(rr'\omega)$ for $A,\ B=p_i,\ \psi$ are functions only of $(\vec{r}-\vec{r}')$ (i.e., they do not have off-diagonal components with higher reciprocal lattice vectors) depends only on $I_{AB}(k\omega)$ and $I_{AB}(\vec{k}\pm2\vec{q}_0,\ \omega)$ and not on $I_{AB}(\vec{k}\pm q_0,\ \omega)$. This is to be expected since the physical periodicity of the cholesteric state is characterized by $\frac{1}{2}\lambda_0$ rather than λ_0, because of its invariance under the transformation $\vec{n}(\vec{r},z)\rightarrow-\vec{n}(\vec{r},z)$. The electromagnetic field couples to both $\rho(\vec{r}t)$ and $Q_{ij}(\vec{r}t)$. Inelastic-light-scattering experiments should, therefore, measure $I_{\rho\rho}$ and $I_{Q_{ij}Q_{kl}}$. However, a calculation of exactly what components and $\vec{k}$ values of these correlation functions are measured is greatly complicated by the nontrivial nature of the eigenmodes for light propagating in a helical structure, especially in off-axis directions.[48] We will leave considerations of this problem until such time as experiments warrant it.

The reactive and dissipative transport coefficients which enter the hydrodynamics of cholesterics can be expressed in the usual way in term of zero $\vec{k}$ and ω limits of correlation functions of currents of "conserved" variables.[29,49] We will concern ourselves here only with this type of expression for the reactive coefficient coupling X to $\vec{v}$ because it will enable us to show in Sec. VII that the hydrodynamics we have developed satisfy the Goldstone theorems for the cholesteric state. $\vec{v}_s(\vec{r}t)$ and $\vec{g}(\vec{r}t)$ have opposite time reversal properties. Changes in the current X are, therefore reactively related to changes in v_k via

$$\delta\langle X(r)\rangle = \int d^3r' \, \frac{\delta\langle X(\vec{r})\rangle}{\delta v_k(\vec{r}\,')}$$
$$= \int \frac{d\omega}{\pi} \int d^3r' \, \frac{\chi''_{Xg_k}(\vec{r}\,\vec{r}\,'\omega)}{\omega} \, \delta v_k(\vec{r}\,') \,, \tag{6.26}$$

which implies from Eq. (4.16)

$$q_0 p_i^0 = \lim_{k\to 0} \int \frac{d\omega}{\pi} \, \frac{\chi''_{Xg_k}(\vec{k},\,\omega)}{\omega} \,. \tag{6.24}$$

VII. GOLDSTONE THEOREMS

Goldstone modes are zero-frequency modes which appear in certain correlation functions as the results of the breaking of a continuous symmetry.[31,32] In cholesteric liquid crystals, they arise from both broken translational and rotational symmetries. Consider the change induced in $\langle Q_{ij}(\vec{r})\rangle$ by an infinitesimal rigid rotation through an angle $\delta\vec{\theta}$,

$$\delta\langle Q_{ij}(\vec{r})\rangle = \langle [Q_{ij}(\vec{r}),\, L_m]\rangle \, \delta\theta_m$$
$$= [\epsilon_{imn}\langle Q_{nj}(\vec{r})\rangle + \epsilon_{jmn}\langle Q_{in}(\vec{r})\rangle]\,\delta\theta_n \,, \tag{7.1}$$

where $[Q_{ij},\, L_m]$ is the Poisson bracket of Q_{ij} and L_m, and $\vec{L}$ is the total angular momentum operator

$$\vec{L} = \int d^3r \, \vec{r}\times\vec{g}(\vec{r}t) \equiv \int d^3r \, \vec{l}(\vec{r}t) \,. \tag{7.2}$$

Equation (7.1) can be rewritten in terms of response functions

$$\int \frac{d\omega}{\pi} \int d^3r' \, \chi''_{Q_{ij}l_m}(\vec{r}\,\vec{r}\,'\omega)$$
$$= i[\epsilon_{imn}\langle Q_{nj}(\vec{r})\rangle + \epsilon_{jmn}\langle Q_{in}(\vec{r})\rangle] \,. \tag{7.3}$$

But since $\vec{L}$ is a conserved quantity, it follows that

$$\omega \int d^3r' \, \chi''_{Q_{ij}l_m}(\vec{r}\,\vec{r}\,'\omega) = 0 \,. \tag{7.4}$$

Using Eqs. (7.3) and (7.4) and the expression for changes of $Q_{ij}(\vec{r}t)$ in terms of changes of $\psi(\vec{r}t)$ and $p_i(\vec{r}t)$, we can derive the following Goldstone theorems:

$$\lim_{k\to 0} \chi''_{p_i l_j}(\vec{k}\omega) = i\pi\epsilon_{ijk} p_k^0 \delta(\omega) \,, \tag{7.5a}$$

$$\lim_{k\to 0} \chi''_{\psi l_m}(\vec{k},\,\omega) = i\pi p_m^0 \,\delta(\omega) \,, \tag{7.5b}$$

where

$$\chi''_{A l_i}(k,\,\omega) = (1/V) \int d^3r\, d^3r' \, e^{-i\vec{k}\cdot(\vec{r}-\vec{r}\,')}$$
$$\times \epsilon_{ijk} r'_j \chi''_{A g_k}(\vec{r}\,\vec{r}\,'\omega) \tag{7.6}$$

for $A = \psi,\ p_i$. By similar arguments regarding the broken translational symmetry we can show that

$$\lim_{k\to 0} \chi''_{\psi g_i}(\vec{k}\omega) = -i\pi q_0 p_i^0 \delta(\omega) \,. \tag{7.7}$$

Using Eq. (7.6) the conservation law for v_{si} [Eq. (4.12)] and the fact that the hydrodynamic part of $p_i(\vec{r})$ is $(1/q_0)\,\delta_{ij}^T\, v_{sj}(\vec{r}t)$, one can easily derive that for small k

$$\chi''_{p_i l_j}(\vec{k},\,\omega) = (1/q_0)\,\epsilon_{jik}\,\delta_{mk}^T\,[\chi''_{Xg_m}(\vec{k}\omega)/i\omega] \,. \tag{7.8}$$

$\chi''_{Xg_m}(\vec{k}\omega)$ can be determined from the mode equations of Sec. V. The frequencies of the hydrodynamical modes tend to zero with $\vec{k}$. We must, therefore, have

$$\lim_{k\to 0} \frac{\chi''_{Xg_m}(k\omega)}{\omega} = \pi\Lambda_m \,\delta(\omega) \,. \tag{7.9}$$

The integral over ω of this quantity has already been evaluated in terms of transport coefficients in Sec. VI. Hence by Eq. (6.27), Λ_m must be $q_0 p_m^0$. Plugging this into Eq. (7.9), we obtain

$$\lim_{k\to 0} \chi''_{p_i l_j}(k\omega) = i\pi\epsilon_{ijk} p_k^0 \delta(\omega) \,. \tag{7.10}$$

This is exactly the form of the correlation function predicted by the Goldstone argument [Eq. (7.5a)]. Verification of Eq. (7.5b) is also straightforward but requires that we retain the $\vec{p}^{\,0}\cdot\nabla\times\vec{v}$ term in the expression for χ [Eq. (4.16)]. Similarly, using $\psi(\vec{r}t) = (1/\nabla^2)\,\nabla\cdot\vec{v}_s(\vec{r}t)$ and Eq. (6.27), we can show that Eq. (7.7) is satisfied.

VIII. CAPILLARY FLOW

The main purpose of this section is to show that the hydrodynamical equations we have derived can be used to describe macroscopic flow as well as fluctuations. We will consider flow of a cholesteric liquid crystal in a cylindrical capillary of radius R. This is the experimental geometry employed by Porter, Barrall, and Johnson.[50] The results we obtain are essentially the same as those obtained by Helfrich[33] using a somewhat different approach.

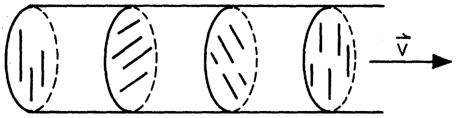

FIG. 4. Schematic diagram of a cholesteric liquid crystal in a cylindrical capillary with pitch axis along the cylinder. Note how the molecules must be attached to the walls at varying angles in order to obtain this configuration.

We will assume that the pitch axis remains parallel to the capillary axis (Fig. 4) and that the helical phase remains constant along the walls of the capillary, i.e., $\phi'(R)=0$. This is a somewhat delicate boundary condition to achieve since the molecules want to align either parallel or perpendicular to the surface rather than of varying angles as is required if there is to be cholesteric order in cylindrical cavity. For a further discussion of this problem, see Ref. 33. We will also assume that the flow takes place at uniform temperature and with a constant pressure gradient along the capillary axis. In steady state, all variables depend only on the radial coordinate r. Let $v_\phi(r)$ be the aximuthal velocity and $v_3(r)$ the component of velocity parallel to the pitch axis. The steady-state equation for $v_3(r)$, $v_\phi(r)$, and $\phi'(r)$ are, from Eq. (5.8), given by

$$\nu_3 \frac{1}{r}\frac{d}{dr}\left(r\frac{dv_3}{dr}\right)+q_0 h_\theta(r)=-\frac{\Delta P}{L} \quad , \tag{8.1a}$$

$$\nu_2\left[\frac{1}{r}\frac{1}{dr}\left(r\frac{dv_\phi}{dr}\right)-\frac{1}{r^2}v_\phi\right]+\frac{1}{2}\frac{dh_\theta}{dr}=0 , \tag{8.1b}$$

$$\frac{1}{2}\frac{1}{r}\frac{d}{dr}(rv_\phi)-q_0 v_3-\frac{1}{\gamma}h_\theta=0 , \tag{8.1c}$$

where ΔP is the pressure drop and L is the length of the capillary. The boundary conditions are that $v_3(R)=0$, $v_\phi(R)=0$, $\phi'(R)=0$ (ϕ' is hidden in h_θ), and that all of these variables be finite at the origin. The solution to Eq. (8.1) subject to these boundary conditions is straightforward. $h_\theta(r)$ can be eliminated from Eqs. (8.1a) and (8.1b) by using Eq. (8.1c). The resulting set of linear coupled equations for $v_3(r)$ and $v_\phi(r)$ is easily solved. The solution for $v_3(r)$ is

$$v_3(r)=v_0[1-I_0(qr)/I_0(qR)], \tag{8.2}$$

where I_0 is the zeroth-order Bessel function of imaginary arguments

$$q^2=\frac{\nu_2}{\nu_3}\frac{\gamma}{\nu_2+\frac{1}{4}\gamma}q_0^2$$

and

$$v_0=\frac{\Delta P}{\nu_3 L q^2}\left[1+\frac{1}{4}\frac{\gamma}{\nu_2}\left(1-\frac{2}{qR}\frac{I_1(qR)}{I_0(qR)}\right)\right]^{-1} . \tag{8.3}$$

Thus the total rate of flow out of the capillary is

$$Q=2\pi\int_0^R rv_3(r)dr$$
$$=\pi v_0 R^2\left(1-\frac{2}{qR}\frac{I_1(qR)}{I_0(qR)}\right) . \tag{8.4}$$

There are two interesting limits to this expression. When $qR \ll 1$, i.e., when the radius of the capillary is much smaller than the pitch, Poiseuille flow is closely approximated and

$$Q \sim (\Delta P/8\nu_3 L)R^4 \quad . \tag{8.5}$$

In this limit, the restoring forces of the cholesteric state play a small role and the flow is like that of an isotropic fluid. The opposite limit, $qR \gg 1$, produces significant differences from Poiseieulle flow

$$Q \sim (\pi\Delta P/\gamma L q_0^2)R^2 \tag{8.6}$$

In this limit, the total flow is proportional to R^2 rather than to R^4. If Poisieulle flow is assumed, this leads to a large effective viscosity

$$\eta_{\text{eff}}=\tfrac{1}{8}\gamma(q_0 R)^2 . \tag{8.7}$$

If R is of the order of a millimeter, η_{eff} is the order of $10^3\gamma$, which is the order of magnitude of the effective viscosity measured by Porter *et al.*

Note that γ is the only "viscosity" that appears in the total flow formula for $qR \gg 1$. In this limit, the amount of flow is controlled by the forces attempting to maintain the cholesteric order. In the opposite limit $qR \ll 1$, ν_3 is the only viscosity that appears in the flow formula. Here, it is the forces that seek to minimize shear stresses that control the flow.

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APPENDIX A

In this appendix, we will derive the entropy production equations (4.17) and (5.1) of the text. In this derivation, we will not consider contributions from terms quadratic in $\vec{v}$. From Eq. (4.6), we can write

$$T\frac{\partial s}{\partial t}=\frac{\partial\epsilon}{\partial t}-\mu\frac{\partial\rho}{\partial t}-v_i\frac{\partial g_i}{\partial t}-h_i\frac{\partial v_{si}}{\partial t} \quad , \tag{A1}$$

$$T\nabla_i s=\nabla_i\epsilon-\mu\nabla_i\rho-v_j\nabla_i g_j-h_j\nabla_i v_{sj} . \tag{A2}$$

To obtain equations (4.17) and (5.1), we express the time derivatives in Eq. (A1) in terms of currents via the conservation laws Eq. (4.12). Before doing this, however, note that since in equilibrium $v_{si}=q_0 p_i^0$, Eq. (4.16) for the current of $\vec{v}_s$ can be written

$$X=\vec{v}_s\cdot\vec{v}-\tfrac{1}{2}\vec{p}^0\cdot\nabla\times\vec{v}+X' . \tag{A3}$$

Using Eqs. (4.12), (4.13), and (A3), we can write Eq. (A1) as

$$T\,\frac{\partial s}{\partial t}=[(\mu\rho-\epsilon)\delta_{ij}-\sigma_{ji}]\nabla_i v_j-\vec{v}\cdot\nabla\epsilon+\mu\vec{v}\cdot\nabla\rho+h_i q_0 p_j^0\nabla_i v_j+h_i v_j\nabla_i v_{sj}-\tfrac{1}{2}h_i\epsilon_{jkl}p_j^0\nabla_i\nabla_k v_l-\vec{h}\cdot\nabla X'-\nabla\cdot\vec{j}'^{\epsilon}\quad.\qquad\text{(A4)}$$

Noting that $h_i v_j\nabla_i v_{sj}=h_i v_j\nabla_j v_{si}$ since v_{si} is a longitudinal vector, and using Eq. (A2) to determine $T\vec{v}\cdot\nabla s$, we can express Eq. (A4) as

$$\begin{aligned}T\left(\frac{\partial s}{\partial t}+\vec{\nabla}\cdot(\vec{v}s+\vec{h}\vec{p}^0\cdot\nabla\times\vec{v})\right)&=-\nabla\cdot\vec{j}'^{\epsilon}+[(\mu\rho+Ts-\epsilon)\delta_{ij}-\sigma_{ji}]\nabla_i v_j\\&\quad+q_0p_j^0h_i\nabla_i v_j+\tfrac{1}{2}p_k^0\epsilon_{kij}\vec{\nabla}\cdot\vec{h}\nabla_i v_j+\vec{h}\cdot\vec{\nabla}X'\quad.\qquad\text{(A5)}\end{aligned}$$

Since both $\vec{h}$ and $\nabla_i v_j$ are zero in equilibrium, the linearized from of Eq. (A5) is just Eq. (4.17) of the text. With $\sigma_{ij}=\sigma_{ij}^R+\sigma_{ij}'$, Eq. (A5) becomes

$$T\left(\frac{\partial s}{\partial t}+\vec{\nabla}\cdot\vec{Q}\right)=-j_i'^{\epsilon}\,\frac{\nabla_i T}{T}-\sigma_{ij}'\nabla_i v_j=X'\vec{\nabla}\cdot\vec{h}\,,\qquad\text{(A6)}$$

where

$$\vec{Q}=\vec{v}+(1/T)\vec{j}'^{\epsilon}+\vec{h}\vec{p}^0\cdot\nabla\times\vec{v}-\vec{h}X'\;.\qquad\text{(A7)}$$

The linearized form of Eq. (A6) is Eq. (5.1) of the text.

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[1] I. B. Chistyakov, Usp. Fiz. Nauk 89, 563 (1966) [Sov. Phys. Usp. 9, 551 (1967)].

[2] George W. Gray, *Molecular Structure and the Properties of Liquid Crystals* (Academic, New York, 1962).

[3] *Liquid Crystals and Ordered Fluids*, edited by J. F. Johnson and R. S. Porter (Plenum, New York, 1970).

[4] Glen H. Brown, J. W. Doane, and Vernon D. Neff, *A Review of the Structure and Properties of Liquid Crystals* (Chemical Rubber Company, Cleveland, 1971).

[5] Mol. Cryst. Liquid Cryst. 12, (1971); 13 (1971).

[6] Mol. Cryst. Liquid Cryst. 7 (1969); 8 (1971).

[7] J. de Phys. 30, Colloque C4 (1969).

[8] G. Friedel, Ann. Phys. (Paris) 19, 273 (1922).

[9] L. Tisza, Nature 141, 913 (1938).

[10] L. Landau, J. Phys. USSR 5, 71 (1941); 11, 91 (1947).

[11] I. M. Khalantnikov, *Introduction to the Theory of Superfluidity* (Benjamin, New York, 1965).

[12] B. I. Halperin and P. C. Hohenberg, Phys. Rev. 188, 898 (1969).

[13] T. C. Lubensky, Ann. Phys. (N. Y.) 64, 424 (1971).

[14] J. L. Ericksen, Arch. Ratl. Mech. Anal. 4, 231 (1960); 9, 371 (1962).

[15] F. M. Leslie, Arch. Ratl. Mech. Anal. 28, 265 (1968).

[16] Dieter Forster, Tom C. Lubensky, Paul C. Martin, Jack Swift, and P. S. Pershan, Phys. Rev. Letters 26, 1016 (1971). The choice of the stress tensor is not unique. In particular, any tensor T_{ij} which satisfies $\nabla_j T_{ij}=0$ can be added to σ_{ij} without changing the physical quantity $\partial g_i/\partial t$. If σ_{ij} contains an antisymmetric part proportional to a spatial derivative, then it is possible to find a T_{ij} such that $\sigma_{ij}+T_{ij}$ is symmetric. Using $h_i=p_i^0(\vec{p}^0\cdot\vec{h})+h_i^T$, where $h_i^T=\delta_{ij}^T h_j=\delta_{ij}^T\nabla_j K_\perp(\nabla)\,\theta$, $\nabla_i\nabla_k v_l=\nabla_i A_{kl}+\nabla_k A_{il}-\nabla_l A_{ik}$, and

$$\epsilon_{jkl}\nabla_i\nabla_k v_l=\epsilon_{jkl}(\nabla_k A_{il}-\nabla_l A_{ik}),$$

where

$$A_{ij}=\tfrac{1}{2}(\nabla_i v_j+\nabla_j v_i),$$

it is possible after integrations by parts to cast the reactive part of $\vec{h}\cdot\vec{\nabla}X$ in the form

$$q_0p_i^0p_j^0(\vec{p}^0\cdot h)\nabla_i v_j+q_0(h_i^Tp_j^0+p_i^0h_j^T-\delta_{ij}^Tq_0\vec{p}^0\cdot\vec{\nabla}K_\perp\theta)\nabla_i v_j-\tfrac{1}{2}p_l^0(\epsilon_{lkj}\nabla_k h_i+\epsilon_{lki}\nabla_k h_j)\nabla_i v_j.$$

This leads to a symmetric stress tensor. $\nabla_j\sigma_{ij}$ is, however, the same as that computed using Eq. (4.18).

[17] Group d'Etudes des Cristaux Liquides (Orsay), J. Chem. Phys. 51, 816 (1968).

[18] O. Parodi, J. Phys. Paris 31, 581 (1970).

[19] F. Jahnig and H. Schmidt, Ann. Phys. (N. Y.) (to be published).

[20] F. C. Frank, Discussions Faraday Soc. 25, 19 (1958).

[21] L. D. Landau and E. M. Lifshitz, *Statistical Physics*, 2nd ed. (Addison-Wesley, Reading, Mass., 1969), pp. 401–404.

[22] N. D. Mermin and H. Wagner, Phys. Rev. Letters 17, 1133 (1966).

[23] P. Hohenberg, Phys. Rev. 158, 383 (1967).

[24] H. Mori, Progr. Theoret. Phys. (Kyoto) 33, 423 (1965).

[25] L. D. Landau and E. M. Lifshitz, *Fluid Mechanics* (Addison-Wesley, Reading, Mass., 1959).

[26] Changpeng Fan, Lorenz Kramer, and Michael J. Stephen, Phys. Rev. A 2, 2482 (1971).

[27] F. M. Leslie, Mol. Cryst. Liquid Cryst. 7, 401 (1969).

[28] F. Brochard, J. Phys. Paris 32, 685 (1971).

[29] Leo P. Kadanoff and Paul C. Martin, Ann. Phys. (N. Y.) 24, 419 (1963).

[30] P. C. Hohenberg and P. C. Martin, Ann. Phys. (N. Y.) 34, 291 (1965).

[31] J. Goldstone, Nuovo Cimento 19, 154 (1961).

[32] A. Katz and Y. Frishman, Nuovo Cimento 42A, 1009 (1966).

[33] W. Helfrich, Phys. Rev. Letters 23, 372 (1969); in Ref. 3, pp. 405–418.

[34] T. C. Lubensky, Phys. Rev. A 2, 2497 (1970).

[35] P. G. de Gennes, Phys. Letters 30A, 454 (1969).

[36] H. Zocher, Trans. Faraday Soc. 29, 915 (1933).

[37] C. W. Oseen, Trans. Faraday Soc. 29, 883 (1933).

[38] A. Saupe, Z. Naturforsch. 15a, 815 (1960).

[39] This analysis was suggested by Leo Kadanoff.

[40] P. G. deGennes, Mol. Cryst. Liquid Cryst. 7, 325 (1969).

[41] P. Pincus, Compt. Rend. 267B, 1290 (1969).

[42] See, for example, R. C. Martin, in *Many-Body Physics*, edited by C. de Witt and R. Balian (Gordon and Breach, New York, 1968), pp. 37–136.

[43] P. M. Morse and H. Fresbach, *Methods of Theoretical Physics* (McGraw-Hill, New York, 1953), p. 555ff.

[44] This was pointed out by P. G. de Gennes.

[45] J. Jenkins, doctoral thesis (Johns Hopkins University, 1969).

[46] *Handbook of Chemistry and Physics*, 50th ed. (Chemical Rubber Company, Cleveland, 1969), p. E–4.

[47] Richard Alban, Mol. Cryst. Liquid Cryst. 10, 24 (1970); H. Arnold, Z. Phys. Chem. Leipzig 226, 146 (1964).

[48] This point was emphasized by Peter Pershan.

[49] R. Kubo, J. Phys. Soc. Japan 12, 570 (1957). See also R. Kubo, in *Lectures in Theoretical Physics* (Interscience, New York, 1959), Vol. I, Chap. 4.

[50] R. S. Porter, E. M. Barrall, II, and J. F. Johnson, J. Chem. Phys. 45, 1452 (1966).