Hydrodynamic Correlation Functions in Nematic Liquid Crystals

Propagating Modes

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The spectral densities of nematic liquid crystals are calculated in the hydrodynamic limit with particular reference to those spectral densities that play a role in the Brillouin lines of the light scattering spectrum. It is found that the contribution of the mixed pressure-director fluctuations to the intensity of the Brillouin lines is comparable to that of the pure pressure fluctuations. Exploitation of this feature allows, in principle, the determination of the flow-director coupling constant from the angular dependence of the intensity of the Brillouin lines.

Spectral densities of fluctuations in nematic liquid crystals were first presented by the Orsay Liquid Crystal group,[1] then calculated in more detail by Forster [2] whose results have been re-examined by the present authors.[3] Most of this attention has been directed to the non-propagating modes. There, the director fluctuations (*i.e.*, the feature characteristic of the nematic phase) make significant contributions; in fact they dominate completely the Rayleigh line in the light scattering spectrum.[4]

In this paper we investigate in detail the propagating (sound) modes. The width of the Brillouin lines is a valuable source of additional information since it is essentially determined by a function of all five viscosity coefficients two of which do not appear in the line-width expression of the Rayleigh line.[5] Further, we find that from the intensity of the Brillouin lines one may extract the flow-director coupling constant λ since the contribution to the intensity by the mixed pressure-director fluctuations, which is a function of λ, is of the same order of magnitude as the contribution of the pure pressure fluctuations.

The spectral densities are calculated in the hydrodynamic limit and we rely on an appropriate choice of fluctuation variables to facilitate a perturbation calculation of the normal modes. Although this procedure has already been outlined in a previous publication [3] we present again those details which are necessary to carry forward the argument.

CALCULATION OF SPECTRAL DENSITIES

Let A_i $i = 1, 2, \ldots, m$ be the variables specifying the hydrodynamic state of the system and $\alpha_i(\boldsymbol{k}, t)$ the spatial Fourier transforms of the fluctuations in these variables. In the hydrodynamic limit the dynamics of these fluctuations are given by

$$\frac{\partial}{\partial t}\langle\alpha(\boldsymbol{k}, t)\rangle_0 = -\mathbf{M}(k)\langle\alpha(\boldsymbol{k}, t)\rangle_0 (t > 0). \quad (1)$$

Here $\mathbf{M}(\boldsymbol{k})$ is the hydrodynamic matrix and $\langle \ldots \rangle_0$ denotes an average of the variable between the brackets subject to an initial condition.

Using standard methods one obtains for the spectral densities†

$$S_{ij}(\boldsymbol{k}, \omega) = \frac{k_B T}{2\pi}[\{\mathbf{M}+\mathrm{i}\omega\mathbf{I}]^{-1}\chi\}_{ji}^{*}+\varepsilon_i^{\mathrm{T}}\varepsilon_j^{\mathrm{T}}\{[\mathbf{M}-\mathrm{i}\omega\mathbf{I}]^{-1}\chi\}_{ji}^{*}] \tag{2}$$

where we have employed $\varepsilon_i^{\mathrm{T}}$ the signature under time reversal of the variable A_i. Here $\chi(\boldsymbol{k})$ is the variance matrix of the fluctuations $\alpha_i(\boldsymbol{k}, t)$.

From the symmetry properties of the spectral density matrix it follows that if $\varepsilon_i^{\mathrm{T}}\varepsilon_j^{\mathrm{T}}\varepsilon_i^{\mathrm{P}}\varepsilon_j^{\mathrm{P}} = +1$ then $S_{ij}(\boldsymbol{k}, \omega)$ is real and symmetric under exchange of i and j whereas if $\varepsilon_i^{\mathrm{T}}\varepsilon_j^{\mathrm{T}}\varepsilon_i^{\mathrm{P}}\varepsilon_j^{\mathrm{P}} = -1$ then $S_{ij}(\boldsymbol{k}, \omega)$ is imaginary and antisymmetric to the same exchange.[6] Here $\varepsilon_i^{\mathrm{P}}$ is the signature under inversion of the variable A_i.

Carrying out a normal mode analysis one can particularize eqn (2) to two cases where

$$S_{ij}(\boldsymbol{k}, \omega) = \frac{k_B T}{\pi}\,\mathrm{Re}\sum_{\mu}\frac{Z_{ij}^{\mu}}{\lambda_{\mu}+\mathrm{i}\omega} \text{ for } \varepsilon_i^{\mathrm{T}}\varepsilon_j^{\mathrm{T}}\varepsilon_i^{\mathrm{P}}\varepsilon_j^{\mathrm{P}} = +1 \tag{3a}$$

or

$$S_{ij}(\boldsymbol{k}, \omega) = \frac{k_B T}{\pi}\,\mathrm{i}\,\mathrm{Im}\sum_{\mu}\frac{Z_{ij}^{\mu}}{\lambda_{\mu}+\mathrm{i}\omega} \text{ for } \varepsilon_i^{\mathrm{T}}\varepsilon_j^{\mathrm{T}}\varepsilon_i^{\mathrm{P}}\varepsilon_j^{\mathrm{P}} = -1. \tag{3b}$$

Here the λ_μ are eigenvalues of the hydrodynamic matrix $\mathbf{M}$. Further we have employed a set of statistically independent and normalized fluctuation variables $\alpha_i(\boldsymbol{k}, t)$ which results in the simple expression for the strength factor matrices

$$\mathbf{Z}^{\mu} = V_{\mu}W_{\mu} \tag{4}$$

where V_μ and W_μ are the right and left eigenvectors of $\mathbf{M}$, respectively and are normalized such that $W_\mu V_\mu = 1$.

APPLICATION TO NEMATIC LIQUID CRYSTALS

The required eigenvalues and eigenvectors are obtained for the hydrodynamic matrix $\mathbf{M}$ which describes the dynamics of the following statistically independent and normalized fluctuation variables

$$\{\alpha_i(\boldsymbol{k}, t)\} = \{N_1\, p(\boldsymbol{k}, t),\, N_2\, \mathrm{d}(\boldsymbol{k}, t),\, N_3\, s(\boldsymbol{k}, t),\, N_4 f(\boldsymbol{k}, t),\, N_5\, \psi(\boldsymbol{k}, t)\} \tag{5}$$

where N_i, $i = 1, \ldots 5$ are normalization factors. Here $d(\boldsymbol{k}, t)$, $\psi(\boldsymbol{k}, t)$ and $f(\boldsymbol{k}, t)$ are fourier transforms of div $\boldsymbol{v}$, (curl curl $\boldsymbol{v})_z$ and $(\partial n_x/\partial x+\partial n_y/\partial y)$, respectively. The thermodynamic state is specified by pressure p and entropy s, $\boldsymbol{v}$ is the velocity field and n_x and n_y describe the fluctuations in the director. For this set of $\alpha_i(\boldsymbol{k}, t)$ the signatures under time reversal are $\{1, -1, 1, 1, -1\}$ and under inversion $\{1, 1, 1, -1, -1\}$. The explicit form of the hydrodynamic matrix $\mathbf{M}$ for these variables is given in ref. (3).

Using standard perturbation theory the eigenvalues correct to order k^2 may be obtained from the hydrodynamic matrix and the result for the sound modes can be written as

$$\lambda_{1,\,2} = \pm\mathrm{i}kc+\tfrac{1}{2}\Gamma k^2. \tag{6}$$

Here $c = (\rho\chi_s)^{-\frac{1}{2}}$ is the adiabatic sound speed and

$$\Gamma = \left(\frac{c_p}{c_v}-1\right)D_{\mathrm{T}}(\phi)+D_{\mathrm{l}}(\phi). \tag{7}$$

† Throughout this paper Boltzmann's constant is represented by k_B, to avoid confusion with the wavevector $\boldsymbol{k}$.

The form of the damping factor Γ is the same as for an isotropic one-component fluid with the notable exception that it now depends on the angle ϕ between the direction of propagation of the sound wave and the director $\boldsymbol{n}^\circ$ as in

$$c_p\rho D_T(\phi) = \kappa_\perp \sin^2\phi + \kappa_\parallel \cos^2\phi$$

$$\rho D_l(\phi) = (2\nu_1+\nu_2-\nu_4+2\nu_5)\cos^2\phi + (\nu_2+\nu_4)\sin^2\phi - \tfrac{1}{2}(\nu_1+\nu_2-2\nu_3)\sin^2 2\phi.$$

The coefficients $\nu_1 \ldots \nu_5$ are the five independent viscosites characteristic of the uniaxial nematic phase and $\kappa_\parallel$ and $\kappa_\perp$ are the heat conductivities parallel and perpendicular to $\boldsymbol{n}^\circ$. The damping constant associated with the heat mode is just $\lambda_3 = D_T(\phi)k^2$. The eigenvalues λ_4 and λ_5 specifying the relaxation times of the longitudinal shear-director modes are

$$\lambda_4 = \left\{\tilde{K}(\phi)\xi + \frac{[1+\lambda\cos 2\phi]^2}{4\tilde{\nu}_t(\phi)}\tilde{K}(\phi)\right\}k^2 \tag{8}$$

$$\lambda_5 = \left\{\frac{\tilde{\nu}_t(\phi)}{\rho} - \frac{[1+\lambda\cos 2\phi]^2}{4\tilde{\nu}_t(\phi)}\tilde{K}(\phi)\right\}k^2. \tag{9}$$

Here ξ is the director relaxation constant, λ is the flow-director coupling constant and $\tilde{\nu}_t(\phi)$ and $\tilde{K}(\phi)$ are defined by

$$\tilde{\nu}_t(\phi) = \nu_3\cos^2 2\phi + \tfrac{1}{2}(\nu_1+\nu_2)\sin^2 2\phi$$

$$\tilde{K}(\phi) = K_{11}\sin^2\phi + K_{33}\cos^2\phi$$

with K_{11} and K_{33} the Frank elasticity constants for splay and bend deformations of the nematic. In writing down λ_4 and λ_5 we have made use of the fact [1] that for nematics, typically, $[\tilde{K}(\phi)\rho/\tilde{\nu}_t^2(\phi)] \ll 1$.

In the hydrodynamic limit the eigenvector matrix corresponding to eigenvalues which are correct to order k^2 is

$$\mathbf{V} = \mathbf{V}^{(0)} + k\mathbf{V}^{(1)}.$$

Here

$$\mathbf{V}^{(0)} = \begin{bmatrix} \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} & 0 & 0 & 0 \\ \frac{i}{\sqrt{2}} & \frac{-i}{\sqrt{2}} & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & q & r \\ 0 & 0 & 0 & r & q \end{bmatrix} \tag{10}$$

where

$$q = \left[\frac{\frac{\tilde{\nu}_t}{\rho}k^2 - \lambda_4}{\lambda_5 - \lambda_4}\right]^{\frac{1}{2}}$$

$$r = \mp\left[\frac{\frac{\tilde{\nu}_t}{\rho}k^2 - \lambda_5}{\lambda_5 - \lambda_4}\right]^{\frac{1}{2}}$$

and in r the upper sign applies when $(1+\lambda \cos 2\phi) < 0$ and the lower when $(1+\lambda \cos 2\phi) > 0$. We write $\mathbf{V}^{(1)}$ as

$$\mathbf{V}^{(1)} = \begin{bmatrix} \frac{-\mathrm{i}b_1}{4\sqrt{2}} & \frac{\mathrm{i}b_1}{4\sqrt{2}} & 0 & -\mathrm{i}(qb_3-rb_4) & \mathrm{i}(qb_4-rb_3) \\ \frac{-b_1}{4\sqrt{2}} & \frac{-b_1}{4\sqrt{2}} & -b_2 & 0 & 0 \\ \frac{-\mathrm{i}b_2}{\sqrt{2}} & \frac{\mathrm{i}b_2}{\sqrt{2}} & 0 & c_{34} & c_{35} \\ \frac{-\mathrm{i}b_3}{\sqrt{2}} & \frac{-\mathrm{i}b_3}{\sqrt{2}} & c_{43}q+c_{53}r & c_{54}r & c_{45}q \\ \frac{-\mathrm{i}b_4}{\sqrt{2}} & \frac{\mathrm{i}b_4}{\sqrt{2}} & c_{43}r+c_{53}q & c_{54}q & c_{45}r \end{bmatrix} \tag{11}$$

where

$$b_1 = \frac{\left(\frac{c_p}{c_v}-1\right)D_{\mathrm{T}}(\phi)-D_{\mathrm{l}}(\phi)}{c}$$

$$b_2 = \frac{\left(\frac{c_p}{c_v}-1\right)^{\frac{1}{2}}D_{\mathrm{T}}(\phi)}{c}$$

$$b_3 = \frac{\frac{1}{2}(\sin 2\phi)\left(\frac{\tilde{K}(\phi)}{\rho}\right)^{\frac{1}{2}}}{c}$$

$$b_4 = \frac{\tilde{\nu}(\phi)/\rho}{c}.$$

Here $\tilde{\nu}(\phi) = \frac{1}{2}(\nu_4-\nu_5-\nu_1)\sin 2\phi+\frac{1}{4}(2\nu_3-\nu_1-\nu_2)\sin 4\phi$ and the $c_{\sigma\mu}$ in eqn (11) are the undetermined coefficients referred to in ref. (3). Given these expressions for $\mathbf{V}^{(0)}$ and $\mathbf{V}^{(1)}$ one can calculate the required left eigenvector matrices $\mathbf{W}^{(0)} = \mathbf{V}^{(0-1)}$ and $\mathbf{W}^{(1)} = -\mathbf{W}^{(0)}\mathbf{V}^{(1)}\mathbf{W}^{(0)}$. The strength factor matrices can now be obtained to order k from

$$Z = V_\mu^{(0)}W_\mu^{(0)}+k[V_\mu^{(0)}W_\mu^{(1)}+V_\mu^{(1)}W_\mu^{(0)}]. \tag{12}$$

The spectral densities now follow on utilizing eqn (3).

RESULTS AND DISCUSSION

Since, as mentioned in the introduction, we are primarily interested in the Brillouin lines, then in selecting the spectral density elements we consider fluctuation variables which contribute to the sound modes and which contribute to the fluctuation in the dielectric constant. Further we shall only be concerned with contributions to the spectral densities which are of hydrodynamic order (*i.e.*, up to order k). Hence we shall be concerned with $S_{pp}(\boldsymbol{k}, \omega)$, $S_{ps}(\boldsymbol{k}, \omega)$ and $S_{pn_1}(\boldsymbol{k}, \omega)$ which can be obtained readily using the methods and results presented in the previous section. We obtain

$$S_{pp}(\boldsymbol{k}, \omega) = \frac{kT_{\mathrm{B}}}{\pi}\chi_{\mathrm{s}}^{-1}\frac{1}{2}\left[\frac{\frac{1}{2}\Gamma k^2-b_1k(\omega+kc)/2}{(\frac{1}{2}\Gamma k^2)^2+(\omega+kc)^2}+\frac{\frac{1}{2}\Gamma k^2+b_1k(\omega-kc)/2}{(\frac{1}{2}\Gamma k^2)^2+(\omega-kc)^2}\right] \tag{13}$$

$$S_{ps}(\boldsymbol{k},\omega) = \frac{k_B T}{\pi}\left(\frac{c_p}{\rho T\chi_s}\right)^{\frac{1}{2}}\left[\frac{-b_2k(\omega+kc)/2}{(\frac{1}{2}\Gamma k^2)^2+(\omega+kc)^2}+\frac{b_2k(\omega-kc)/2}{(\frac{1}{2}\Gamma k^2)^2+(\omega-kc)^2}\right] \tag{14}$$

$$S_{pn_1}(\boldsymbol{k},\omega) = \frac{k_B T}{\pi}(\tilde{K}\chi_s)^{-\frac{1}{2}}\left[\frac{\frac{1}{2}b_3\frac{1}{2}\Gamma k^2}{(\frac{1}{2}\Gamma k^2)^2+(\omega+kc)^2}+\frac{\frac{1}{2}b_3\frac{1}{2}\Gamma k^2}{(\frac{1}{2}\Gamma k^2)^2+(\omega-kc)^2}+\frac{(qrb_4-q^2b_3)\lambda_4}{\lambda_4^2+\omega^2}+\frac{(-qrb_4+r^2b_3)\lambda_5}{\lambda_5^2+\omega^2}\right]. \tag{15}$$

Here we have reverted to the commonly used variable n_1 which is related to our original variable f by $f = (-ik\sin\phi)n_1$.

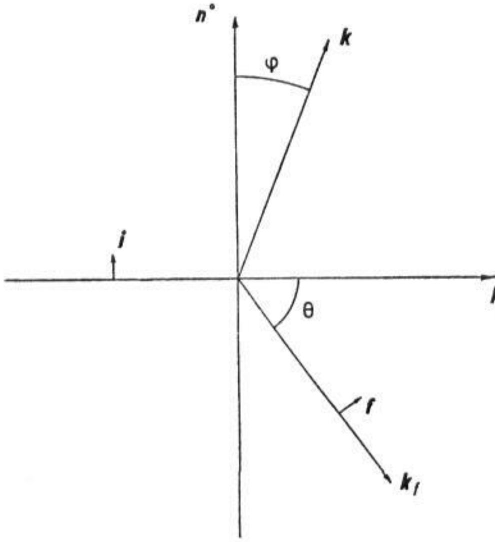

FIG. 1.—The scattering geometry.

The form of $S_{pp}(\boldsymbol{k},\omega)$ and $S_{ps}(\boldsymbol{k},\omega)$ is exactly the same as in the ordinary one component fluid although, as mentioned earlier, Γ does reflect the uniaxiallity of the system. The additional term $S_{pn_1}(\boldsymbol{k},\omega)$ is a distinct contribution of the nematic phase. It should be noted that the sum of the strength factors of the four lorentizian contributions is however zero [as it must be since $\langle p(\boldsymbol{k})n_1(\boldsymbol{k})^*\rangle = 0$]. The fact that the contributions to the mixed spectral density $S_{pn_1}(\boldsymbol{k},\omega)$ are lorentzian, whereas those which contribute to the mixed term $S_{ps}(\boldsymbol{k},\omega)$ are non-lorentzian, can be traced to the fact that the coupling which gives rise to the mixed term is, in the case of $S_{pn_1}(\boldsymbol{k},\omega)$, to the odd variable div $\boldsymbol{v}$ whereas in the case of $S_{ps}(\boldsymbol{k},\omega)$ it is to be the even variable p.

Although the contributions of $S_{pn_1}(\boldsymbol{k},\omega)$ to the Rayleigh line are of minor importance (they are smaller by a factor of k^2 than the contribution of $S_{n_1n_1}$) their contribution to the Brillouin line is of the same order in k as that of the pure pressure fluctuations. This makes the contribution of $S_{pn_1}(\boldsymbol{k},\omega)$ to the Brillouin line of some interest and we shall consider it in the context of the scattering configuration utilized by the Orsay Group to study the Rayleigh line [7] (see fig. 1). In this configuration the polarization vectors $\boldsymbol{i}$ and $\boldsymbol{f}$ of the incident and scattered wave and $\boldsymbol{n}^\circ$ lie in the scattering plane defined by the wave vectors $\boldsymbol{k}_i$ and $\boldsymbol{k}_f$ of the incident and scattered wave.

The spectrum of scattered light is proportional to the spectral density of $\delta\varepsilon_{fi}(k, t) = \boldsymbol{f}.\delta\varepsilon(\boldsymbol{k}, t).\boldsymbol{i}$ which in this case is just

$$\delta\varepsilon_{fi}(\boldsymbol{k}, t) = \left(\frac{\partial\varepsilon_{\parallel}}{\partial p}\right)_s (\cos\theta) p(\boldsymbol{k}, t) + \left(\frac{\partial\varepsilon_{\parallel}}{\partial s}\right)_p (\cos\theta) s(\boldsymbol{k}, t) + \varepsilon_a (\sin\theta) n_1(\boldsymbol{k}, \mathrm{t}). \tag{16}$$

Here $\varepsilon_a = \varepsilon_{\parallel} - \varepsilon_{\perp}$ where $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ are the components of the dielectric tensor parallel and perpendicular to the director $\boldsymbol{n}^{\circ}$. Neglecting the non-lorentzian contributions, which are smaller by a factor k, we obtain for the intensity of the Brillouin line

$$I^{\mathrm{B}}(\boldsymbol{k}, \omega) = C\left[\left(\frac{\partial\varepsilon_{\parallel}}{\partial\rho}\right)_s \rho\cos^2\theta + \varepsilon_a\lambda\cos\theta\sin\theta\sin 2\phi\right]\left[\frac{\frac{1}{2}\Gamma k^2}{(\frac{1}{2}\Gamma k^2)^2 + (\omega + kc)^2} + \frac{\frac{1}{2}\Gamma k^2}{(\frac{1}{2}\Gamma k^2)^2 + (\omega - kc)^2}\right]. \tag{17}$$

Here C is a collection of constants which need not concern us for the moment. Since $(\partial\varepsilon_{\parallel}/\partial\rho)_s\rho$ is of the same order of magnitude as ε_a for nematics [4] the contribution to the intensity by the mixed pressure director fluctuation is of the same order of magnitude as that from the pure pressure fluctuation. Thus by measuring the angular dependency of the intensity of the Brillouin lines it is, in principle, possible to extract a value for the flow director coupling constant λ. In contrast to the determination of λ from measurements on the width of the Rayleigh line [7] this procedure would not require prior knowledge of the elastic constants.

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APPENDIX

List of symbols that enter the " Harvard presentation " of nematodynamics [2, 5, 8]

$\boldsymbol{n}$: director

K_{11}, K_{22}, K_{33} : elasticity constants for splay, twist and bend formations

λ_6: flow-director coupling constant

$\nu_1, \nu_2, \nu_3, \nu_4, \nu_5$: independent viscosity coefficients

$\kappa_{\parallel}, \kappa_{\perp}$: heat conductivities parallel and perpendicular to $\boldsymbol{n}$.

ξ : director relaxation constant.

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(PAPER 7/1525)