

## Hydrodynamics of Liquid Crystals\*

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The linearized hydrodynamic behavior of liquid crystals is systematically deduced and earlier theories reconciled and simplified. Predictions for ordinary and depolarized light scattering are obtained and the latter compared with experiment.

Some months ago three of us<sup>1</sup> proposed an alternative description of liquid-crystal hydrodynamics. We were dissatisfied with the Leslie-Ericksen<sup>2,3</sup> picture because of these features: (1) The long-wavelength modes of the liquid crystal should follow from rigorous thermodynamic and hydrodynamic arguments and the proposed equation for the director was not rigorous. It was a Bloch- or Langevin-like equation, second order in the time, purporting to describe processes decaying in microscopic times, as well as the hydrodynamic relaxation processes whose rates were proportional to the square of the wave number. (2) Their theory insisted on an asymmetrical stress tensor although it can be proven that whenever angular momentum is locally conserved there must be an equivalent symmetric stress tensor. Independently we know that the averaged microscopic theory will give the macroscopic theory and the microscopic stress tensor can be taken to be symmetric. Failure to use this symmetry leads to cumbersome arguments about angular momentum. (3) The theory did not introduce fluxes and forces in the fashion appropriate to the underlying microscopic theory and thereby introduced parameters with inappropriate time-reversal properties. (4) Their parametrization of physical processes obscured simple symmetries and the positivity of the natural decay constants.

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Unfortunately, the proposed alternative was more seriously deficient. It failed to include, for certain geometries and polarizations, the dominant relaxation mechanism for depolarized light scattering. The purpose of this Letter (which attempts to codify similar conclusions reached by the many authors) is to eliminate all of these difficulties, to give a complete, straightforward derivation of liquid-crystal hydrodynamics, to compare its consequences with existing experiments,<sup>4,5</sup> and to summarize its predictions for Rayleigh- and Brillouin-scattering experiments not yet performed.

The fundamental problem in *deriving* hydrodynamic equations is to *deduce* what independent dynamic variations persist for arbitrarily long times when they vary arbitrarily slowly in space. Not all fluctuations of the order parameter have this character. Thus, in an Ising antiferromagnetic or in a superfluid, fluctuations in the *magnitude* of the order parameter are not hydrodynamic. The order parameter in a liquid crystal is proportional to the quadrupolar term in the mass density,<sup>6</sup>

$$Q_{ij}(\vec{r}) = \sum_{\alpha k} m^{\alpha k} [(r^{\alpha k} - r^{\alpha})_i (r^{\alpha k} - r^{\alpha})_j - \frac{1}{3} \delta_{ij} (\vec{r}^{\alpha k} - \vec{r}^{\alpha})^2] \delta(\vec{r} - \vec{r}^{\alpha}),$$

where  $\vec{r}^{\alpha k}$  and  $m^{\alpha k}$  are the coordinate and mass of the  $k$ th particle in the  $\alpha$ th molecule and  $\vec{r}^{\alpha}$  is the molecular center of mass. Assuming axial symmetry we may write

$$\langle Q_{ij}(\vec{r}) \rangle = CS(\vec{r}) [n_i(\vec{r}) n_j(\vec{r}) - \frac{1}{3} \delta_{ij}],$$

where  $n_i(\vec{r})$  is the  $i$ th component of the unit vector defining the local symmetry axis,  $S(\vec{r})$  is the conventional dimensionless order parameter normalized to unity at zero temperature, and  $C$  is a multiplicative constant. In a homogeneous nematic  $\vec{n}(\vec{r}) = \vec{n}^0$  is independent of  $\vec{r}$ . We shall take our 3 axis in the direction of  $\vec{n}^0$ .

Although there is no microscopic conservation law for  $Q_{ij}$ , two of its components, those with  $(i, j) = (1, 3)$  or  $(2, 3)$  must have low-frequency (hydrodynamic) fluctuations. These are the fluctuations that we may identify in a rigorous fashion with the two components  $\delta n_1(\vec{r}, t)$  and  $\delta n_2(\vec{r}, t)$  of the director in an unstressed nematic liquid crystal. They are defined by

$$\delta\langle Q_{ij}(\vec{r}, t) \rangle \cong CS(\vec{r})[\delta n_i(\vec{r}, t)n_j^0 + n_i^0\delta n_j(\vec{r}, t)];$$

they play a role similar to the phase or superfluid velocity in a superfluid; and they must be included, along with fluctuations of the conserved densities of mass  $\rho$ , energy  $\epsilon$ , and total momentum  $\vec{g}$ , in the linearized liquid-crystal hydrodynamic equations.

The proof that  $\delta n_i$  has hydrodynamic character (i.e., that it is a low-frequency Goldstone mode) follows orthodox lines.<sup>7</sup> We observe that in the ordered state an infinitesimal rotation of  $Q_{31}$  about the 2 axis is generated by the 2 component  $L_2$  of the angular momentum, i.e., that

$$\delta\langle Q_{31}(\vec{r}, t) \rangle = (i/\hbar)\langle [Q_{31}(\vec{r}, t), L_2(t)] \rangle \delta\theta = [\langle Q_{33}(\vec{r}, t) \rangle - \langle Q_{11}(\vec{r}, t) \rangle] \delta\theta \neq 0,$$

and that since angular momentum is conserved,

$$\delta\langle \dot{Q}_{31}(\vec{r}, t) \rangle = (i/\hbar)\langle [Q_{31}(\vec{r}, t), \dot{L}_2(t)] \rangle \delta\theta = 0.$$

(As usual the square brackets indicate a commutator or  $\hbar/i$  times a Poisson bracket.) From these two equations and their restatement in terms of Fourier components  $l_2(\vec{q})$  of the angular momentum density  $L_2(\vec{r})$ , it follows that the long-wavelength fluctuations of  $Q_{31}$  are nonvanishing when  $\langle Q_{33} \rangle - \langle Q_{11} \rangle \neq 0$ , and that these long-wavelength fluctuations must have vanishing frequency.<sup>8</sup> If a finite field were applied along the director to stabilize it, the fluctuations in  $\delta n$  would cease to be hydrodynamic, acquiring a finite frequency, and more phenomenological arguments would have to be used. This would be reflected in the above argument by the nonvanishing of  $\dot{L}_2$ .

We may summarize the "conservation laws" of the resulting hydrodynamics<sup>9</sup> by an entropy differential  $ds$  with

$$Tds = de - \vec{v} \cdot d\vec{g} - \mu d\rho - \psi_{ij} \nabla_j dn_i. \quad (1)$$

This equation applies to the temporally slow (lossless) changes in the state of the system that can be described in a purely thermodynamic fashion. The necessity for the last term is a consequence of the argument that the relaxation frequency of a spatially varying deviation in  $n_i$  vanishes with vanishing wave number. The variable conjugate to  $\nabla_j n_i$ ,  $\psi_{ij}$ , must be proportional to the wave vector  $q$  of the disturbance, that is,  $\psi_{ij} = K_{ijkl} \nabla_l dn_k$ , and thus the  $K$  are the Frank elastic constants;  $v = \rho^{-1} dg$ ;  $T$  is the temperature; and  $\mu$  is the chemical potential. Associated with each of the "conserved" dynamical variables is a current

$$\dot{\rho} + \nabla \cdot \vec{g} = 0, \quad \dot{\epsilon} + \nabla \cdot \vec{j}^\epsilon = 0, \quad \dot{\vec{g}}_i + \nabla_j \sigma_{ij} = 0, \quad \dot{n}_i + \nabla_k X_{ik} = 0. \quad (2)$$

To complete the hydrodynamic description we need expressions for the currents in terms of the variables conjugate to the conserved densities. Using Galilean invariance, the isotropy of the liquid pressure, and the uniaxial symmetry of the nematic, we have for the reactive terms (terms relating currents to densities with the same time-reversal properties are reactive)

$$\vec{g}^R = \rho \vec{v}, \quad \vec{j}^{\epsilon R} = (\epsilon + p) \vec{v}, \quad X_{ij}^R = \frac{1}{2}(-\lambda + \varphi + 1)(\delta_{ij} - n_i^0 n_j^0) n_k^0 v_k - \frac{1}{2}(\lambda + \varphi + 1)(\delta_{ik} - n_i^0 n_k^0) n_j^0 v_k. \quad (3)$$

The dissipative terms in the currents are given by

$$\vec{g}^D = 0, \quad j_i^{\epsilon D} = \kappa_\perp \nabla_i \delta T - (\kappa_\parallel - \kappa_\perp) n_i^0 (\vec{n}^0 \cdot \nabla) \delta T, \quad X_{ij}^D = -\xi_{ijkl} \psi_{kl}. \quad (4)$$

$K_{ijkl}$  and  $\xi_{ijkl}$  are each described by three invariants. The three contained in  $K_{ijkl}$  are the usual Frank constants,<sup>10</sup>

$$K_{ijkl} = K_3(\delta_{ik} - n_i^0 n_k^0) n_j^0 n_l^0 + (K_2 - K_1) \epsilon_{ijp} n_p^0 \epsilon_{klq} n_q^0 + K_1(\delta_{ik} - n_i^0 n_k^0)(\delta_{jl} - n_j^0 n_l^0). \quad (5)$$

Stability requires that they be positive.

Two further conditions may be imposed on these equations. The first,  $\varphi = 0$ , follows from the condition that in the equilibrium rotating state  $\dot{n}_i = (\vec{\omega} \times \vec{n}^0)_i$  where  $\vec{\omega} = \frac{1}{2}(\nabla \times \vec{v})$ . This condition may be demonstrated microscopically.<sup>11</sup> The second very probable, but not compelling, condition is that despite the long-range fluctuations of the director, the fluctuations in  $\dot{n}_i = -\nabla_j X_{ij}$  have finite range. This condition [which prohibits invariants like  $(\hat{q} \cdot \vec{n}^0)^2$  in the  $\vec{n}$  fluctuation spectrum] implies that  $\xi_{ijkl} = \gamma_1^{-1} \delta_{ji} (\delta_{ik} - n_i^0 n_k^0)$ .

With both restrictions, and with  $A_{ij} \equiv \frac{1}{2}(\nabla_i v_j + \nabla_j v_i)$ , the director equation reduces to the one previously employed,<sup>12</sup>

$$\delta \dot{n}_i = \lambda A_{ij} n_j^0 + (\vec{\omega} \times \vec{n}^0)_i + \gamma_1^{-1} K_{ijkl} \nabla_j \nabla_l \delta n_k. \quad (6)$$

We next consider the stress tensor. Although it is not unique, a perfectly acceptable symmetric reactive stress tensor may be deduced by using the identity  $\nabla_i \epsilon_{jkl} \omega_l = \nabla_j A_{ik} - \nabla_k A_{ij}$ , and the identity between the reactive coefficients,  $\partial \hat{g}_k / \partial (\nabla_j \psi_{ij}) = -\partial \dot{n}_i / \partial v_k$ . The latter follows from the energy conservation law implied by Eq. (1) in the absence of dissipation (i.e., with  $Tds/dt = 0$ ). We have

$$\delta \sigma_{jk}^R = (\delta p) \delta_{jk} + \left\{ \frac{1}{2} \lambda [K_{kpqr} (\nabla_p \nabla_r \delta n_q) n_j^0] + \frac{1}{2} [K_{jkqr} n_p^0 \nabla_p \nabla_r \delta n_q - K_{pkqr} n_j^0 \nabla_p \nabla_r \delta n_q] + (jk - kj) \right\}. \quad (7)$$

The dissipative invariants in the stress tensor are identical with the viscosities of a uniaxial single crystal or a gas in a magnetic field. They are conveniently represented by

$$\delta \sigma_{ij}^D = -2\nu_2 A_{ij} - 2(\nu_3 - \nu_2) [A_{ik} n_k^0 n_j^0 + A_{jk} n_i^0 n_k^0] - (\nu_4 - \nu_2) \delta_{ij} A_{kk} - 2(\nu_1 + \nu_2 - 2\nu_3) n_i^0 n_j^0 n_k^0 n_l^0 A_{kl} - (\nu_5 - \nu_4 + \nu_2) [\delta_{ij} n_k^0 n_l^0 A_{kl} + n_i^0 n_j^0 A_{kk}]. \quad (8)$$

The positivity of the entropy production then implies that

$$\nu_4(2\nu_1 + \nu_2) \geq (\nu_5 - \nu_4)^2, \quad \nu_2 \geq 0, \quad \nu_3 \geq 0, \quad \nu_4 \geq 0, \quad 2(\nu_1 + \nu_5) - \nu_4 + \nu_2 \geq 0, \quad \kappa_{\parallel} > 0, \quad \kappa_{\perp} > 0, \quad \gamma_1 > 0.$$

An incompressibility condition eliminates two parameters, i.e.,  $\nu_4 = \nu_2$  and  $\nu_5 = 0$ . Note that  $\lambda$  does not appear in any differential stability condition. Moreover, while  $\lambda$  is usually larger than unity there is no physical requirement to this effect.

Leslie's parameters for an incompressible fluid are given by

$$2\nu_2 = \alpha_4, \quad 2\nu_3 = \alpha_4 + \alpha_5 - (\gamma_2 \alpha_2 / \gamma_1), \quad \gamma_1 = \alpha_3 - \alpha_2, \quad \lambda = -\gamma_2 / \gamma_1, \quad 2\nu_1 = \alpha_1 + \alpha_4 + \alpha_5 + \alpha_6, \quad \alpha_6 - \alpha_5 = \gamma_2 = \alpha_3 + \alpha_2;$$

Miesowicz's<sup>5</sup> are given by

$$\eta_3^M = \nu_2, \quad \eta_1^M = \nu_3 + (1 - \lambda)^2 \gamma_1 / 4, \quad \eta_2^M = \eta_1^M + \lambda \gamma_1;$$

and the parameters of MPS are given by

$$L_4 = 0, \quad 4L_5 = (1 - \lambda)^2 K_1, \quad L_6 + K_1 - \lambda(K_1 + K_3), \quad 4M_5 = (1 + \lambda)^2 K_3, \quad M_4 + M_6 + L_6 = K_1 + K_3,$$

$$K_2 M_5 = K_3 (M_4 + L_5), \quad \eta_4^{\text{MPS}} = \nu_2, \quad \eta_5^{\text{MPS}} = \nu_3, \quad \eta_4^{\text{MPS}} + \eta_6^{\text{MPS}} = 2(\nu_1 + \nu_2).$$

Even in the compressible fluid the frequency  $\omega_{s2}$  of the slow mode polarized perpendicular to its propagation direction is obtained from the equations

$$\begin{aligned} i\omega \rho \delta v_2 + \frac{1}{2} i(1 + \lambda)(K_2 q_1^2 + K_3 q_3^2) q_3 \delta n_2 - (\nu_3 q_3^2 + \nu_2 q_1^2) \delta v_2 &= 0, \\ i\omega \delta n_2 - \frac{1}{2} i(1 + \lambda) q_3 \delta v_2 + \gamma_1^{-1} (K_2 q_1^2 + K_3 q_3^2) \delta n_2 &= 0, \\ i\omega_{s2} (K_2 q_1^2 + K_3 q_3^2)^{-1} \cong \gamma_1^{-1} + \frac{1}{4} (1 + \lambda)^2 q_3^2 (\nu_3 q_3^2 + \nu_2 q_1^2)^{-1}. \end{aligned} \quad (10)$$

The frequency of the other slow mode,  $\omega_{s1}$ , is approximately given by

$$i\omega_{s1} (K_3 q_3^2 + K_1 q_1^2)^{-1} \cong \gamma_1^{-1} + \frac{1}{4} [q_3^2 + q_1^2 + \lambda(q_3^2 - q_1^2)]^2 [\nu_3(q_1^2 - q_3^2)^2 + 2(\nu_1 + \nu_2) q_1^2 q_3^2]^{-1}; \quad (11)$$

fast modes have frequencies

$$i\omega_{f2} = [\nu_3 q_3^2 + \nu_2 q_1^2] / \rho, \quad i\omega_{f1} = [\nu_3(q_1^2 - q_3^2)^2 + 2(\nu_1 + \nu_2) q_1^2 q_3^2] / \rho(q_1^2 + q_3^2). \quad (12)$$

The equality of attenuation of  $\omega_{f_1}$  under the interchange of the one and three axes is an immediate consequence of the stress tensor symmetry. The reader is urged to examine the corresponding expressions in the Leslie and Erickson notation. An anisotropic  $\xi_{ijkl}$  would lead to the replacement of  $\gamma_1^{-1}$  in Eqs. (10) and (11) by  $(\bar{\xi}_3 q_3^2 + \bar{\xi}_2 q_1^2)/(K_3 q_3^2 + K_2 q_1^2)$  and  $(\bar{\xi}_3 q_3^2 + \bar{\xi}_1 q_1^2)/(K_3 q_3^2 + K_1 q_1^2)$ , respectively.

Using only the Miesowicz measurements  $\eta_1^M = 0.024 \pm 0.001$ ,  $\eta_2^M = 0.092 \pm 0.008$  (our error estimate), and  $\eta_3^M = 0.034 \pm 0.003 = \nu_2$ , and using the Orsay value for  $\gamma_1 = 0.059 \pm 0.003$ , it is possible to estimate  $\lambda$  and  $\nu_3$  and the three other parameters measured in light scattering.<sup>4,13</sup> They give, for para-azoxyanisole at 125°C,

$$\lambda = 1.15 \pm 0.10, \quad \nu_3 = 0.024 \pm 0.001,$$

and the values listed in the following table:

| Orsay parameter   | Calculated        | Measured          |
|---|-------------------|-------------------|
| $t \equiv \gamma_1 \eta_1^M / \nu_3$                      | $0.059 \pm 0.003$ | $0.051 \pm 0.013$ |
| $\alpha_v' \equiv \eta_2^M / (\eta_2^M - \nu_3) \gamma_1$ | $23 \pm 2$        | $21 \pm 3$        |
| $\alpha_4' \equiv \eta_3^M / (\eta_2^M - \nu_3) \gamma_1$ | $8.5 \pm 1$       | $10 \pm 1.5$      |

This display of the Orsay data circumvents the large uncertainties introduced in going from the light scattering to the viscosities. The data clearly suggest that no dissipative parameter beyond  $\gamma_1$  is necessary.

While all five modes are contained in the correlation functions linking the director with  $\rho$ ,  $\epsilon$ , and  $g_i \equiv (\hat{q} \cdot \hat{g})/q$ , those linking the latter three contain only the sound and heat diffusion poles. Indeed, they differ from those of a simple liquid<sup>14</sup> only in that the heat diffusion constant  $D_T$  and the sound attenuation constant  $\Gamma$  depend on the angle  $\varphi$  between  $n$  and the propagation direction in a simple fashion:

$$\begin{aligned} \rho c_p D_T &= [\kappa_{\perp} \sin^2 \varphi + \kappa_{\parallel} \cos^2 \varphi]; \\ \Gamma &= D_T (c_p c_v^{-1} - 1) + D_i; \\ \rho D_i &= (2\nu_1 + \nu_2 - \nu_4 + 2\nu_3) \cos^2 \varphi \\ &\quad + (\nu_2 + \nu_4) \sin^2 \varphi - \frac{1}{2}(\nu_1 + \nu_2 - 2\nu_3) \sin^2 2\varphi. \end{aligned}$$

The bulk viscosities can be determined from sound attenuation and thermal conduction.

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<sup>1</sup>P. C. Martin, P. S. Pershan, and J. Swift, Phys. Rev. Lett. **25**, 844 (1970) (henceforth referred to as MPS).

<sup>2</sup>J. L. Erickson, Arch. Ration. Mech. Anal. **4**, 231 (1960); Phys. Fluids **9**, 1205 (1966).

<sup>3</sup>F. M. Leslie, Quart. J. Mech. Appl. Math. **19**, 356 (1966), and Arch. Ratl. Mech. Anal. **28**, (1968), 265-283.

<sup>4</sup>P. Chatelain, Acta Crystallogr. **1**, 315 (1948); P. G. de Gennes, C. R. Acad. Sci. Paris **266**, 15 (1968); Orsay Liquid Crystal Group, Phys. Rev. Lett. **22**, 1361 (1969), and more recent work to be published.

<sup>5</sup>M. Miesowicz, Nature **158**, 27 (1946).

<sup>6</sup>T. C. Lubensky, Phys. Rev. A **2**, 2497 (1970). The model  $R_{ij}$  is to be replaced by the molecular moment-of-inertia tensor  $Q_{ij}$  in a real fluid.

<sup>7</sup>See, for example, A. Katz and Y. Frishman, Nuovo Cimento **42A**, 1009 (1966).

<sup>8</sup>There is, however, considerably greater difficulty in constructing a Bogoliubov inequality.

<sup>9</sup>Cf. B. I. Halperin and P. C. Hohenberg, Phys. Rev. **188**, 898 (1969).

<sup>10</sup>C. W. Oseen, Trans. Faraday Soc. **29**, 883 (1933); F. C. Frank, Discuss. Faraday Soc. **25**, 19 (1958).

<sup>11</sup>The only term of order  $q$  in the expression  $\delta \dot{h}_i \approx \delta Q_{3i}$  is determined by the correlation function of  $g_K$  and  $\delta Q_{3i}$ , and the expression for  $\varphi$  involves the combination  $\hat{r} \times \hat{g} = \hat{I}$  whose value is determined by rotations. The intuitive argument cannot be circumvented.

<sup>12</sup>Groupe d'Etudes des Cristaux Liquides (Orsay), J. Chem. Phys. **51**, 816 (1970).

<sup>13</sup>The Orsay values also incorporate the results of V. Zwetkoff, Acta Physicochim. URSS **6**, 865 (1937), as corrected in V. Zwetkoff, Acta Physicochim. URSS **18**, 358 (1943).

<sup>14</sup>L. P. Kadanoff and P. C. Martin, Ann. Phys. **24**, 419 (1963). Pages 443 and 456 indicate how these expressions are incorporated in the relevant correlation functions.