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Molecular Description of Nematic Liquid Crystals

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Liquid crystals are considered as gases of long barlike molecules. Variables describing the position and orientation of individual molecules are introduced. These are used to arrive at a microscopic definition of the order in liquid crystals in terms of a symmetric traceless tensor. The Frank and Leslie-Ericksen directors are shown to be equivalent to the unit eigenvector associated with the largest eigenvalue of this symmetric traceless tensor. Attention is then restricted to nematics. It is shown that the Frank free energy gives a valid description of equilibrium properties of nematics to order $\chi^a H^2/\rho k T m^{-1}$, where χ^a is the anisotropic magnetic susceptibility, H the external magnetic field, ρ the mass density, T the temperature, k the Boltzmann constant, and m the molecular mass. Microscopic justification is given for the linearized Leslie-Ericksen hydrodynamic theory for nematics. A microscopic response-function description of nematics is then presented, and contact is made between the general frequency- and wave-number-dependent response functions and those calculated from the phenomenological hydrodynamic theory. Applications to light scattering and nuclear magnetic resonance are considered. $1/T_1$ calculated here differs from that calculated from the Pincus theory by a factor of S^2, where S is the parameter measuring the degree of nematic order.

I. INTRODUCTION

The liquid-crystalline state of matter is a state intermediate between a solid crystal and a liquid.[1,2] This state of matter has been the subject of much research since its discovery by the Austrian botanist Reinitzer at the end of the last century.[3] Early experiments showed that certain organic crystals when melted produced a liquid of turbid appearance which upon further heating underwent another transition to an isotropic transparent liquid. This turbid-appearing state was soon shown to have anisotropic optical, electrical, and magnetic properties and was named the liquid-crystalline state by Lehman.[4] This state, though anisotropic, still flowed like a liquid. Furthermore, x-ray experiments indicated a random arrangement of the centers of mass of the molecules in the liquid.[1,2] Later, experiments were able to link the observed anisotropies with alignment along a certain direction of the long molecules which compose the liquid crystal. In 1922 Friedel[5] distinguished the following subclasses of the liquid-crystalline state according to the properties of single-crystal samples:

Nematic state. The centers of mass of the elongated molecules are randomly oriented but their long axes are oriented along a specific direction. There is rotational invariance about the direction of alignment [Fig. 1(a)].

Smectic state. The centers of mass of the molecules are arranged in parallel equidistant planes. Motion of the centers of mass in each plane is allowed. The long axes of the molecules are aligned along a specific direction [Fig. 1(b)].

Cholesteric state. A subclass of the nematic state in which the direction of orientation rotates in a screwlike motion [Fig. 1(c)].

In order to describe deformations in liquid crystals, Frank[6] and later Ericksen[7] following an idea of Oseen[8] introduced at each point in space a phenomenological unit vector $n_i(\vec{r})$ describing the orientation of the molecules at that point. Frank then discussed the possible functional dependence of the free energy on $n_i(\vec{r})$ and its first spatial derivative subject to the condition that $n_i(\vec{r})$ and $-n_i(\vec{r})$ be equivalent configurations. He found that the free energy in a nematic could be expressed as

$$F=\tfrac{1}{2}\int d^3r\,\{K_{11}(\vec{\nabla}\cdot\vec{n})^2+K_{22}[\vec{n}\cdot(\vec{\nabla}\times\vec{n})]^2+K_{33}[\vec{n}\times(\vec{\nabla}\times\vec{n})]^2 - (K_{22}+K_{24})[(\vec{\nabla}\cdot\vec{n})^2-\nabla_i n_j\nabla_j n_i]\}, \tag{1.1}$$

where K_{11}, K_{22}, K_{33}, and K_{24} are elastic constants. The first term in this equation, in the language of Frank, gives the energy associated with splay [Fig. 2(a)], the second that associated with torsion, and the third that associated with flexion [Fig. 2(c)].

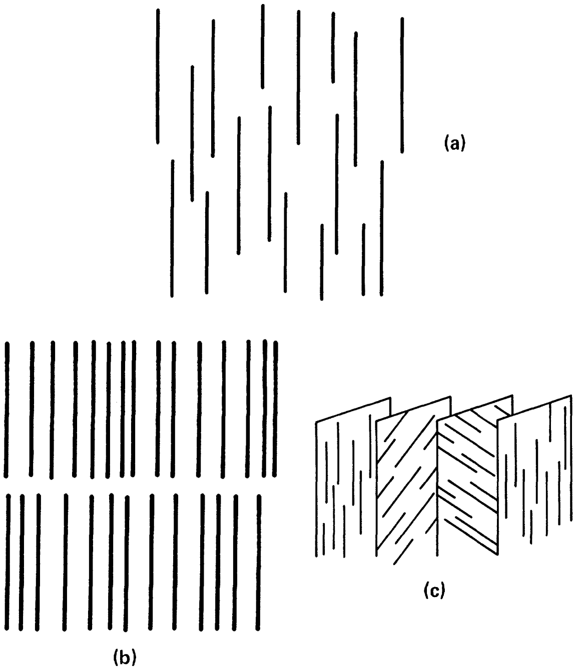

FIG. 1. (a) Schematic arrangement of molecules in a nematic liquid crystal. (b) Schematic arrangement of molecules in a smectic liquid crystal. (c) Schematic arrangement of molecules in a cholesteric liquid crystal.

The fourth term does not contribute to the volume free energy[9] and is usually neglected. It will, nevertheless, be important for us to bear in mind that this term exists. The Frank free energy has been used successfully to explain many equilibrium properties of nematics.[10] The elastic constants K_{11}, K_{22}, and K_{33} have been experimentally determined to be to the order of 10^{-6} dyn with $K_{33} > K_{11} > K_{22}$.[11]

A dynamical continuum theory for anisotropic liquids was first introduced by Ericksen[12] and later elaborated upon and applied to the specific case of liquid crystals by Leslie.[13] The Leslie-Ericksen theory assumes that in a liquid crystal there exists at each point in space a time-dependent director $n_i(\vec{r}t)$, which in the static limit reduces to the Frank director $n_i(\vec{r})$. In addition, there are the velocity, temperature, and pressure fields that appear in the hydrodynamic theory of an isotropic fluid. Starting from the standard conservation laws for energy, mass, and momentum and a balance law for the director, Leslie introduced constitutive relations between the various currents and the spatially and temporally varying thermodynamic variables, including $n_i(\vec{r}t)$ and its time derivative. In particular, he introduced viscosities coupling velocity gradients and the director. The resulting hydrodynamic theory can be used to explain various flow configurations in liquid crystals.[14] It was also used by the Orsay Liquid Crystal Group[15] to derive the fluctuation spectrum associated with local variation in direction of the director.

The Frank and Leslie-Ericksen theories have been very successful in explaining many of the properties of nematic and cholesteric liquid crystals. However, they suffer from a lack of a concise microscopic definition of the director $n_i(\vec{r}t)$. As has been pointed out by de Gennes,[16] the natural way to describe the macroscopic order in a liquid crystal is via a symmetric traceless tensor rather than by a vector. [A vector cannot be used to describe a system in which the directions $n_i(\vec{r})$ and $-n_i(\vec{r})$ are equivalent.] In this paper, we will introduce a microscopic definition of a symmetric traceless tensor which varies in space and time and which in equilibrium reduces to the tensor describing the macroscopic liquid-crystal order. We will then show how a theory using this tensor yields the Frank and Leslie-Ericksen theories under almost all conditions realized in nematics. We will always consider single-crystal samples.

Section II introduces a microscopic model of a liquid crystal and defines the symmetric traceless tensor characterizing liquid-crystal order. Section III considers in detail the equilibrium theory for a nematic and shows how the Frank theory depending only on the two independent variables of a unit director can be obtained from a theory in which the five independent components of a symmetric traceless tensor are allowed to vary. Section IV discusses transport and nonequilibrium behavior of a nematic and presents a microscopic justification of the Leslie-Ericksen theory when there is no component of angular momentum parallel to the director. Section V presents a microscopic response-function description of liquid crystals. Contact is made between the phenomenological response functions derived from the Leslie-Ericksen theory and the general frequency- and wave-number-dependent response functions. Finally, Sec. VI discusses application of the theory developed in the previous sections to light scattering and nuclear magnetic resonance. In particular, it shows that the Pincus formula[17] for the inverse nuclear relaxation time should be multiplied by the square of the parameter describing the degree of liquid-crystal order.

II. INTRODUCTION OF MODEL FOR A LIQUID CRYSTAL

We will consider a liquid crystal to be a classical gas of long thin cylindrical bars. In reality, of course, the molecules of a typical liquid crystal are more like flat plates with a length of no more than four or five times their width [paraazoxyanisol (PAA) is approximately 17×7 Å]. In addition, the molecules can have complicated internal degrees of freedom such as twisting of the plate about a given direction, stretching, or electronic excitations. However, the interesting collective phenomena unique to liquid crystals can be described quite well in terms of long thin molecules. In the treatment to be presented, additional internal degrees of freedom can be included as they become necessary to explain observed phenomena.[18]

The Hamiltonian and Poisson-bracket description of classical mechanics is the one best suited to the discussion of dynamic-response functions and is the one which we will use. Each molecule α can be described in terms of its c.m. coordinates r_i^α and the angles θ^α and φ^α, which give the orientation of the bar in the c.m. frame. Hence, for each molecule there are five generalized coordinates χ_t^α ($t = 1, \cdots, 5$) where $\chi_t^\alpha = r_i^\alpha$ for ($t = 1, 2, 3$), $\chi_4^\alpha = \theta^\alpha$, and $\chi_5^\alpha = \varphi^\alpha$, and five conjugate momenta $P_t^\alpha = (p_i^\alpha, P_\theta^\alpha, P_\varphi^\alpha)$ satisfying

$$[X_t^\alpha, P_{t'}^{\alpha'}] = \delta_{\alpha\alpha'}\delta_{tt'}, \tag{2.1}$$

where $[A, B]$ is the Poisson bracket of A and B.

The Hamiltonian is

$$\mathcal{H} = \sum_\alpha \frac{1}{2m} \vec{\mathrm{p}}^\alpha \cdot \vec{\mathrm{p}}^\alpha + \sum_\alpha \frac{1}{2I}\left(P_\theta^{\alpha 2} + \frac{1}{\sin^2\theta^\alpha} P_\varphi^{\alpha 2}\right) + V(\{X_t^\alpha\}), \tag{2.2}$$

where m is the mass of the molecule, I is its moment of inertia, and $V(\{X_t^\alpha\})$ is the potential energy, which does not depend on the momenta. I is $\frac{1}{12} m l_0^2$, where l_0 is the length of the molecule. To the extent that the molecules are not really long thin bars, the factor $\frac{1}{12}$ in the above expression may change. Nevertheless, $(I/m)^{1/2}$ is always a length of molecular dimension. Given any function A of X_t^α and P_t^α, its time rate of change in the absence of time-varying external fields can be calculated by

$$\frac{\partial A}{\partial t} = [\mathcal{H}, A]. \tag{2.3}$$

In principle, Eqs. (2.4)–(2.3) with a specification of the potential V are all we need to describe the dynamics of a gas of long bars. We, of course, will not attempt any such description, but we will use the fact that such a Hamiltonian formulation of the problem exists.

For our purposes, it is convenient to introduce a unit vector ν_i^α designating the instantaneous orientation of molecule α:

$$\vec{\nu}^\alpha(t) = \cos\theta^\alpha \vec{\mathrm{e}}_z + \sin\theta^\alpha (\cos\varphi^\alpha \vec{\mathrm{e}}_x + \sin\varphi^\alpha \vec{\mathrm{e}}_y), \tag{2.4}$$

where $\vec{\mathrm{e}}_x$, $\vec{\mathrm{e}}_y$, and $\vec{\mathrm{e}}_z$ are unit vectors pointing along the x, y, and z axes. We may associate with each ν_i^α, a "momentum" $\Pi_i^\alpha = I\partial\nu_i^\alpha/\partial t$, which satisfies a Poisson-bracket relation with ν_i^α:

$$[\nu_i^\alpha, \Pi_j^\alpha] = (\delta_{ij} - \nu_i^\alpha \nu_j^\alpha). \tag{2.5}$$

In other words, $[\nu_i^\alpha, \Pi_j^\alpha]$ is the projection operator onto directions perpendicular to ν_i^α.

The two ends of our long-bar molecules are physically indistinguishable.[19] Hence external fields will not couple to ν_i^α itself but to bilinear forms built from ν_i^α. The most interesting of these forms is the symmetric traceless tensor

$$Q_{ij}^\alpha = \nu_i^\alpha \nu_j^\alpha - \tfrac{1}{3}\delta_{ij}. \tag{2.6}$$

In particular, we can express single-particle magnetic and electric polarizabilities in terms of δ_{ij} and Q_{ij}:

$$P_{Hij}^\alpha(t) = \kappa_H^0 \delta_{ij} + \kappa_H^a Q_{ij}^\alpha, \tag{2.7a}$$

$$P_{Eij}^\alpha(t) = \kappa_E^0 \delta_{ij} + \kappa_E^a Q_{ij}^\alpha, \tag{2.7b}$$

where κ_H^0 and κ_E^0 are the isotropic parts, and κ_E^a and κ_H^a are the anisotropic parts of the magnetic and electric polarizabilities of a single molecule. In the isotropic phase, the average value of Q_{ij}^α is rigorously zero:

$$\langle Q_{ij}^\alpha \rangle \equiv \mathrm{Tr}\rho Q_{ij}^\alpha = 0. \tag{2.8}$$

In this expression, ρ is the density matrix, and Tr implies an integration over all generalized coordinates and momenta. In homogeneous nematics, in the ordered phase, $\langle Q_{ij}^\alpha \rangle$ is simply related to the order parameter S. Let n_i be the unit vector defining the preferred direction of molecular orientation, then

$$n_i \langle Q_{ij}^\alpha \rangle n_j = \langle \cos^2\theta^\alpha \rangle - \tfrac{1}{3} = \tfrac{2}{3}S, \tag{2.9}$$

where we have used the summation convention over

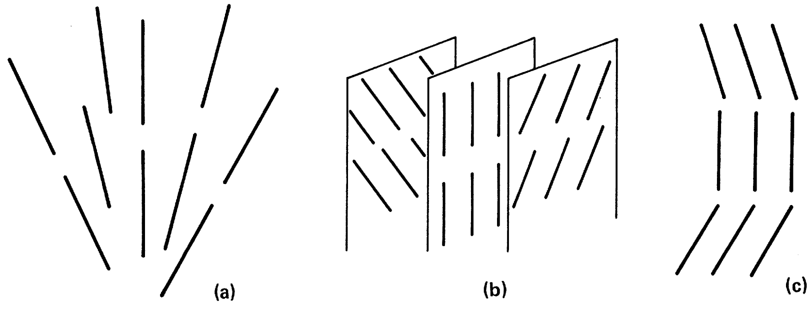

FIG. 2. (a) Splay deformation in a nematic. (b) Torsion in a nematic. Note the similarity between the arrangement of molecules in a nematic undergoing torsion and in a cholesteric [Fig. 1(c)]. (c) Flexion in a nematic.

repeated Latin subscripts. [Note that the averages in Eqs. (2.8) and (2.9) are independent of the particle index α.] In order to generalize the concept of an order parameter to cholesteric, smectic, and inhomogeneous nematic liquid crystals, it is convenient to introduce the density

$$R_{ij}(\vec{r}t) = \Sigma_\alpha Q^\alpha_{ij}(t)\delta\,[\vec{r} - \vec{r}^\alpha(t)], \tag{2.10a}$$

$$\langle R_{ij}(\vec{r}t)\rangle \equiv [\langle\rho(\vec{r}t)\rangle/m]Q_{ij}(\vec{r}t). \tag{2.10b}$$

The bracket $\langle\;\rangle$ signifies an average over any ensemble, including nonequilibrium ensembles. $\langle\rho(\vec{r}t)\rangle$ is the mass density of the fluid at the point $\vec{r}$, and m is the mass of a molecule. Eq. (2.10b) constitutes a definition of the liquid-crystal order, $Q_{ij}(\vec{r}t)$, when it can vary in space and time. In all equilibrium ensembles, $\langle R_{ij}(\vec{r}t)\rangle$, $\langle\rho(\vec{r}t)\rangle$, and $Q_{ij}(\vec{r}t)$ are of course independent of time. $Q_{ij}(\vec{r}t)$ is zero in all isotropic phases. In the homogeneous nematic mesophase, it is given by

$$Q_{ij}(\vec{r}t) = S(n_i n_j - \tfrac{1}{3}\delta_{ij}). \tag{2.11}$$

In the smectic mesophase, $Q_{ij}(\vec{r})$ is periodic in space along the direction perpendicular to the ordered lamina. In cholesterics, $Q_{ij}(\vec{r})$ has basically the form of Eq. (2.11), except that the preferred direction n_i rotates in a helical pattern along a specific direction.

$Q_{ij}(\vec{r})$ given by Eq. (2.11) is uniaxial; i.e., in the coordinate system defined by n_i, it has the form

$$Q_{ij} = \tfrac{2}{3}\begin{pmatrix} S & 0 & 0 \\ 0 & -\tfrac{1}{2}S & 0 \\ 0 & 0 & -\tfrac{1}{2}S \end{pmatrix}. \tag{2.12}$$

It is useful to keep in mind that $Q_{ij}(\vec{r})$ can, in general, be biaxial. In other words, in the appropriate coordinate system, it can assume the form

$$Q_{ij} = \begin{pmatrix} \tfrac{2}{3}S & 0 & 0 \\ 0 & -\tfrac{1}{3}S + \xi & 0 \\ 0 & 0 & -\tfrac{1}{3}S - \xi \end{pmatrix}. \tag{2.13}$$

where ξ is a measure of the degree of biaxiality of $Q_{ij}(\vec{r})$. Note that it takes only three independent variables to specify completely an uniaxial symmetric traceless tensor (the magnitude of the maximum eigenvalue and the polar angles of the associated unit eigenvector), and five independent variables to specify a biaxial symmetric traceless tensor (the magnitude of the second largest eigenvalue and one angle giving the direction of its eigenvector in addition to the three variables for an uniaxial tensor).

$Q_{ij}(\vec{r}t)$ [Eq. (2.10b)] is the quantity describing the liquid-crystal order. It will be used extensively in the following sections in deriving the Frank and Leslie-Ericksen theories.

III. EQUILIBRIUM PROPERTIES

In this section we consider the equilibrium theory for a nematic liquid crystal in which the order parameter $Q_{ij}(\vec{r})$ is allowed to vary from point to point in space. In particular, we show how Frank's free energy, which depends on the two independent variables associated with a unit vector, can be obtained from a free energy which in general depends on the five independent variables of a symmetric traceless tensor.

To clarify our ideas on $Q_{ij}(\vec{r})$, let us note that it can, in general, be written in the form

$$Q_{ij}(\vec{r}) = S(\vec{r})[n_i(\vec{r})n_j(\vec{r}) - \tfrac{1}{3}\delta_{ij}] + \xi(\vec{r})\{n'_i(\vec{r})n'_j(\vec{r}) - [\vec{n}(\vec{r})\times\vec{n}'(\vec{r})]_i\,[\vec{n}(\vec{r})\times\vec{n}'(\vec{r})]_j\}, \tag{3.1}$$

where $n_i(\vec{r})$ is the direction corresponding to the maximum eigenvalue $\tfrac{2}{3}S(\vec{r})$ of $Q_{ij}(\vec{r})$, and $n'_i(\vec{r})$ the direction corresponding to the second-largest eigenvalue $-\tfrac{1}{3}S(\vec{r}) + \xi(\vec{r})$. In the orthogonal coordinate system defined at each point in space by $n_i(\vec{r})$ and $n'_i(\vec{r})$, $Q_{ij}(\vec{r})$ has the canonical form expressed in Eq. (2.12). For a homogeneous nematic configuration [$Q_{ij}(\vec{r})$ independent of $\vec{r}$], the biaxial term ξ is zero. When $Q_{ij}(\vec{r})$ is allowed to vary, the possibility of a nonvanishing biaxial component has to be admitted[20] even in nematics.

The free energy of a liquid crystal can be expressed as a sum of three parts:

$$F = F_0 + F_1 + F_H = \int d^3r\, \mathcal{F}(\vec{r}) = \int d^3r\,[\mathcal{F}_0(\vec{r}) + \mathcal{F}_1(\vec{r}) + \mathcal{F}_H(\vec{r})]. \tag{3.2}$$

$\mathcal{F}(\vec{r})$ is the total free-energy density, and $\mathcal{F}_0(\vec{r})$, $\mathcal{F}_1(\vec{r})$, and $\mathcal{F}_H(\vec{r})$ are the free-energy densities associated with F_0, F_1, and F_H. $\mathcal{F}_0(\vec{r})$ is a local function of $Q_{ij}(\vec{r})$ at the point $\vec{r}$. It is, therefore, a function only of $S(\vec{r})$ and $\xi(\vec{r})$, and not of $n_i(\vec{r})$ and $n'_i(\vec{r})$. $\mathcal{F}_1(\vec{r})$ is a function of $Q_{ij}(\vec{r})$ at different points in space; alternatively, if variations in space are small, it can be viewed as a functional of the spatial derivatives of $Q_{ij}(\vec{r})$ at the point $\vec{r}$. F_H is the free energy associated with an external magnetic field[21]:

$$F_H = -\tfrac{1}{2}\int d^3r\,\chi^a_{ij}(\vec{r})H_i(\vec{r})H_j(\vec{r}), \tag{3.3}$$

where

$$\chi^a_{ij}(\vec{r}) = \kappa^a_H\langle R_{ij}(\vec{r})\rangle \equiv \chi^a Q_{ij}(\vec{r}), \tag{3.4a}$$

$$\chi^a = \kappa^a_H\langle\rho\rangle/m. \tag{3.4b}$$

In stable equilibrium, the free energy must be a minimum with respect to variation of all five independent components of $Q_{ij}(\vec{r})$. In homogeneous systems, F_1 is zero by definition. In nematics, the minimization of $F_0 + F_H$ then yields $\xi = 0$, $S = \text{const}$, and n_i parallel to the homogeneous external field

H_i. If the state of stable equilibrium is inhomogeneous, a more complete analysis is necessary. We will restrict ourselves to systems in which either the existence of boundaries can be ignored (infinite systems) or in which the value of $Q_{ij}(\vec{r})$ at any boundaries is rigidly fixed. In this case, the condition for stable equilibrium is that F be a minimum with respect to variations of $Q_{ij}(\vec{r})$ at each point in the interior of the sample. In other words,

$$\delta F=\int d^3r\ \frac{\delta F}{\delta S(\vec{r})}\,\delta S(\vec{r})+\frac{\delta F}{\delta\xi(\vec{r})}\,\delta\xi(\vec{r})+\frac{\delta F}{\delta n_i(\vec{r})}\,\delta n_i(\vec{r})+\frac{\delta F}{\delta n_i'(\vec{r})}\,\delta n_i'(\vec{r})=0, \tag{3.5}$$

where the variations in $n_i(\vec{r})$ and $n_i'(\vec{r})$ are understood to conform to the constraints that $n_i(\vec{r})$ and $n_i'(\vec{r})$ be orthogonal unit vectors. Hence the equilibrium state is determined by the equations

$$\frac{\delta F}{\delta S(\vec{r})}=0, \tag{3.6a}$$

$$\frac{\delta F}{\delta \xi(\vec{r})}=0, \tag{3.6b}$$

$$\frac{\delta F}{\delta n_i(\vec{r})}-\lambda_1 n_i(\vec{r})-\lambda_2 n_i'(\vec{r})=0, \tag{3.6c}$$

$$\frac{\delta F}{\delta n_i'(\vec{r})}-\lambda_3 n_i(\vec{r})-\lambda_4 n_i'(\vec{r})=0. \tag{3.6d}$$

The Lagrange multipliers λ_1, λ_2, λ_3, and λ_4 are determined by the conditions that $n_i n_i=1$, $n_i' n_i'=1$, and $n_i n_i'=0$. Consider first Eq. (3.6d). Using Eqs. (3.2) and (3.3), this can be written as

$$\frac{\delta F_1}{\delta n_i'(\vec{r})}-\chi^{\alpha}\xi(\vec{r})\{[\vec{n}'(\vec{r})\cdot\vec{H}]n_i'-[\vec{n}\cdot(\vec{n}\times\vec{H})](\vec{n}\times\vec{H})_i\}-\lambda_3 n_i-\lambda_4 n_i'=0. \tag{3.7}$$

From this it follows that

$$\vec{n}'(\vec{r})\cdot[\vec{n}(\vec{r})\times\vec{H}(\vec{r})]=0, \tag{3.8}$$

which completely determines $\vec{n}'(\vec{r})$ if we require $\vec{n}$, $\vec{n}'$ and $\vec{n}\times\vec{n}'$ to form a right-handed coordinate system (Fig. 3). Equation (3.8) holds regardless of the form of F_1.

The equations determining $S(r)$ and $\xi(r)$ are

$$\frac{\delta F_0}{\delta S(\vec{r})}+\frac{\delta F_1}{\delta S(\vec{r})}-\tfrac{1}{2}\chi^a\{[\vec{n}(\vec{r})\cdot\vec{H}(\vec{r})]^2-\tfrac{1}{3}H^2(\vec{r})\}=0, \tag{3.9a}$$

$$\frac{\delta F_0}{\delta \xi(\vec{r})}+\frac{\delta F_1}{\delta \xi(\vec{r})}-\tfrac{1}{2}\chi^a[\vec{n}'(\vec{r})\cdot\vec{H}(\vec{r})]^2=0. \tag{3.9b}$$

If we restrict ourselves to slow variations in space, $\mathfrak{F}_1$ can be taken as some quadratic function of $\nabla_i Q_{jk}$. If we further assume that deviations of $S(\vec{r})$ and $\xi(\vec{r})$ from their values in homogeneous equilibrium are small, we can linearize Eq. (3.9):

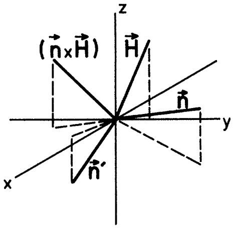

FIG. 3. Diagram showing the relation between the magnetic field $\vec{H}$ and the directors $\vec{n}$ and $\vec{n}'$.

$$A_{SS}\delta S(\vec{r})+A_{S\xi}\delta\xi(\vec{r})+f_S(\vec{r},\vec{\nabla})\delta S(\vec{r})-\tfrac{1}{2}\chi^a[(\vec{n}\circ\vec{H})^2-\tfrac{1}{3}H^2]=0, \tag{3.10a}$$

$$A_{\xi\xi}\delta\xi(\vec{r})+A_{\xi S}\delta\xi(\vec{r})+f_\xi(\vec{r},\vec{\nabla})\delta\xi(\vec{r})-\tfrac{1}{2}\chi^a(\vec{n}'\cdot\vec{H})^2=0, \tag{3.10b}$$

where

$$A_{SS}=\frac{\partial^2\mathfrak{F}_0}{\partial S^2}\ ,\quad A_{\xi\xi}=\frac{\partial^2\mathfrak{F}_0}{\partial\xi^2},\ \text{and}\ A_{S\xi}=A_{\xi S}=\frac{\partial^2\mathfrak{F}_0}{\partial S\,\partial\xi}\ ,$$

and $f_S(\vec{r},\vec{\nabla})$ and $f_\xi(\vec{r},\vec{\nabla})$ are second-order differential operators operating on $\delta S(\vec{r})$ and $\delta\xi(\vec{r})$. All of the A's have units of energy over volume and are of order $\rho kT/m$. ($\rho/m=N/V$, where N is the total number of particles and V is the volume of the system.) After Fourier transformation, Eq. (3.10) becomes an algebraic equation which can be solved by standard techniques. The determinant of this equation is positive definite. If we assume that there is no tendency for the systems in question to undergo a phase transition to a biaxial state, we can assume that the determinant is of order $(\rho kT/m)^2$. Hence, $\delta S(\vec{r})$ and $\delta\xi(\vec{r})$ are of order $\chi^a H^2/\rho kTm^{-1}$ which at 100 °C in a field of 10 kG is of order 10^{-7} for $\chi^a=10^{-7}$. This is certainly small and justifies the linearization of Eq. (3.9).[22] Hence, $\delta S(\vec{r})$ and $\xi(\vec{r})$ are always small relative to S itself, which in the ordered state is never less than 0.3. We can, therefore, take $Q_{ij}(\vec{r})$ to be a uniaxial tensor with a homogeneous eigenvalue but with principal axes which can vary in space:

$$Q_{ij}(\vec{r})=S[n_i(\vec{r})n_j(\vec{r})-\tfrac{1}{3}\delta_{ij}]. \tag{3.11}$$

We now consider in more detail the form of $\mathfrak{F}_1$ to lowest order in the derivatives of the order parameter. Since the only spatial variation in $Q_{ij}(\vec{r})$ is in $n_i(\vec{r})$, any quadratic form in $\nabla_i Q_{jk}(\vec{r})$ can be expressed as some function of S multiplied by the independent combinations of $n_i(\vec{r})$ and $\nabla_j n_k(\vec{r})$ quadratic in ∇_i. There are four such combinations which can be expressed in terms of the four independent contributions to the Frank free energy [Eq. (3.1)]. Hence, F_1 as a function of $Q_{ij}(\vec{r})$ is equivalent to Frank's free energy to order $\chi^a H^2/\rho kTm^{-1}$. The elastic constants are now, of course, functions of S. It is interesting to note that there are only three independent combinations of $\nabla_i Q_{jk}$ which are quadratic in both ∇_i and Q_{jk}:

$$C_1 = \nabla_i Q_{ik} \nabla_j Q_{jk} = S^2[(\nabla_i n_i)^2 + (n_i \nabla_i n_k)(n_j \nabla_j n_k)], \tag{3.12a}$$

$$C_2 = \nabla_i Q_{jk} \nabla_i Q_{jk} = 2S^2 \nabla_i n_j \nabla_i n_j, \tag{3.12b}$$

$$C_3 = \nabla_i Q_{jk} \nabla_j Q_{ik} = S^2[(\nabla_i n_j)(\nabla_j n_i) + (n_i \nabla_i n_k)(n_j \nabla_j n_k)]. \tag{3.12c}$$

Hence $(\vec{\nabla}\cdot\vec{n})^2$, $[\vec{n}\cdot(\vec{\nabla}\times\vec{n})]^2$, and $[\vec{n}\times(\vec{\nabla}\times\vec{n})]^2$ cannot be expressed in terms of C_1, C_2, and C_3. To obtain the fourth independent term, it is necessary to go to third order in Q_{ij} and consider terms like

$$Q_{ij} \nabla_i Q_{kl} \nabla_j Q_{kl} = S^3[\tfrac{2}{3}(n_i \nabla_j n_k)(n_j \nabla_j n_k) - \tfrac{1}{3}(\nabla_i n_j)(\nabla_j n_i)]. \tag{3.13}$$

On the other hand, it is possible to express C_1, C_2, and C_3 in terms of $(\vec{\nabla}\cdot\vec{n})^2$, $[\vec{n}\cdot(\vec{\nabla}\times\vec{n})]^2$, $[\vec{n}\times(\vec{\nabla}\times\vec{n})]^2$, and $(\vec{\nabla}\cdot\vec{n})^2 - (\nabla_i n_j)(\nabla_j n_i)$:

$$C_1 = S^2\{(\vec{\nabla}\cdot\vec{n})^2 + [\vec{n}\times(\vec{\nabla}\times\vec{n})]^2\}, \tag{3.14a}$$

$$C_2 = 2S^2\{(\vec{\nabla}\cdot\vec{n})^2 + [\vec{n}\cdot(\vec{\nabla}\times\vec{n})]^2 - [(\vec{\nabla}\cdot\vec{n})^2 - \nabla_i n_j \nabla_j n_i]\}, \tag{3.14b}$$

$$C_3 = S^2\{(\vec{\nabla}\cdot\vec{n})^2 + [\vec{n}\times(\vec{\nabla}\times\vec{n})]^2 - [(\vec{\nabla}\circ\vec{n})^2 - \nabla_i n_j \nabla_j n_i]\}. \tag{3.14c}$$

Hence C_1, C_2, and C_3 together contain all of the terms which contribute to the Frank free energy. It is perhaps more than coincidental that K_{11}, K_{22}, and K_{33} of Frank's theory are experimentally determined to be proportional to S^2 as a function of temperature,[11] while the simplest expression for the free energy in terms of $\nabla_i Q_{jk}$ is also proportional to S^2. Of course, in general, there can always be an essentially arbitrary function of S multiplying each term quadratic in the space derivatives.

Now that we have established that Frank's equilibrium theory for a nematic is rigorous in the long-wavelength limit to order $\chi^a H^2/\rho k T m^{-1}$, let us review some of its consequences. $n_i(\vec{r})$ is determined by

$$(\delta_{ij} - n_i n_j)[\delta F/\delta n_i(\vec{r})] = 0, \tag{3.15}$$

$$\frac{\delta F}{\delta n_i(\vec{r})} = \frac{\partial \mathfrak{F}}{\partial n_i} - \nabla_j \frac{\partial \mathfrak{F}}{\partial(\nabla_j n_i)}. \tag{3.16}$$

Equation (3.16) for the functional derivative of F is valid because we have restricted our attention to variations in the bulk of the sample. The Orsay Liquid Crystal Group[15] has calculated this derivative from the Frank free energy:

$$-\frac{\delta F}{\delta n_i(\vec{r})} = K_{11} \nabla_i(\vec{\nabla}\cdot\vec{n}) - K_{22}\{C(\vec{\nabla}\times\vec{n})_i + [\vec{\nabla}\times(C\vec{n})]_i\} + K_{33}\{[\vec{D}\times(\vec{\nabla}\times\vec{n})]_i + [\vec{\nabla}\times(\vec{n}\times\vec{D})]_i\} + \chi_a(T) n_j(\vec{r}) H_{ij}(\vec{r}), \tag{3.17}$$

where $\vec{C} = \vec{n}\cdot(\vec{\nabla}\times\vec{n})$, $\vec{D} = \vec{n}\times(\vec{\nabla}\times\vec{n})$, and where we have introduced the notation $H_{ij}(\vec{r}) = H_i(\vec{r}) H_j(\vec{r})$ and $\chi_a(T) = \chi^a S$. In the case where all of the elastic constants are equal, Eq. (3.17) assumes a particularly simple form:

$$-\frac{\delta F}{\delta n_i(\vec{r})} = K \nabla^2 n_i(\vec{r}) + \chi_a(T) n_j(\vec{r}) H_{ij}(\vec{r}). \tag{3.18}$$

These equations can be used to determine $n_i(\vec{r})$ in systems subject to a variety of external fields and rigid boundary conditions.[10] Of particular interest to us is the change in $n_i(\vec{r})$ produced by an infinitesimal spatially varying external field $\tilde{H}_{ij}(\vec{r})$ in systems where $n_i(\vec{r})$ is homogeneous and parallel to any nonspatially varying field H_i. In these systems, if we take $\vec{n} = \vec{e}_z$ parallel to $\vec{H}$ when $\tilde{H}_{ij}(\vec{r})$ is zero, then $n_x(\vec{r})$ and $n_y(\vec{r})$ must be proportional to $\tilde{H}_{ij}(\vec{r})$ for infinitesimal $\tilde{H}_{ij}(\vec{r})$ and $n_z = 1 - (n_x^2 + n_y^2) = 1 + O(\tilde{H}_{ij}^2)$. To lowest order, Eqs. (3.15) and (3.18) give, after Fourier transformation,

$$K q^2 n_x(\vec{q}) = \chi_a(T) \tilde{H}_{xz}(\vec{q}) + O(\tilde{H}^2), \tag{3.19a}$$

$$K q^2 n_y(\vec{q}) = \chi_a(T) \tilde{H}_{yz}(\vec{q}) + O(\tilde{H}^2). \tag{3.19b}$$

Hence we have

$$\frac{\partial n_x(\vec{q})}{\partial \tilde{H}_{xz}(\vec{q})} = \frac{\partial n_y(\vec{q})}{\partial \tilde{H}_{yz}(\vec{q})} = \frac{\partial n_x(\vec{q})}{\partial \tilde{H}_{zx}(\vec{q})} = \frac{\partial n_y(\vec{q})}{\partial \tilde{H}_{zy}(\vec{q})} = \frac{\chi_a(T)}{K q^2}. \tag{3.20}$$

All other derivatives of $n_x(\vec{q})$, $n_y(\vec{q})$, or $n_z(\vec{q})$ with respect to $\tilde{H}_{ij}(\vec{q})$ are of higher order in $\tilde{H}_{ij}(\vec{q})$ or q^2. The derivatives in Eq. (3.20) are thermodynamic derivatives. They diverge at $\vec{q} = 0$ because $n_i(\vec{r})$ will align along any homogeneous external field.

In closing this section, we should perhaps stress that the $n_i(\vec{r})$'s encountered in a static theory are properties of the system in equilibrium in the presence of a static external field. As such, they are not quantities which fluctuate. The individual particle directors $\nu_i^a(t)$ do fluctuate in equilibrium, and one can discuss their equilibrium fluctuation spectrum. Hence, when we speak of order parameter fluctuations, we mean fluctuations in $R_{ij}(\vec{r}t)$ which are usually expressed in terms of the equilibrium average $\langle R_{ij}(\vec{r}t) R_{kl}(\vec{r}'t')\rangle$. $n_i(\vec{r})$, on the other hand, is expressed in terms of the equilibrium average $\langle R_{ij}(\vec{r}t)\rangle$ and does not fluctuate.

IV. TRANSPORT IN A LIQUID CRYSTAL

The transport properties of any system are determined by its differential conservation laws. A liquid crystal is characterized by the laws governing the conservation of mass, momentum, energy, and angular momentum:

$$\frac{\partial \rho(\vec{r}t)}{\partial t} + \nabla_i j_i(\vec{r}t) = 0, \tag{4.1a}$$

$$\frac{\partial j_i(\vec{r}t)}{\partial t} + \nabla_j \sigma_{ij}(\vec{r}t) = 0, \tag{4.1b}$$

$$\frac{\partial \epsilon(\vec{r}t)}{\partial t} + \nabla_i j_i^\epsilon(\vec{r}t) = 0, \tag{4.1c}$$

$$\frac{\partial L_i(\vec r t)}{\partial t}+\frac{\partial M_i(\vec r t)}{\partial t}+\nabla_j \tau_{ij}(\vec r t)=0. \tag{4.1d}$$

$\rho(\vec r t)$ is the mass density

$$\rho(\vec r t)=\textstyle\sum_\alpha m\,\delta[\vec r-\vec r^{\alpha}(t)], \tag{4.2}$$

and $j_i(\vec r t)$ is the momentum density of c.m. motion:

$$j_i(\vec r t)=\textstyle\sum_\alpha p_i^\alpha \delta[\vec r-\vec r^{\alpha}(t)]. \tag{4.3}$$

$\epsilon(\vec r t)$ is the energy density, $\sigma_{ij}(\vec r t)$ the stress tensor, and $j^{\epsilon}(\vec r t)$ the energy current. $L_i(\vec r t)$ is the angular momentum density due to c.m. motion, and $M_i(\vec r t)$ is the angular momentum density due to rotational motion of the barlike molecules:

$$L_i(\vec r t)=\Sigma_\alpha(\vec r^{\alpha}\times\vec p^{\alpha})_i\delta[\vec r-\vec r^{\alpha}(t)]=[\vec r\times\vec j(\vec r t)]_i, \tag{4.4a}$$

$$M_i(\vec r t)=\Sigma_\alpha I[\vec\nu^{\alpha}\times\dot{\vec\nu}^{\alpha}(t)]_i\delta[\vec r-\vec r^{\alpha}(t)], \tag{4.4b}$$

where

$$\dot\nu_i^\alpha(t)=\frac{\partial\nu_i^\alpha(t)}{\partial t}\;.$$

In an isotropic fluid (even one composed of long molecules), one can always define $\rho(\vec r t)$ and $j_i(\vec r t)$ so that $L_i(\vec r t)=[\vec r\times\vec j(rt)]_i$. In this case, the angular-momentum-conservation equation imposes the condition that $\sigma_{ij}(\vec r t)$ be symmetric. Hence, in discussions of isotropic fluids, one usually quotes only the first three conservation laws of Eq. (4.1) and assumes that σ_{ij} is symmetric. In liquid crystals, angular momentum conservation plays a more important role and, in particular, determines the antisymmetric part of σ_{ij}.

If variations in space and time are slow, the system can be treated as if it were in thermodynamic equilibrium locally. The equilibrium state of a liquid crystal is characterized by the eight conserved variables: particle number, momentum, energy, and total angular momentum, and by the order parameter $Q_{ij}(\vec r t)$. We expect local equilibrium to be described by densities of the conserved quanties and $\langle R_{ij}(\vec r t)\rangle$ or alternatively by associated spatially and temporally varying intensive quantities. For nematics, a convenient choice of intensive variables is pressure, temperature, order parameter $S(\vec r t)$, director $n_i(\vec r t)$, local velocity $v_i(\vec r t)$, and frequency $\Omega_i(\vec r t)$ defined by

$$\langle j_i(\vec r t)\rangle=\langle\rho(\vec r t)\rangle\, v_i(\vec r t), \tag{4.5a}$$

$$\langle M_i(\vec r t)\rangle=[\langle\rho(\vec r t)\rangle/m]I_{ij}(\vec r t)\Omega_j(\vec r t), \tag{4.5b}$$

where

$$\begin{aligned}\langle\rho(\vec r t)\rangle I_{ij}(\vec r t)&=I\langle\textstyle\sum_\alpha(\delta_{ij}-\nu_i^\alpha\nu_j^\alpha)\delta[\vec r-\vec r^{\alpha}(t)]\rangle\\ &=\langle\rho(\vec r t)\rangle\,(I/m)\{\tfrac{2}{3}\delta_{ij}-S(\vec r t)\,[n_i(\vec r t)n_j(\vec r t)-\tfrac{1}{3}\delta_{ij}]\}.\end{aligned} \tag{4.6}$$

Consider now a rigid rotation of the liquid crystal with a constant angular frequency. In this case, $M_i(\vec r t)$ is given by Eq. (4.5b) with Ω_j a constant independent of space and time. Since we are considering a rigid rotation, that part of Ω_j perperpendicular to n_i must be given identically by

$$\Omega_{\perp i}=[\vec n\times\dot{\vec n}(t)]_i, \tag{4.7}$$

where $\dot n_i(t)=\partial n_i/\partial t$. Hence, for rigid rotations the intensive variable $\Omega_{\perp i}(\vec r t)$ can be replaced by $\dot n_i(\vec r t)$.

If we now consider nonrigid rotations, Eq. (4.7) is no longer compatible with the definition of $\Omega_j(\vec r t)$ given by Eq. (4.5b). However, for variations [of $\Omega_j(\vec r t)$] which are slow in space and time, the error made in replacing $\Omega_{\perp i}(\vec r t)$ by $[\vec n(\vec r t)\times\dot{\vec n}(\vec r t)]_i$ is of order $\omega\tau$, where τ is a characteristic molecular decay time and ω is the frequency characterizing the time variation of $\Omega_i(\vec r t)$. This follows because although each molecule is not necessarily instantaneously aligned with $n_i(\vec r t)$ its component perpendicular to $n_i(\vec r t)$ averages to zero over several decay times. Hence, to order $\omega\tau$ one can assume that the molecules at each point in space are parallel to the director at that point. Therefore, if we restrict ourselves to states in which the component of Ω_i parallel to n_i is zero, we can write

$$\langle M_i(\vec r t)\rangle=(\rho I/m)(\tfrac{2}{3}+\tfrac{1}{3}S)(\vec n\times\dot{\vec n})_i\equiv J(\vec r t)[\vec n(\vec r t)\times\dot{\vec n}(\vec r t)]_i. \tag{4.8}$$

(We drop here the notational distinction between the operator ρ and its average value $\langle\rho\rangle$.) We may further suppose that the complete equilibrium system is at rest and consider only linear deviations from that state. Then $J(\vec r t)$ can be considered as a constant independent of space and time. The angular-momentum-conservation equation now reads

$$J\frac{\partial}{\partial t}[\vec n\times\dot{\vec n}(\vec r t)]_i-\epsilon_{ijk}\sigma_{jk}(\vec r t)+\nabla_j\tau'_{ij}(\vec r t)=0, \tag{4.9}$$

where we have used Eqs. (4.4a) and (4.1b) to express $\partial L_i(\vec r t)/\partial t$ in terms of $\sigma_{jk}(\vec r t)$:

$$\tau'_{ij}(\vec r t)=\tau_{ij}(\vec r t)-\epsilon_{ikl}r_k\sigma_{lj}(\vec r t), \tag{4.10}$$

where ϵ_{ikl} is the Levi-Civita symbol, and J from Eq. (4.8) is $(\rho I/m)\,(\frac{2}{3}+\frac{1}{3}S)$.[23]

Instead of writing an equation for $[\vec n\times\dot{\vec n}(\vec r t)]$, one could equally as well write, as Leslie has chosen to do,[13] an equation for $\dot{\vec n}(\vec r t)$,

$$\frac{\partial^2 n_i(\vec r t)}{\partial t^2}+g_i(\vec r t)+\nabla_j\Pi_{ij}(\vec r t)=0\;\;. \tag{4.11}$$

(Since we are considering only linear deviations from equilibrium, we need not distinguish between material and spatial time derivatives.) Equation (4.11) must of course be compatible with Eq. (4.8). Hence, we have

$$\epsilon_{ijk}(n_jg_k-\Pi_{kl}n_{j,l})=-\epsilon_{ijk}\sigma_{jk}, \tag{4.12a}$$

$$\nabla_j(\epsilon_{ilk}n_l\Pi_{kj})=\nabla_j\tau'_{ij}\;, \tag{4.12b}$$

where

$$n_{j,l} = \nabla_l n_j \ .$$

In Appendix B, we rederive Ericksen's[7] expression for σ_{ij} in equilibrium,

$$\sigma_{ij} = p\delta_{ij} + \frac{\partial \mathfrak{F}}{\partial n_{k,j}} n_{k,i}, \qquad (4.13)$$

where p is the pressure, and $\mathfrak{F}$ is the Frank free-energy density [Eqs. (3.1) and (3.3)]. From this and Eq. (4.11) one can easily see that at equilibrium

$$g_i = \frac{\partial \mathfrak{F}}{\partial n_i} + \gamma n_i - \beta_j n_{i,j} \ , \qquad (4.14a)$$

$$\Pi_{ij} = -\frac{\partial \mathfrak{F}}{\partial n_{i,j}} + \beta_j n_i, \qquad (4.14b)$$

where γ and β_j are undetermined constants. They indicate the indeterminacy of the specification of g_i and Π_{ij} by Eq. (4.12); they do not, however, affect Eq. (4.9), which contains the physics of the problem. The form of g_i and Π_{ij} in Eq. (4.14) is just that given by Leslie. Plugging Eq. (4.14) into Eq. (4.9), one obtains

$$J\frac{\partial}{\partial t}(\vec{n}\times\dot{\vec{n}}) = -\epsilon_{ijk} n_j\left(\frac{\partial \mathfrak{F}}{\partial n_k} - \nabla_l \frac{\partial \mathfrak{F}}{\partial n_{k,l}}\right) \ . \qquad (4.15)$$

But $\partial \mathfrak{F}/\partial n_k - \nabla_l\, \partial \mathfrak{F}/\partial n_{k,l}$ is just the functional derivation $\partial F/\delta n_k(\vec{r})$ of the free energy F with respect to $n_k(\vec{r})$. In equilibrium, the cross product of this with n_i is zero, so that Eq. (4.15) says that $\dot{\vec{n}}$ is zero in equilibrium as it should be.

To discuss transport in systems slightly away from total equilibrium but in equilibrium locally, it is necessary to introduce constitutive relations between the currents of Eq. (4.1) and (4.11) and variations in the spatially varying intensive quantities characterizing the local equilibrium state. This is discussed in detail in Leslie's papers.[13] In particular, he finds that the dissipative part of the stress tensor can be written as

$$\sigma'_{ij} = -\alpha_1 n_k n_l A_{kl} n_i n_j - \alpha_2 N_i n_j - \alpha_3 n_i N_j - \alpha_4 A_{ij} - \alpha_5 n_j n_k A_{ki} - \alpha_6 n_i n_k A_{kj} \ , \qquad (4.16)$$

where

$$A_{ij} = \tfrac{1}{2}(\nabla_i v_j + \nabla_j v_i) \ , \qquad (4.17a)$$

$$N_i = \frac{\partial n_i}{\partial t} - (\vec{\omega}\times\vec{n})_i \ , \qquad (4.17b)$$

$$\omega_i = \tfrac{1}{2}(\vec{\nabla}\times\vec{v})_i \ . \qquad (4.17c)$$

The coefficients α all have dimensions of a viscosity. Taking into account the remarks of Parodi[24] regarding the Onsager relations, there are only five independent viscosities with $\alpha_2 + \alpha_3 = \alpha_6 - \alpha_5$. α_4 is the only viscosity which remains in the isotropic phase. In the nematic phase, α_2 and α_3 represent a direct coupling between the velocity and the time rate of change of the director. α_1, α_5, and α_6 represent the dissipation due to velocity gradients in different directions relative to $n_i(\vec{r})$.

If we now use Eqs. (4.9) and (4.12a) (bearing in mind that they are only valid for $\omega\tau \ll 1$), we obtain zero for the dissipative part of Π_{ij} and

$$\epsilon_{ijk} n_j g'_k = -\epsilon_{ijk}\sigma'_{jk} = +\epsilon_{ijk} n_j (\gamma_1 N_k + \gamma_2 A_{lk} n_l) \qquad (4.18)$$

for the dissipative part of g_i, where $\gamma_1 = \alpha_3 - \alpha_2$ and $\gamma_2 = \alpha_6 - \alpha_5$. Hence, for linear deviations from equilibrium in the hydrodynamic regime, the equation determining the director is

$$J\left(\vec{n}\times\frac{\partial^2\vec{n}}{\partial t^2}\right) = -\left(\vec{n}\times\frac{\delta F}{\delta\vec{n}}\right) - \gamma_1 \vec{n}\times\vec{N} - \gamma_2 \vec{n}\times\hat{A}n \ , \qquad (4.19)$$

where $(\hat{A}n)_i = A_{ij} n_j$. This is the equation used by the Orsay Liquid Crystal Group to determine the fluctuation spectrum of the director in a nematic.[15] We will now quickly outline the derivation of this fluctuation spectrum in a way that guarantees the existence of local equilibrium at all times so that the hydrodynamic equations of Leslie are always applicable. To do this, we create at time $t=0$ a local equilibrium state with a spatially varying order parameter by the adiabatic application of an external magnetic field from time equals minus infinity to time zero[25]:

$$H_{ij}(rt) = \begin{cases} H_{ij}(r)e^{\epsilon t}, & t<0 \\ 0 \ , & t>0 \end{cases} \qquad (4.20)$$

where ϵ is an infinitesimal.

For $H_{ij}(\vec{r})$ slowly varying in space, the field (4.18) will induce a director at $t=0$ of the form

$$\delta n_i(\vec{q}) = \frac{\partial n_i(\vec{q})}{\partial H_{jk}(\vec{q})}\,\delta H_{jk}(\vec{q}) \ , \qquad (4.21)$$

where $\partial n_i(\vec{q})/\partial H_{jk}(\vec{q})$ is a thermodynamic derivative. Or, using Eq. (4.20), we have

$$n_x(\vec{q}) = [\chi_a(T)/Kq^2]\, H_{xz}(\vec{q}) \ , \qquad (4.22a)$$

$$n_y(\vec{q}) = [\chi_a(T)/Kq^2]\, H_{yz}(\vec{q}) \ , \qquad (4.22b)$$

$$n_z(\vec{q}) = 1 + O((\delta n)^2) \ . \qquad (4.22c)$$

For $t>0$, we can now use Leslie's equations to determine $n_i(\vec{q}t)$ subject to the condition that at $t=0$ it reduces to Eq. (4.22).

Following closely the procedure and notation of Ref. 15, one can easily show that

$$n_i(\vec{q}\omega) = \left(\frac{1}{-i\omega + u_{is}} - \frac{C_i Q_i}{\gamma_i P_i}\,\frac{1}{-i\omega + u_{iF}}\right) n_i(\vec{q}t=0), \qquad i = x, y \qquad (4.23)$$

where $n_i(\vec{q}\omega) = \int_0^\infty e^{i\omega t} n_i(\vec{q}t)$ (ω is understood to have a small positive imaginary part).

The directions x and y correspond to directions 1 and 2 of Ref. 15, i.e., y is parallel to $\vec{n}\times\vec{q}$, and x is parallel to $(\vec{n}\times\vec{q})\times\vec{n}_0$ where $\vec{n}_0$ is the direction of preferred orientation in complete equilibrium. Similarly γ_x is identical to γ_1, and γ_y is identical to γ_2. In arriving at Eq. (4.23), we used the standard approximation that $K\rho/\eta^2 \ll 1$, where η is a characteristic viscosity. u_{is} and u_{iF} are, respectively, the frequencies of the slow and fast modes. u_{is}/u_{iF} is of order $K\rho/\eta^2$. The general expressions for C_i, Q_i, and P_i are relatively complicated. They, however, have the general form

$$P_i(\vec{q}) \sim \eta q^2, \quad C_i(\vec{q}) \sim Q_i(\vec{q}) \sim \eta q \quad . \tag{4.24}$$

The contribution of the second term of Eq. (4.23) to the total power spectrum is of order $K\rho/\eta^2$ relative to the first and can, in general, be neglected. Hence Eq. (4.23) obtains the simple form

$$n_i(\vec{q}t) = (-i\omega + u_{is})^{-1} n_i(\vec{q}t=0) \quad . \tag{4.25}$$

Even if one lets all the elastic constants be equal, the exact expressions for u_{is} are complicated [cf. Eq. (4.25) of Ref. 15].

Fortunately, for most purposes the schematic representation suggested in Ref. 15 is sufficient:

$$u_{xs} \sim u_{ys} \sim Kq^2/\eta \quad . \tag{4.26}$$

Here, η is a viscosity averaged over angles. It, however, is proportional to γ_1 or γ_2 and thus vanishes in the isotropic phase. Using Eqs. (4.21), (4.22), and (4.26), we can now write

$$\frac{\delta n_x(\vec{q}\omega)}{\delta H_{xz}(\vec{q})} = \frac{\chi_a(T)}{Kq^2} \frac{1}{-i\omega + (Kq^2/\eta)} = \frac{\delta n_y(\vec{q}\omega)}{\delta H_{yz}(\vec{q})} \quad . \tag{4.27}$$

All other derivatives are zero to the order in question. This is the formula which we will use for comparison with a general response-function treatment in Sec. V.

Before closing this section, it might be useful to make some general comments about the Leslie theory and transport in liquid crystals. The intensive parameter $n_i(\vec{r}t)$ is *defined* to be a unit vector at all points in space and time. It specifies the preferred orientation of the molecules at the point r and time t. Alternatively, it specifies the direction of the maximum eigenvalue of $Q_{ij}(\vec{r}t)$. One cannot speak of fluctuations in $n_i(\vec{r}t)$ without contradicting the assumption that $n_i(\vec{r}t)$ is a unit vector. One can, however, speak of fluctuations in the total order parameter $Q_{ij}(\vec{r}t)$. Physically, fluctuations in $Q_{ij}(\vec{r}t)$ are fluctuations in the direction of the individual molecules about their preferred directions. One can calculate the fluctuation in Q_{ij} via the fluctuation dissipation theorem and the response functions calculated in this section. We will do this in Sec. V. Since $n_i(\vec{r}t)$ is a unit vector defined in terms of a symmetric traceless tensor (rather than simply a symmetric tensor), it is doubtful that the Leslie theory for a director of variable magnitude is applicable to liquid crystals. It is also worth noting again that the Leslie theory is incapable of giving any information about the transport properties of liquid crystals in which there is a non-negligible biaxial term or component of angular momentum parallel to n. This does not constitute a restriction on the first-order theory which we are considering as long as the initial states contain no biaxial component or component of angular momentum parallel to n. However, in higher order, there may be spontaneous creation of biaxial terms and parallel angular momentum components. Hence the Leslie theory is probably only valid for first-order deviations from complete equilibrium.

V. RESPONSE-FUNCTION DESCRIPTION

As is well known, the linear change in the expectation value of any observable due to the presence of an external field is conveniently described in terms of linearized response functions. In Appendix B, we review the pertinent definitions and properties of response functions in classical systems. For our present purpose, we need only know that the change in the average value of $\langle R_{ij}(\vec{r}t)\rangle$ due to a time-varying external magnetic field is

$$\delta\langle R_{ij}(\vec{r}t)\rangle = -2i\kappa_H^a \int d^3r \int_{-\infty}^{t} \tilde{\chi}''_{ijkl}(\vec{r}\vec{r}'tt')\, \delta H_{kl}(\vec{r}'t') \ , \tag{5.1}$$

where $\tilde{\chi}''_{ijkl}(\vec{r}\vec{r}'tt')$ is $\frac{1}{2}$ times the equilibrium average of the Poisson bracket of $R_{ij}(\vec{r}t)$ with $R_{kl}(\vec{r}'t')$:

$$\tilde{\chi}''_{ijkl}(\vec{r}\vec{r}'tt') = \tfrac{1}{2}\langle [R_{ij}(\vec{r}t), R_{kl}(\vec{r}'t')]\rangle \ . \tag{5.2}$$

If we choose an external magnetic field with time dependence of the form of Eq. (4.19), we obtain

$$\delta\langle R_{ij}(\vec{q}\zeta)\rangle = \kappa_H^a \int \frac{d\omega'}{\pi i} \frac{\chi''_{ijkl}(\vec{q}\omega')}{\omega'(\omega'-\zeta)}\, \delta H_{kl}(\vec{q}) \ , \tag{5.3}$$

where $\delta\langle R_{ij}(\vec{q}\zeta)\rangle$ is the Laplace transform in time (ζ is a complex frequency variable in the upper half-plane) and the Fourier transform in space of $\delta\langle R_{ij}(\vec{r}t)\rangle$. $\chi''_{ijkl}(\vec{q}\omega')$ is the Fourier transform of $\tilde{\chi}''_{ijkl}(\vec{r}\vec{r}'tt')$, and $\delta H_{ij}(\vec{q})$ is the external magnetic field at $t = 0$ just prior to being shut off. Hence we have

$$\delta\langle R_{ij}(\vec{q}\zeta)\rangle = (\kappa_H^a/i\zeta)[\chi_{ijkl}(\vec{q}\zeta) - \chi_{ijkl}(\vec{q})]\, \delta H_{kl}(q) \ , \tag{5.4}$$

where $\chi_{ijkl}(\vec{q}\zeta)$ is the familiar dynamic response function and $\chi_{ijkl}(\vec{q})$ the static susceptibility. This equation is valid for all frequencies and wave numbers, provided the external field is small enough that the linear approximation is valid. However, as it stands, it is not very interesting since the form of $\chi_{ijkl}(\vec{q}\zeta)$ can be almost arbitrary. Fortunately, we can use the results of the previous sections to give us the form of $\chi_{ijkl}(\vec{q}\zeta)$ in the hydrodynamic limit (i.e., for $\omega\tau \ll 1$, where τ is the longest characteristic molecular time of the system). For the moment, let us restrict ourselves to a consideration of changes in $\langle R_{xz}(\vec{q}t)\rangle$ due to an external field $H_{xz}(\vec{q})$. From Eq. (4.22), the linear change in $\langle R_{xz}(\vec{q}t)\rangle$ is

$$\delta\langle R_{xz}(\vec{q}t)\rangle = (\rho/m)\,\delta Q_{xz}(\vec{q}t) = (\rho S/m)\,\delta(n_x(\vec{q}t)\,n_z(\vec{q}t))$$
$$= (\rho S/m)\,\delta n_x(\vec{q}t) \ . \tag{5.5}$$

We have ignored changes in ρ and S because they appear only in second order. A similar equation holds for static changes in $\langle R_{xz}(\vec{q})\rangle$:

$$\delta\langle R_{xz}(\vec{q})\rangle = \frac{\rho}{m}\,S\,\frac{\partial n_x(\vec{q})}{\partial H_{xz}(\vec{q})}\,\delta H_{xz}(\vec{q}) \ , \tag{5.6}$$

where as before $\partial n_x(\vec{q})/\partial H_{xz}(\vec{q})$ is a thermodynamic derivative. For classical systems, thermodynamic derivatives are always equal to the static response functions (cf. Appendix B), so that we can deduce from Eq. (5.6) that

$$\chi_{xzxz}(\vec{q}) = (\rho/m)^2\,(S^2/Kq^2) \ . \tag{5.7}$$

Using Eqs. (5.4), (5.5), and (5.7), it follows that

$$\frac{\rho}{m}\,S\,\frac{\delta n_x(\vec{q}\zeta)}{\delta H_{xz}(\vec{q})} = \frac{\kappa_H^a}{i\zeta}\,[\chi_{xzxz}(\vec{q}\zeta) - \chi_{xzxz}(\vec{q})] \ . \tag{5.8}$$

Using the schematic form of $\delta n_x(\vec{q}\zeta)/\delta H_{xz}(\vec{q})$ of Eq. (4.13), this gives immediately

$$\frac{1}{i\zeta}\,[\chi_{xzxz}(\vec{q}\zeta) - \chi_{xzxz}(\vec{q})] = \left(\frac{\rho}{m}\right)^2 \frac{S^2}{Kq^2}\,\frac{1}{-i\zeta + (K/\eta)\,q^2} \ , \tag{5.9a}$$

$$\chi_{xzxz}(\vec{q}\zeta) = \left(\frac{\rho}{m}\right) \frac{S^2}{Kq^2}\,\frac{iKq^2/\eta}{\zeta + iKq^2/\eta} \ . \tag{5.9b}$$

The imaginary part of this expression is $\chi''_{xzxz}(\vec{q}\omega)$:

$$\frac{1}{\omega}\,\chi''_{xzxz}(\vec{q}\omega) = \left(\frac{\rho}{m}\right)^2 \frac{S^2}{Kq^2}\,\frac{(K/\eta)q}{\omega^2 + [(K/\eta)\,q^2]^2} \ . \tag{5.10}$$

This function is plotted in Fig. 4(a). In a similar way, one can obtain the expression for $\chi_{yzyz}(\vec{q}\,\zeta)$ [which in the approximation of Eq. (4.27) is the same as $\chi_{xzxz}(\vec{q}\zeta)$].

By Eq. (3.20), the derivation of the Frank free energy, and the form of $\delta\langle R_{ij}(\vec{q}\zeta)\rangle$, one can easily see that χ_{abxy}, χ_{aaxz}, χ_{aayz}, and χ_{xzyz} for $a, b = x, y, z$ are zero in the hydrodynamic limit. In other words, they are at least of order $q\lambda \ll 1$, where λ is the characteristic length determining the domain of validity of hydrodynamics. There remain only the components χ_{zzzz}, χ_{xxxx}, χ_{yyyy}, χ_{xxzz}, χ_{yyzz}, and χ_{xxyy}. These all involve variations in the order parameter S *and* in the density ρ. The Frank-Leslie theories cannot give us any information about these response functions even in the hydrodynamic limit.

To avoid complicated notation, let us now assume that the schematic hydrodynamic limit of Eq. (5.9) is valid and set $\chi_\perp(\vec{q}\zeta) = \chi_{xzxz} = \chi_{yzyz}$. $\omega\chi''_\perp(\vec{q}\omega)$ is positive definite. Hence, according to standard procedure,[25,26] one can introduce a wave-number-dependent elastic constant $K(\vec{q})$ and a frequency- and wave-number-dependent quantity $(K/\eta)(\vec{q}\zeta)$ such that

$$\chi_\perp(\vec{q}\zeta) = \frac{S^2}{K(q)q^2}\left(\frac{\zeta}{\zeta + i(K/\eta)(\vec{q}\zeta)q^2} - 1\right) \tag{5.11}$$

for all $\vec{q}$ and ζ. For small $\vec{q}$, $K(\vec{q})$ reduces to the elastic constant; and for small q and ζ, $(K/\eta)(\vec{q}\zeta)$ reduces to the constant value K/η. $i(K/\eta)(\vec{q}\zeta)$ has a spectral representation similar to that of $\chi_\perp(\vec{q}\zeta)$:

$$i\frac{K}{\eta}(\vec{q}\zeta) = \int_{-\infty}^{\infty} \frac{d\omega}{\pi}\,\frac{\Delta'(\vec{q}\omega)}{\omega - \zeta} \ . \tag{5.12}$$

At high frequencies, $\chi(\vec{q}\zeta)$ behaves like

$$\chi_\perp(\vec{q}\zeta) = -(1/\zeta^2)M_1 - (1/\zeta^4)M_2 + \cdots \ , \tag{5.13}$$

where the high-frequency moments are defined as

$$M_n = \int \frac{d\omega}{\pi}\,\omega^{2n}\,\frac{\chi''_\perp(\vec{q}\omega)}{\omega} \ . \tag{5.14}$$

Using Eq. (5.11) this gives

$$i\frac{K}{\eta}(\vec{q}\zeta) = -\frac{1}{\zeta^2}\int \frac{d\omega}{\pi}\,\Delta'(\vec{q}\omega) + \cdots$$
$$= -\frac{1}{\zeta^2}\,\frac{M_1}{\chi_\perp(\vec{q})q^2} + \cdots \ . \tag{5.15}$$

The high-frequency moments can easily be evaluated in terms of equal-time Poisson brackets of $R_{ij}(rt)$

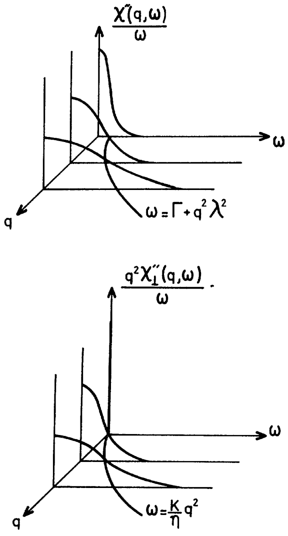

FIG. 4. (a) $q^2\chi''_\perp(q\omega)/\omega$ in the ordered nematic phase. Note that it is a delta function in ω at $q=0$ and is a Lorentzian with width proportional to q^2 for $q>0$. (b) Schematic plot of $\chi''(q\omega)/\omega$ in the isotropic phase of a nematic. Note that it has a finite width at $q=0$ and that for $q^2\lambda^2 \gg \Gamma$, its width is proportional to q^2.

and its time derivatives. In particular,

$$\int \frac{d\omega}{\pi}\,\omega\chi''_{ijkl}(\vec{q}\omega) = \frac{\rho}{mI}\,[2\langle Q^{\alpha}_{jl}Q^{\alpha}_{ik}\rangle + 2\langle Q^{\alpha}_{jk}Q^{\alpha}_{il}\rangle$$
$$-\tfrac{1}{3}(\delta_{jl}\langle Q^{\alpha}_{ik}\rangle + \delta_{ik}\langle Q^{\alpha}_{jl}\rangle + \delta_{jk}\langle Q^{\alpha}_{il}\rangle + \delta_{il}\langle Q^{\alpha}_{jk}\rangle)$$
$$-\tfrac{4}{9}(\delta_{jl}\delta_{ik} + \delta_{jk}\delta_{il})]$$
$$-(\rho/m)(q^2/m)\langle Q^{\alpha}_{ij}Q^{\alpha}_{kl}\rangle\ . \qquad (5.16)$$

Notice that the second term in this expression is negligible compared to the first unless q^{-1} is of the order of a molecular dimension. This is merely a reflection of the fact that the only natural length in the liquid crystal is the length of the molecules. $M_{\perp}$ can be obtained from Eq. (5.16) by taking its $xzxz$ component.

The hydrodynamic form for $\chi_{\perp}(\vec{q}\zeta)$ [Eq. (5.9)] becomes invalid when either q or ω becomes too large. [We are speaking somewhat loosely here since the frequency of the pole of $\chi_{\perp}(q\omega + i\epsilon)$ is determined once q is given.] The frequency that determines the breakdown at large q is $\omega_q \sim K/\eta\lambda^2 < K(2\pi)^2/\eta l_0^2$, where λ is again the length determining the validity of hydrodynamics, and l_0 is a molecular length. With $K \sim 10^{-6}$ dyn, $\eta \sim 10^{-1}$ P and $l_0 \sim 20$ Å, this gives $\omega_q < 10^{10}$. One can arrive at an estimate of the frequency determining the validity of the hydrodynamic (i.e., constant) form of K/η at small q by introducing a phenomenological form for $(K/\eta)(\vec{q}, \omega + i\epsilon)$ which satisfies the first high-frequency sum rule (5.16):

$$\Delta'(\vec{q}\omega) = \frac{M_1}{\chi_{\perp}(\vec{q})q^2}\,\frac{\tau_c}{1 + (\omega\tau_c)^2}\ . \qquad (5.17)$$

At $\omega = 0$, this reduces to K/η, so

$$\tau_c^{-1} = \frac{M_1}{\chi_{\perp}(\vec{q})q^2}\,\frac{\eta}{K}$$
$$\cong \frac{\eta^2}{K\rho}\,\frac{K}{\eta l_0^2} \sim 10^4\omega_q\ . \qquad (5.18)$$

Hence, the hydrodynamic form of the response function breaks down more rapidly as a function of q than as a function of ω.[27]

The response function introduced in Eq. (5.1) is, of course, not restricted to the ordered phase; it is equally well defined in the isotropic and other phases. A few words about χ in the disordered phase might be of interest. $\chi_{ijkl}(\vec{q}\zeta)$ can be written as

$$\chi_{ijkl}(\vec{q}\zeta) = \tfrac{1}{2}\chi_0(\vec{q}\zeta)(\delta_{ik}\delta_{jl} + \delta_{il} + \delta_{jk} - \tfrac{2}{3}\delta_{ij}\delta_{kl}) + \chi^{(1)}_{ijkl}(\vec{q}\zeta)\ , \qquad (5.19)$$

where the zero ζ, zero $\vec{q}$ limit of $\chi_0(\vec{q}\zeta)$ is the static response function χ_0, and the zero $\vec{q}$ limit of $\chi^{(1)}_{ijkl}(\vec{q}\zeta)$ is zero for all ζ.

The nematic liquid-crystal phase transition is a first-order phase transition characterized by a transition temperature T_c. However, the behavior of the susceptibility and other quantities for $T > T_c$ is similar to that of a system with a second-order phase transition characterized by a temperature $T^* < T_c$ with $(T_c - T^*)/T_c \ll 1$. In particular, for $T > T_c$, the static susceptibility $\chi_0(\vec{0}0)$ measured by magnetic birefringence[28] appears to diverge at a temperature of the order of 1° less than the transition temperature. The dynamical susceptibility also exhibits such critical behavior. To a good approximation,[29] we have

$$\lim_{\vec{q}\to 0}\frac{\chi_0''(\vec{q}\omega)}{\omega} = \chi_0\,\frac{\Gamma}{\omega^2 + \Gamma^2}\ . \qquad (5.20)$$

This function is plotted in Fig. 4(b). The width Γ is observed to be proportional to $(T - T^*)^{\tilde{\gamma}}$, where $\tilde{\gamma}$ seems to be 1 (corresponding to a mean field theory) for PAA[30] and $\frac{4}{3}$ for p-methoxy benzylidene-p-nbutylaniline (MBBA).[31] At higher values of q, there is evidence that $\chi_0''(\vec{q}\omega)/\omega$ obtains the same form as $\chi_{\perp}''(\vec{q}\omega)/\omega$ in the ordered phase.[30] This is analogous to the appearance of "sloppy spin-wave" peaks for q greater than an inverse coherence length in the response functions of magnetic and antiferromagnetic systems above

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T_c.[32] One can argue that these result from the existence of a short-range order above T_c giving rise to ordered domains whose size is determined by the above coherence length and within which the modes of the ordered phase propagate freely.[30]

We close this section with a note about the striking resemblance between the response functions for liquid crystals and those for magnetic systems. In a ferromagnet, the perpendicular static response function in the ordered phase is

$$\chi_{\perp}(\vec{q}) = \gamma\langle M\rangle/\mu q^2\ , \qquad (5.21)$$

where μ is a stiffness constant, and μq^2 is the magnon energy.[33] $\langle M\rangle$ is, of course, the magnetic order parameter. $\langle M\rangle$ plays the same role as $(\rho/m)S$ and μ the same role as K in liquid crystals. Equation (5.21) is to be compared with Eq. (5.6) for $\chi_{xzxz}(\vec{q})$. Perhaps a more interesting comparison is with the correlation function for the staggered magnetization in antiferromagnetic systems[34]:

$$S_{xx}(\vec{q}) = \int d^3r\, e^{-i\vec{q}\cdot(\vec{r}-\vec{r}')}$$
$$\langle[B_x(\vec{r}) - \langle B_x(\vec{r})\rangle]\,[B_x(\vec{r}') - \langle B_x(\vec{r}')\rangle]\rangle$$

$$= (4\pi\langle B_z\rangle^2/q^2)\,a\ . \qquad (5.22)$$

$B_i(\vec r)$ is the staggered magnetization and $\langle B_z\rangle$ is the order parameter. a is a coherence length. The analogous quantity for a liquid crystal is

$$S_{Q_{xz}Q_{xz}}(\vec q) = kT\left(\frac{\rho}{m}\right)^2 \frac{S^2}{Kq^2} = \left(\frac{\rho}{m}S\right)^2 \frac{a}{q^2}\,, \qquad (5.23)$$

where $a = kT/K$. Equations (5.22) and (5.23) have exactly the same form: an order parameter squared times a coherence length divided by q^2. Furthermore, neither $R_{ij}(\vec r t)$ nor $B_i(\vec r t)$ are conserved quantities, so that in the disordered phase, the power spectra of these quantities have finite width at $q=0$. The analogy between magnetic and liquid-crystal systems cannot be pressed too far, however. The hydrodynamic modes associated with long-range order are propagating modes in both antiferromagnets and ferromagnets; in liquid crystals, they are diffusive modes. Furthermore, the existence of zero-energy modes at $\vec q = 0$ in the magnetic system is associated with a rotationally invariant Hamiltonian. Introduction of nonrotationally invariant interactions (such as dipolar interactions) changes the nature of the modes at low $\vec q$. At the moment, one cannot associate the existence of hydrodynamic modes in ordered liquid crystals with a similar rotationally invariant Hamiltonian.

VI. APPLICATIONS

A. Light Scattering

In this section, we will consider the application of the formalism developed in the preceding sections to two specific problems: light scattering and NMR linewidths. Each molecule in a liquid crystal has an anisotropic electric polarizability of the form of Eq. (2.7b) from which we can define a polarizability density

$$P_{ij}(\vec r t) = \textstyle\sum_\alpha P^\alpha_{ij}(t)\,\delta(\vec r - \vec r^{\,\alpha}(t))\ . \qquad (6.1)$$

Using classical scattering theory and ignoring multiple scattering effects one arrives at the well-known formula[35, 36] for the differential scattering cross section per unit scattering volume per unit solid angle of the outgoing beam ($d\Omega$) per unit angular frequency $d\omega$:

$$\frac{d^2\sigma}{V d\Omega\, d\omega} = \frac{\pi}{2}\,\frac{1}{\lambda^4}\, e^F_i e^I_j e^I_k e^F_l S_{P_{ij}P_{kl}}(\vec q\omega)\,, \qquad (6.2)$$

where λ is the vacuum wavelength of the incident beam, e^I_i is the incident polarization vector, and e^F_i is the outgoing polarization vector. $S_{P_{ij}P_{kl}}(\vec q\omega)$ is the fluctuation in $P_{ij}(\vec r t)$,

$$S_{P_{ij}P_{kl}}(\vec q\omega) = \int d^3r \int dt\, e^{-i(\vec q\cdot\vec r - \omega t)} \langle [P_{ij}(\vec r t) - \langle P_{ij}\rangle] \times [P_{kl}(\vec 0 0) - \langle P_{kl}\rangle]\rangle\ . \qquad (6.3)$$

Using Eq. (2.7), the differential cross section can be written as

$$\frac{d^2\sigma}{V d\Omega\, d\omega_f} = \frac{\pi}{2\lambda^2}\, e^F_i e^I_j e^I_k e^F \big[(m\chi^0_E)^2 \delta_{ij}\delta_{kl} S_{\rho\rho}(\vec q\omega) + (\chi^a_E)^2 S_{Q_{ij}Q_{kl}}(\vec q\omega) + (m\chi^a_E\chi^0_E)\,\delta_{ij} S_{\rho Q_{kl}}(\vec q\omega) + (m\chi^a_E\chi^0_E)\delta_{kl} S_{Q_{ij}\rho}(\vec q\omega)\big]\ . \qquad (6.4)$$

The first term represents the familiar density fluctuations which appear in Newtonian fluids. The second term represents fluctuations in the liquid-crystal order. The third and fourth represent interference between density and order fluctuations. Note that if the outgoing polarization is perpendicular to the incoming polarization, the only term that contributes to the cross section is the second. $S_{Q_{ij}Q_{kl}}(\vec q\omega)$ can be related to $\chi''_{ijkl}(\vec q\omega)$ by the classical fluctuation dissipation theorem (Appendix B)

$$Q_{Q_{ij}Q_{kl}}(\vec q\omega) = (\beta\omega)^{-1}\chi''_{ijkl}(\vec q\omega)\ , \qquad (6.5)$$

where $\beta = 1/kT$. The wavelengths accessible to light scattering experiments are quite long so that one is in the hydrodynamic regime. Hence, choosing the incident beam to be polarized parallel to $\vec n_0$ (z axis), one can measure $\chi''_{xzxz}(\vec q\omega)$ and $\chi''_{yzyz}(\vec q\omega)$ by observing the scattered beam in the two polarizations perpendicular to $\vec n_0$ (see Fig. 5). Using the schematic form of $\chi''_{xzxz}(\vec q\omega)$, the cross section in this configuration is

$$\frac{d^2\sigma}{V d\Omega\, d\omega} = \frac{\pi kT}{2\lambda^2}\,\frac{[\epsilon^a(T)]^2}{Kq^2}\,\frac{Kq^2/\eta}{\omega^2 + (Kq^2/\eta)^2}\,, \qquad (6.6)$$

where we have replaced $\chi^a_E(\rho/m)S$ by $\epsilon^a(T)$, the bulk anisotropic dielectric constant (at the frequency of the light source). This formula is valid at all temperatures where the liquid-crystal order exists and does not require the molecules to be perfectly aligned (i.e., S does not have to be nearly 1). The total area under the power spectrum curve (6.6) is proportional to $[\epsilon^a(T)]^2/Kq^2$. $\epsilon^a(T)$ is proportional to S and, as already stated, K is proportional to S^2; so as a function of temper-

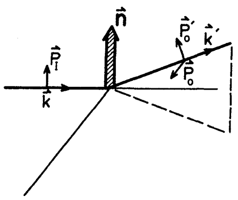

FIG. 5. Experimental configuration for measurement of $(1/\omega)\chi''_{xzxz}(\vec q\omega)$ by light scattering. The incident beam $\vec k$ has polarization $\vec P_I$ parallel to the equilibrium liquid-crystal director $\vec n$. The scattered beam $\vec k'$ can be polarized along $\vec P_0$, which is perpendicular to $\vec n$ and $\vec k'$, or along $\vec P_0'$, which is perpendicular to k' and P_0. Polarizers then pick the component of $\vec P_0'$ perpendicular to $\vec n$.

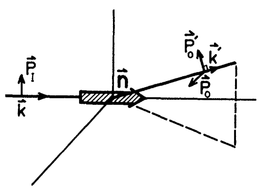

FIG. 6. Experimental configuration for measurement of $(1/\omega)\chi''_{xyxy}(\vec{q}\omega)$ by light scattering. The incident polarization $\vec{P}_I$ is perpendicular to $\vec{n}$. The outgoing polarization $\vec{P}_0$ is also perpendicular to $\vec{n}$. Polarizers pick the component perpendicular to $\vec{n}$ of the other possible outgoing polarization $\vec{P}_0'$.

ature, the area under the power curve should not be strongly dependent on T (at least to the extent that K really is proportional to S^2).

There is another geometry in which only order parameter fluctuations are seen. That is the one in which the polarization vectors of the incoming and outgoing beams are perpendicular to each other and both are perpendicular to $\vec{n}_0$ (Fig. 6). This configuration measures $\chi''_{xyxy}(\vec{q}\omega)$, which is zero in the hydrodynamic limit. The other possible experimental configurations have the polarization vectors of the incoming and outgoing beams parallel to each other. They measure fluctuations in ρ and S. In principle, it should be possible by using all possible polarizations to disentangle the fluctuations in S from those in ρ. Experimentally it may be less feasible.

B. NMR

We consider here the model for NMR in liquid crystals proposed by Pincus.[17] Each molecule in the liquid crystal is assumed to have two identical nuclear spins located on the axis and separated by a distance a. Interactions between spins on neighboring molecules are neglected. Following Pincus and Abragam,[17, 37] the longitudinal decay time due to a dipolar interaction between nuclear spins on the same molecule for the case with external magnetic field $\vec{H}$ parallel to the liquid-crystal order $\vec{n}_0$ is given by

$$(T_1)=\tfrac{3}{2}\gamma^4\hbar^2[I(I+1)/a^6]\,[J^{(1)}(\omega_0)+J^{(2)}(\omega_0)]\ . \quad (6.7$$

γ is the nuclear gyromagnetic ratio, I is the nuclear spin, and ω_0 is the nuclear resonance frequency γH:

$$J^{(1)}(\omega_0)=\int_{-\infty}^{\infty} e^{-i\omega_0 t}\langle F^{(1)}(t)F^{(1)*}(0)\rangle\, dt\ , \qquad (6.8\text{a})$$

$$J^{(2)}(\omega_0)=\int_{-\infty}^{\infty} e^{-i\omega_0 t}\langle F^{(2)}(t)F^{(2)*}(0)\rangle\, dt\ , \qquad (6.8\text{b})$$

where

$$F^{(1)}(t)=\sin\theta^\alpha\cos\theta^\alpha e^{-i\varphi^\alpha}=Q^\alpha_{zx}-iQ^\alpha_{zy}\ , \qquad (6.9\text{a})$$

$$F^{(2)}(t)=\sin^2\theta^\alpha\, e^{-2i\varphi^\alpha}=(Q^\alpha_{xx}-Q^\alpha_{yy})-i(Q^\alpha_{xy}+Q^\alpha_{yx})\ . \qquad (6.9\text{b})$$

Note that $1/T_1$ is expressed in terms of individual-particle correlation functions and not in terms of correlation functions of the density $R_{ij}(\vec{r}t)$.

However, an individual particle at the point $\vec{r}$ should on the average be aligned parallel to the liquid-crystal order at that point. Stated differently, the individual-particle correlation function $\langle Q^\alpha_{ij}(t)Q^\alpha_{kl}(0)\rangle$ should be expressible in terms of the density correlation function $\langle R_{ij}(\vec{r}t)R_{kl}(\vec{r}'t')\rangle$. If the position of the center of mass of each particle is fixed, the relation between $\langle Q^\alpha_{ij}(t)\,Q^\alpha_{kl}(0)\rangle$ and $\langle R_{ij}(\vec{r}t)\,R_{kl}(\vec{r}'t')\rangle$ is relatively straightforward. In this case, $\delta[\vec{r}-\vec{r}^\alpha(t)]\ \delta[\vec{r}-\vec{r}^{\alpha'}(t')]$ is zero unless $\alpha=\alpha'$. Hence

$$\langle R_{ij}(\vec{r}t)R_{kl}(\vec{r}0)\rangle=\Big\langle\sum_{\alpha\alpha'} Q^\alpha_{ij}(t)\,Q^{\alpha'}_{kl}(0) \times \delta[\vec{r}-\vec{r}^\alpha(t)]\delta[\vec{r}-\vec{r}^{\alpha'}(0)]\Big\rangle$$
$$=(\rho/m)^2\langle Q^\alpha_{ij}(t)Q^\alpha_{kl}(0)\rangle\ . \qquad (6.10)$$

When the centers of mass of the particles are allowed to move, relation (6.10) becomes more complicated. $\delta[\vec{r}-\vec{r}^\alpha(t)]\,\delta[\vec{r}'-\vec{r}^{\alpha'}(t')]$ would be proportional to $\delta^{\alpha\alpha'}$ if $\vec{r}-\vec{r}'$ were always equal to $\vec{r}^\alpha(t)-\vec{r}^{\alpha'}(t')$. If $t=t'$, this condition is satisfied if $\vec{r}=\vec{r}'$. If $t\neq t'$, it is not possible to choose $\vec{r}$ and $\vec{r}'$ so that $\vec{r}-\vec{r}'=\vec{r}^\alpha(t)-\vec{r}^\alpha(t')$ for all α and α'. Nevertheless, an approximate average statement can be made. If a particle is at position $\vec{r}$ at time t, the probability that it will be at position $\vec{r}'$ at time t' is given by the familiar diffusion function

$$P(\vec{r}\vec{r}'tt')=-(4\pi D|t-t'|)^{-3/2}e^{-(\vec{r}-\vec{r}')^2/4Dt}\ , \qquad (6.11)$$

where D is the diffusion constant. In a liquid crystal, D should be direction dependent. However, to prevent a proliferation of confusing algebra, we will assume for the moment that it is isotropic. In some average sense, $\delta[\vec{r}-\vec{r}^\alpha(t)]\,\delta[\vec{r}'-\vec{r}^\alpha(t')]$ multiplied by $P(\vec{r}\vec{r}'tt')$ and integrated over $\vec{r}'$ is proportional to $\delta^{\alpha\alpha'}$. Hence

$$\int d^3r'\, P(\vec{r}\vec{r}'tt')\langle R_{ij}(\vec{r}t)R_{kl}(\vec{r}'t')\rangle$$
$$=(\rho/m)^2\langle Q^\alpha_{ij}(t)Q^\alpha_{kl}(0)\rangle\ . \qquad (6.12)$$

Using Eq. (6.12), the fluctuation dissipation theorem, and $\chi''_{ijkl}(\vec{q}\omega)$ from Eq. (5.10), one obtains

$$J^{(1)}(\omega_0)=S^2\int\frac{d^3q}{(2\pi)^3}\,\frac{k_BT}{Kq^2}\,\frac{(K/\eta+D)q^2}{\omega_0^2+[(K/\eta+D)q^2]^2}\ . \qquad (6.13)$$

If we neglect $J^{(2)}(2\omega_0)$ and plug Eq. (6.13) into Eq. (6.7), we obtain the Pincus formula for $1/T_1$ with a factor of S^2 rather than S:

$$1/T_1\cong\omega_D^2 t_c\ , \qquad (6.14)$$

where ω_D is a dipolar frequency, and

$$t_c \sim \frac{k_B T}{K} S^2 \frac{1}{[\omega_0(D+K/\eta)]^{1/2}} . \tag{6.15}$$

A few words regarding the neglect of $J^{(2)}(2\omega_0)$ and the use of Eq. (6.13) for $J^{(1)}(\omega_0)$ are now in order. First, the hydrodynamic form for $\chi''_{xzxz}(\vec{q}\,\omega)$ is valid only for $q\lambda < 1$. Hence, from a rigorous point of view, one cannot use the hydrodynamic form for $(\beta\omega)^{-1}\chi''_{xzxz}(\vec{q}\omega)$ throughout the entire region of integration. However, if q_c defined by $(K/\eta + D)q_c^2 = \omega_0$ is such that $q_c\lambda \ll 1$, one can break up the integration in Eq. (6.13) into two parts. The first part would extend from $q = 0$ to $q = 1/\lambda$. This gives a contribution to $1/T_1$ of the same form as Eq. (6.14) with a t_c the same as that in Eq. (6.15), but multiplied by a slowly varying (logarithmic) function of ω_0 which can be set equal to 1. In addition, there will be a contribution to the integral of Eq. (6.13) for $q > 1/\lambda$. It is difficult to say exactly what form this term will have except that it will probably be a slowly varying function of ω_0 and, in particular, not have the $\omega_0^{-1/2}$ dependence of Eq. (6.15). An analysis of $J^{(2)}(2\omega_0)$ similar to that of $J^{(1)}(\omega_0)$ shows that $J^{(2)}(2\omega_0)$ is related to an integral over q of $(\beta\omega)^{-1}\chi''_{xxxx}(\vec{q}\omega)$ and $(\beta\omega)^{-1}\chi_{xyxy}(\vec{q}\omega)$. The first term contains fluctuations in the magnitude of the order parameter S, and the second vanishes in the hydrodynamic regime. In neither of these is there an important accumulation of low-frequency modes necessary to give the characteristic $\omega_0^{-1/2}$ dependence of Eq. (6.15). Hence, $1/T_1$, taking into account $J^{(2)}(\omega_0)$ and large q contributions to $J^{(1)}(\omega_0)$, can be written as

$$1/T_1 \sim \omega_D^2 t_c + 1/T_1' , \tag{6.16}$$

where $1/T_1'$ is relatively independent of ω_0 for small ω_0. $1/T_1'$ represents fluctuations in the magnitude of the order parameter S and large q (short distance) variations in the direction of preferred order. As such, it should become more and more important as the clarification temperature is approached. However, since the liquid-crystal transition is first order, it could be that throughout the liquid-crystal phase $\omega_D^2 t_c$ dominates at NMR frequencies.

It is worth noting that for frequencies accessible to NMR experiments (~0–50 MHz), q_c remains in the hydrodynamic regime. However, for higher frequencies (accessible to EPR say), q_c approaches molecular dimensions (cf. Table I). This suggests that it may be possible to estimate λ (wavelength determining the hydrodynamic regime) by performing measurements of $1/T_1$ by NMR and EPR over several decades of frequency. The frequency at which there is no longer an apparent $\omega_0^{-1/2}$ dependence of $1/T_1$ should give a measure of λ.

Recent experiments[38–40] show clearly that T_1 in the ordered phase is proportional to $\omega_0^{1/2}$ over at least two decades in frequency. However, the temperature dependence predicted by the Pincus theory is not at all in agreement with experiment. The factor of S^2 [41] introduced in this paper changes the theoretically predicted temperature dependence of $1/T_1$ in the direction of greater agreement with experiment. Given the lack of experimental data on the diffusion constant D and viscosity η, it is not possible to say at the moment whether theory and experiment agree quantitatively. We should stress that the viscosity that appears in the equation for $1/T_1$ is not the total viscosity but only that related to the liquid-crystal order. It is zero in the isotropic phase. Hence, its temperature dependence will be more pronounced than that of the total viscosity.

TABLE I. Wavelength of excitations produced by external magnetic fields of different frequencies. $\omega_0 = 2\pi n \times 10^6$ Hz, $\lambda_c = 2\pi/q_c$, and $(D+K/\eta)q_c^2 = \omega_0$.

n	0.1	1	10	50	100	10^3	10^4
λ_c(Å)	200	710	250	110	11	25	7.7

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APPENDIX A

In this appendix, we will derive the Leslie stress tensor in equilibrium. First, consider the free energy of a nematic at rest. It is a function of the temperature T, the volume of the system V, the order parameter S, the director $n_i(\vec{r})$, and its first spatial derivative $\nabla_j n_i(\vec{r})$. It must be invariant with respect to infinitesimal rigid rotations of the entire system. Under such rotations the scalars T, S, and V remain unchanged, whereas $n_i(\vec{r})$ and $n_{i,j}(\vec{r})$ are changed according to

$$\delta n_i(\vec{r}) = \delta\theta_{il} n_l(\vec{r}) , \tag{A1}$$

$$\delta n_{i,j}(\vec{r}) = \delta\theta_{il} n_{l,j}(\vec{r}) + \delta\theta_{jl} n_{i,l}(\vec{r}) , \tag{A2}$$

where $\delta\theta_{il}$ is the antisymmetric tensor characterizing the infinitesimal rotation. The change in the free-energy density is therefore

$$\begin{aligned}\delta\mathfrak{F} &= \frac{\partial\mathfrak{F}}{\partial n_i}\delta n_i + \frac{\partial\mathfrak{F}}{\partial n_{i,j}}\delta n_{i,j} \\ &= \left(\frac{\partial\mathfrak{F}}{\partial n_i} n_l + \frac{\partial\mathfrak{F}}{\partial n_{i,j}} n_{l,j} + \frac{\partial\mathfrak{F}}{\partial n_{j,i}} n_{j,l}\right)\delta\theta_{il} .\end{aligned} \tag{A3}$$

But this must be zero, hence

$$n_j \frac{\partial \mathcal{F}}{\partial n_i} + n_{j,l} \frac{\partial \mathcal{F}}{\partial n_{i,l}} + n_{l,j} \frac{\partial \mathcal{F}}{\partial n_{l,i}} = n_i \frac{\partial \mathcal{F}}{\partial n_j} + n_{i,l} \frac{\partial \mathcal{F}}{\partial n_{j,l}} + n_{l,i} \frac{\partial \mathcal{F}}{\partial n_{l,j}} . \tag{A4}$$

Now, consider a coordinate system moving with velocity $\vec{v}$ relative to that in which the nematic is at rest. By Galilean invariance, the energy density and energy current in the moving coordinate system are

$$\epsilon = \tfrac{1}{2}\rho v^2 + \vec{v}\cdot \vec{j}_0 + \epsilon_0 , \tag{A5}$$

$$j_i^{\epsilon} = (\tfrac{1}{2}\rho v^2 + \vec{v}\cdot \vec{j}_0 + \epsilon_0) v_i + \tfrac{1}{2} v^2 j_{0i} + \sigma^0_{ji} v_j + j^{\epsilon}_{0i} , \tag{A6}$$

where $\epsilon_0, j_0^{\epsilon}$, and σ^0_{ij} are, respectively, the energy density, momentum density, energy current, and stress tensor in the rest system. In addition, there is the thermodynamic relation for infinitesimal changes in the energy density ϵ_0:

$$d\epsilon_0 = d[(F + T\Sigma)/V] , \tag{A7}$$

where Σ is the entropy. Using the facts that the derivative of F with respect to the total momentum is $-\vec{v}$ and $dV/V = -d\rho/\rho$ if the number of particles is held constant, Eq. (A7) reads, for constant temperature and external fields,

$$d\epsilon_0 = \left(-\frac{\partial F}{\partial V} + \epsilon_0 - Ts\right)\frac{d\rho}{\rho} - \vec{v}\cdot d\vec{j}_0 + \frac{\partial \mathcal{F}}{\partial n_i} dn_i + \frac{\partial \mathcal{F}}{\partial n_{i,j}} dn_{i,j} + \frac{\partial \mathcal{F}}{\partial S} dS - T\,ds , \tag{A8}$$

where $s = \Sigma/V =$ entropy density. To find σ^0_{ij}, we require that Eqs. (A5) and (A6) satisfy the energy conservation equation in the moving coordinate system. For uniform translations,

$$\frac{dn_i}{\partial t} = -\nabla_j(n_i v_j) , \tag{A9}$$

$$\frac{\partial n_{i,j}}{\partial t} = -\nabla_l(n_{i,j} v_l) , \tag{A10}$$

$$\frac{\partial S}{\partial t} = -\nabla_i(v_i S) , \tag{A11}$$

$$\frac{\partial s}{\partial t} = -\nabla_i(v_i s) . \tag{A12}$$

Hence we have

$$\frac{\partial \epsilon_0}{\partial t} = -\left(-\frac{\partial F}{\partial V} + \epsilon_0 - Ts\right)\frac{1}{\rho}\nabla_i(\rho v_i) - \vec{v}\cdot\frac{\partial \vec{j}_0}{\partial t} - \frac{\partial \mathcal{F}}{\partial n_i}\nabla_j(n_i v_j) - \frac{\partial \mathcal{F}}{\partial n_{i,j}}\nabla_l(v_l n_{i,j}) - \frac{\partial \mathcal{F}}{\partial S}\,{}_i(v_i S) + T\nabla_i(v_i s) \tag{A13}$$

or

$$\frac{\partial \epsilon_0}{\partial t} = -\nabla_i\left(-\frac{\partial F}{\partial V} + \frac{\partial \mathcal{F}}{\partial S} S + \epsilon_0\right) - \vec{v}\cdot\frac{\partial \vec{j}_0}{\partial t} - \nabla_i\left(\frac{\partial \mathcal{F}}{\partial n_{k,i}} n_{k,j} v_j\right), \tag{A14}$$

where we have used the facts that in equilibrium, in the rest frame,

$$\vec{j}_0 = 0 , \tag{A15}$$

$$\frac{\partial \mathcal{F}}{\partial S} = 0 , \tag{A16}$$

$$\frac{\partial \mathcal{F}}{\partial n_i} - \nabla_j \frac{\partial \mathcal{F}}{\partial n_{i,j}} = 0 , \tag{A17}$$

$$\nabla_i\left[\frac{1}{\rho}\left(-\frac{\partial F}{\partial V} + \epsilon_0 - Ts\right)\right] = 0 . \tag{A18}$$

Equating $\partial\epsilon/\partial t$ to $-\vec{\nabla}\cdot\vec{j}^{\,\epsilon}$, we obtain for the stress tensor in the rest frame

$$\sigma^0_{ij} = p\delta_{ij} + \frac{\partial \mathcal{F}}{\partial n_{k,j}} n_{k,i} , \tag{A19}$$

where

$$P = -\frac{\partial F_0}{\partial V} + \frac{\partial \mathcal{F}}{\partial S} S = -\frac{\partial F_0}{\partial V} .$$

This is the stress tensor found by Ericksen and Leslie for a nematic in equilibrium and the one used in the text.

APPENDIX B

The purpose of this appendix is to present a review of response-function theory in a classical context. More complete discussions can be found in Refs. 25 and 26.

A classical system is completely described in terms of a distribution function $f(q^{\alpha}(t), p^{\alpha}(t), t)$. q^{α} and p^{α} are the generalized coordinates and momenta for the particle α. In equilibrium, f reduces to the familiar cannonical distribution function

$$f_0 = Z^{-1} e^{-\beta \mathcal{H}_0(\vec{q}^{\alpha}, \vec{p}^{\alpha})} , \tag{B1}$$

where

$$Z = \operatorname{Tr} e^{-\beta \mathcal{H}_0(\vec{q}^{\alpha}, \vec{p}^{\alpha})} .$$

$\mathcal{H}^0$ is the unperturbed Hamiltonian, and $\beta = 1/kT$. (Tr again means to integrate over all variables $\vec{q}^{\alpha}$ and $\vec{p}^{\alpha}$.) Linear deviations in f can be expressed as

$$f = f_0 + \delta f = f_0 + \sum_{\alpha}\left(\delta\vec{q}^{\alpha}(t)\frac{\partial}{\partial \vec{q}^{\alpha}(t)} + \delta\vec{p}^{\alpha}(t)\frac{\partial}{\partial \vec{p}^{\alpha}(t)}\right) f_0 \cdot , \tag{B2}$$

and δf can be rewritten in the following form:

$$\delta f = \sum_{\alpha}\int_{t_0}^{t} dt'\left(\delta\dot{\vec{q}}(t')\frac{\partial}{\partial \vec{q}^{\alpha}(t)} + \delta\dot{\vec{p}}^{\alpha}(t')\frac{\partial}{\partial \vec{p}^{\alpha}(t)}\right) f_0 , \tag{B3}$$

where

$$\delta\dot{\vec{q}}^{\alpha} = \frac{\partial\,\delta\vec{q}^{\alpha}(t)}{\partial t} \quad .$$

We now assume that the changes in f from f_0 are produced by an external disturbance which can be expressed in terms of an external Hamiltonian $\mathcal{H}^{\mathrm{ext}}$ added to $\mathcal{H}_0$. Then, by Hamilton's equations,

$$\delta\dot{\vec{q}}^{\alpha}(t) = \frac{\partial\mathcal{H}^{\mathrm{ext}}}{\partial\vec{p}^{\alpha}(t)} , \quad \delta\dot{\vec{p}}^{\alpha}(t) = -\frac{\partial\mathcal{H}^{\mathrm{ext}}}{\partial\vec{q}^{\alpha}(t)} \quad . \tag{B4}$$

This equation is valid even if $\mathcal{H}^{\mathrm{ext}}$ includes velocity-dependent forces. Equations (B3) and (B4) combine to give

$$\delta f = \int_{t_0}^{t} [f_0(t),\ \mathcal{H}^{\mathrm{ext}}(t')]\, dt' \quad , \tag{B5}$$

where $[f_0(t),\ \mathcal{H}^{\mathrm{ext}}(t')]$ is the Poisson bracket defined by

$$[f_0(t),\ \mathcal{H}^{\mathrm{ext}}(t')] = \sum_{\alpha}\left(\frac{\partial f_0(t)}{\partial\vec{q}^{\alpha}(t)}\cdot\frac{\partial\mathcal{H}^{\mathrm{ext}}(t')}{\partial\vec{p}^{\alpha}(t')} - \frac{\partial f_0(t)}{\partial\vec{p}^{\alpha}(t)}\cdot\frac{\partial\mathcal{H}^{\mathrm{ext}}(t')}{\partial\vec{q}^{\alpha}(t')}\right). \tag{B6}$$

Now, let

$$\mathcal{H}^{\mathrm{ext}}(t') = -\int d^3r'\, B(\vec{r}\,'t')\, h(\vec{r}\,'t').$$

The change in the average value of an operator $A(\vec{r}\,t)$ due to the presence of $\mathcal{H}^{\mathrm{ext}}$ is

$$\begin{aligned}\delta\langle A(\vec{r}\,t)\rangle &= -\int d^3r' \int_{t_0}^{t} dt'\, \mathrm{Tr}\{A(\vec{r}\,t)[f_0, B(\vec{r}\,'t')]\, h(\vec{r}\,'t')\} \\ &= +\int d^3r' \int_{t_0}^{t} dt' \langle [A(\vec{r}\,t), B(\vec{r}\,'t')]\rangle\, h(\vec{r}\,'t') \quad .\end{aligned} \tag{B7}$$

Letting $t_0 \to -\infty$, we can write

$$\delta\langle A(\vec{r}\,t)\rangle = \int d^3r' \int_{-\infty}^{\infty} dt'\, \tilde{\chi}_{AB}(\vec{r}\vec{r}\,'tt')\, h(\vec{r}\,'t') \quad . \tag{B8}$$

Here

$$\tilde{\chi}_{AB}(\vec{r}\,\vec{r}\,'t-t') = 2i\eta(t-t')\,\tilde{\chi}''_{AB}(\vec{r}\,\vec{r}\,'t-t') \quad , \tag{B9}$$

$$\chi''_{AB}(\vec{r}\,\vec{r}\,'t-t') = (2i)^{-1}\langle[A(\vec{r}\,t), B(\vec{r}\,'t')]\rangle \quad , \tag{B10}$$

where $\eta(t-t')$ is the Heaviside unit step function. $\chi''_{AB}(\vec{r}\,\vec{r}\,'t-t')$ has a real Fourier transform

$$\chi''_{AB}(rr'\omega) = \int d(t-t')\, e^{i\omega(t-t')}\tilde{\chi}''_{AB}(\vec{r}\,\vec{r}\,'t-t') \quad . \tag{B11}$$

From Eq. (B9), one can see that $\tilde{\chi}_{AB}(\vec{r}\,\vec{r}\,'t-t')$ has a Fourier transform in terms of a complex frequency ζ in the upper half-plane:

$$\begin{aligned}\chi_{AB}(\vec{r}\,\vec{r}\,'\zeta) &= \int_{-\infty}^{\infty} e^{i\zeta(t-t')}\tilde{\chi}_{AB}(\vec{r}\,\vec{r}\,'\,t-t')\, d(t-t') \\ &= \int_{-\infty}^{\infty} \frac{d\omega}{\pi}\, \frac{\chi''_{AB}(\vec{r}\,\vec{r}\,'\omega)}{\omega-\zeta} \quad .\end{aligned} \tag{B12}$$

As ζ approaches the real axis (i.e., $\zeta = \omega + i\epsilon$), $\chi_{AB}(\vec{r}\,\vec{r}\,'\zeta)$ obtains the form

$$\chi_{AB}(\vec{r}\,\vec{r}\,'\omega) = \chi'_{AB}(\vec{r}\,\vec{r}\,'\omega) + i\chi''_{AB}(\vec{r}\,\vec{r}\,'\omega) \quad . \tag{B13}$$

$\chi'_{AB}(\vec{r}\,\vec{r}\,'\omega)$ and $\chi''_{AB}(\vec{r}\,\vec{r}\,'\omega)$ satisfy the Kramers-Kronig relations

$$\begin{aligned}\chi'_{AB}(\vec{r}\,\vec{r}\,'\omega) &= P\int \frac{d\omega'}{\pi}\, \frac{\chi''_{AB}(\vec{r}\,\vec{r}\,'\omega')}{\omega'-\omega} \quad , \\ \chi''_{AB}(\vec{r}\,\vec{r}\,'\omega) &= -P\int \frac{d\omega'}{\pi}\, \frac{\chi'_{AB}(\vec{r}\,\vec{r}\,'\omega)}{\omega'-\omega} \quad .\end{aligned} \tag{B14}$$

For translationally invariant systems $\chi_{AB}(\vec{r}\,\vec{r}\,'\zeta)$ can be expressed in terms of a single spatial Fourier transform

$$\chi_{AB}(\vec{r}\,\vec{r}\,'\zeta) = \int d^3(r-r')\, e^{-i\vec{q}\cdot(\vec{r}-\vec{r}\,')}\chi_{AB}(\vec{q}\zeta) \quad . \tag{B15}$$

Using the preceding definitions and properties of response functions, one can determine the change in $\langle A(\vec{r}\,t)\rangle$ due to an adiabatically applied external field such as discussed in Sec. IV of the text:

$$h(\vec{r}\,t) = \begin{cases} h(\vec{r})e^{\epsilon t} , & t<0 \\ 0 , & t>0 \end{cases} \tag{B16}$$

$$\delta\langle A(\vec{r}\,t)\rangle = \begin{cases} 2i\int_{-\infty}^{t} dt'\, e^{\epsilon t'} \int d^3r'\, \chi''_{AB}(\vec{r}\,\vec{r}\,'t-t')\, h(\vec{r}\,') , & t<0 \\ 2i\int_{-\infty}^{0} dt'\, e^{\epsilon t'} \int d^3r'\, \chi''_{AB}(\vec{r}\,\vec{r}\,'t-t')\, h(\vec{r}\,') , & t>0 \end{cases} \quad . \tag{B17}$$

Hence we have

$$\delta\langle A(\vec{r}t)\rangle = \begin{cases} \displaystyle\int \frac{d^3k}{(2\pi)^3}\, h(\vec{k})\, e^{i\vec{k}\cdot\vec{r}} \int \frac{d\omega}{\pi}\, \frac{\chi''_{AB}(\vec{k}\omega)}{\omega} , & t\leqslant 0 \\ \displaystyle\int \frac{d^3k}{(2\pi)^3}\, h(\vec{k})\, e^{i\vec{k}\cdot\vec{r}} \int \frac{d\omega}{\pi}\, \frac{\chi''_{AB}(\omega)}{\omega}\, e^{-iwt} , & t>0 . \end{cases} \tag{B18}$$

Taking the Laplace Fourier transform of this we obtain the formula quoted in the text [Eq. (5.3)]:

$$\delta\langle B(\vec{k}\zeta)\rangle = \int \frac{d\omega}{\pi i}\, \frac{\chi''_{BA}(\vec{k}\omega)}{\omega(\omega-\zeta)}\, h(\vec{k}) \tag{B19}$$

Fluctuation Dissipation Theorem

Consider any operator A such that $\langle \partial A/\partial t\rangle = 0$ in the equilibrium ensemble. Let

$$S_{AA}(\vec{r}\,\vec{r}\,'tt') = \langle [A(\vec{r}\,t) - \langle A(\vec{r}\,'t')\rangle][A(\vec{r}\,'t') - \langle A(\vec{r}\,'t')\rangle]\rangle. \tag{B20}$$

In equilibrium,

$$\begin{aligned}\frac{\partial S_{AA}}{\partial t} &= \langle [A(\vec{r}\,t), \mathcal{H}]A(\vec{r}\,'t')\rangle \\ &= \mathrm{Tr}\left(\frac{\partial A(\vec{r}t)}{\partial\vec{q}^{\alpha}}\cdot\frac{\partial\mathcal{H}}{\partial\vec{p}^{\alpha}} - \frac{\partial A(\vec{r}t)}{\partial\vec{p}^{\alpha}}\cdot\frac{\partial\mathcal{H}}{\partial\vec{q}^{\alpha}}\right)A(\vec{r}\,'t')f_0 \quad ,\end{aligned} \tag{B21}$$

but

$$\frac{\partial\mathcal{H}}{\partial\vec{q}^{\alpha}}f_0 = -\frac{1}{\beta}\frac{\partial f_0}{\partial\vec{q}^{\alpha}} , \quad \frac{\partial\mathcal{H}}{\partial\vec{p}^{\alpha}}f_0 = -\frac{1}{\beta}\frac{\partial f_0}{\partial\vec{p}^{\alpha}} \quad . \tag{B22}$$

Hence

$$\frac{\partial S_{AA}}{\partial t}=-\frac{1}{\beta}\operatorname{Tr}\left(\frac{\partial A(\vec{r}t)}{\partial\vec{q}^{\alpha}}\cdot\frac{\partial f_0}{\partial\vec{p}^{\alpha}}-\frac{\partial A(\vec{r}t)}{\partial\vec{p}^{\alpha}}\cdot\frac{\partial f_0}{\partial\vec{q}^{\alpha}}\right)A(\vec{r}'\,t')\quad . \tag{B23}$$

Integrate by parts

$$\frac{\partial S_{AA}}{\partial t}=\frac{1}{\beta}\operatorname{Tr}f_0[A(\vec{r}t),A(\vec{r}'t')]=\frac{2i}{\beta}\,\tilde{\chi}''_{AA}(\vec{r}\,\vec{r}'tt')\quad . \tag{B24}$$

After Fourier transformation, this reads

$$\chi''_{AA}(\vec{r}\,\vec{r}'\omega)=\tfrac{1}{2}\beta\omega\,S_{AA}(\vec{r}\,\vec{r}'\omega)\quad . \tag{B25}$$

This is the classical fluctuation dissipation theorem.

The thermodynamic derivative of $\langle A\rangle$ with respect to the external field that couples to A can be calculated as follows. The distribution function f in the presence of an infinitesimal external field h is

$$f=f_0+f_0\beta h\int d^3r\,[A(\vec{r})-\langle A(\vec{r})\rangle_0]\ , \tag{B26}$$

where f_0 is the distribution function when $h=0$ and $\langle A(\vec{r})\rangle_0=\operatorname{Tr}f_0A(\vec{r})$. Hence

$$\begin{aligned}\frac{\partial\langle A(\vec{r})\rangle}{\partial h}&=\frac{\partial\operatorname{Tr}fA(\vec{r})}{\partial h}\\&=\beta\int d^3r'\,[\langle A(\vec{r})A(\vec{r}')\rangle_0-\langle A(\vec{r})\rangle_0\langle A(\vec{r}')\rangle_0]\\&=\beta\int d^3r'\int\frac{d\omega}{2\pi}\,S_{AA}(\vec{r}\,\vec{r}'\omega)\quad .\end{aligned} \tag{B27}$$

Using Eq. (B25), we can now identify the thermodynamic derivative (B27) with the zero k limit of the static response function

$$\lim_{\vec{k}\to 0}\chi_{AA}(\vec{k})=\lim_{\vec{k}\to 0}\int\frac{d\omega}{\pi}\,\frac{\chi''_{AA}(\vec{k}\omega)}{\omega}=\frac{\partial\langle A(\vec{r})\rangle}{\partial h}\quad . \tag{B28}$$

Symmetry properties

The correlation function of interest in liquid crystals is $\chi_{R_{ij}R_{kl}}\equiv\chi_{ijkl}$. We now list the important symmetry properties of $\tilde{\chi}''_{ijkl}(\vec{r}\,\vec{r}'tt')$ and $\chi''_{ijkl}(\vec{q}\omega)$.

(i) $R_{ij}(\vec{r}\,t)$ is symmetric and traceless:

$$\chi''_{ijkl}=\chi''_{jikl}=\chi''_{ijlk}=\chi''_{jilk}\ , \tag{B29a}$$

$$\chi''_{iikl}=\chi''_{ijkk}=\chi''_{iijj}=0\quad . \tag{B29b}$$

(ii) $\tilde{\chi}''_{ijkl}(\vec{r}\,\vec{r}'tt')$ is a Poisson bracket:

$$\tilde{\chi}''_{ijkl}(\vec{r}\,\vec{r}'tt')=-\tilde{\chi}''_{klij}(\vec{r}'\vec{r}t't)\ , \tag{B30a}$$

$$\chi''_{ijkl}(\vec{q}\omega)=-\chi''_{klij}(-\vec{q}-\omega)\quad . \tag{B30b}$$

(iii) $R_{ij}(\vec{r}\,t)$ is real:

$$[\tilde{\chi}''_{ijkl}(\vec{r}\,\vec{r}'tt')]^*=\tilde{\chi}''_{klij}(\vec{r}'\vec{r}t't)=-\tilde{\chi}_{ijkl}(\vec{r}\,\vec{r}'tt')\ , \tag{B31a}$$

$$[\chi''_{ijkl}(\vec{q}\omega)]^*=\chi''_{ijkl}(\vec{q}\omega)\quad . \tag{B31b}$$

(iv) $R_{ij}(\vec{r}t)$ is time-reversal invariant [i.e., $R_{ij}(\vec{r}t)=R_{ij}(\vec{r}-t)$]:

$$\tilde{\chi}''_{ijkl}(\vec{r}\,\vec{r}'tt')=\tilde{\chi}''_{klij}(\vec{r}'\vec{r}tt')=-\chi''_{ijkl}(\vec{r}\,\vec{r}'t't)\ , \tag{B32a}$$

$$\chi''_{ijkl}(\vec{q}\omega)=\chi''_{klij}(-\vec{q}\omega)=-\chi''_{ijkl}(\vec{q}-\omega)\quad . \tag{B32b}$$

Hence $\chi''_{ijkl}(q\omega)$ is real and odd in ω.

Sum rules

For $|\zeta|$ much greater than any characteristic frequency in the system, one can obtain an asymtotic expansion for $\chi_{ijkl}(\vec{q}\zeta)$ from Eq. (B12):

$$\begin{aligned}\chi_{ijkl}(\vec{q}\zeta)=&-\frac{1}{\zeta^2}\int\frac{d\omega}{\pi}\,\omega\chi''_{ijkl}(\vec{q}\omega)\\&-\frac{1}{\zeta^4}\int\frac{d\omega}{\pi}\,\omega^3\chi''_{ijkl}(\vec{q}\omega)+\cdots\ ,\end{aligned} \tag{B33}$$

where we used the fact that $\chi''_{ijkl}(\vec{q}\omega)$ is odd in ω. But

$$\begin{aligned}&\left\langle\left(\frac{\partial^nR_{ij}(\vec{r}t)}{\partial t^n},\ R_{kl}(\vec{r}'t')\right)\right\rangle\Bigg|_{t=t'}\\&\qquad=i\int\frac{d\omega}{\pi}\,(-i\omega)^n\,\chi''_{ijkl}(\vec{r}\,\vec{r}'\omega)\quad .\end{aligned} \tag{B34}$$

Hence we have

$$\int\frac{d\omega}{\pi}\,\omega\chi''_{ijkl}(\vec{r}\,\vec{r}'\omega)=\left\langle\left(\frac{\partial R_{ij}(\vec{r}\,t)}{\partial t},\ R_{kl}(\vec{r}'t')\right)\right\rangle\Bigg|_{t=t'}\ , \tag{B35a}$$

$$\int\frac{d\omega}{\pi}\,\omega^3\chi''_{ijkl}(\vec{r}\,\vec{r}'\omega)=-\left\langle\left(\frac{\partial^3R_{ij}(\vec{r}\,t)}{\partial t^3},\ R_{kl}(\vec{r}'t')\right)\right\rangle\Bigg|_{t=t'}\ . \tag{B35b}$$

Formula (B35a) was used to derive the sum rule Eq. (5.15) in the text.

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Computer "Experiments" on Classical Fluids. III. Time-Dependent Self-Correlation Functions

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Molecular dynamics experiments made on a system of 864 particles interacting through a Lennard-Jones potential for various high-density states are used to study the self-correlation in classical fluids. The self-diffusion constant is computed and interpreted in terms of a hard-sphere model. The memory-function formalism is used to give a simple phenomenological fit for the computed velocity autocorrelation function and for the self-intermediate-scattering function. A detailed comparison is made with the various existing theories for the latter quantity.

I. INTRODUCTION

This paper is devoted to the phenomenological description of the self-motion of atoms in liquids. We would like to interpret for instance the self-diffusion coefficient and the incoherent scattering of neutrons in simple liquids. In order to establish