

Classification
Physics Abstracts
 7.130

HYDRODYNAMIC CORRELATION FUNCTIONS IN NEMATIC LIQUID CRYSTALS

H. N. W. LEKKERKERKER

Fakulteit van de Wetenschappen Vrije Universiteit Brussel, 1050 Brussel, Belgium

D. CARLE and W. G. LAIDLAW

Department of Chemistry University of Calgary, Calgary, Alberta, Canada

(Reçu le 28 octobre 1975, révisé le 19 mars 1976, accepté le 13 avril 1976)

Résumé. — L'objet du présent article consiste en un réexamen du résultat suivant récemment obtenu par Forster : dans le cas des cristaux liquides nématiques, il n'est pas possible de déterminer de manière complète, à partir de la matrice hydrodynamique, les amplitudes liées à tous les modes diffusifs. Nous montrons qu'à partir des lois de symétrie d'inversion spatiale et d'inversion de temps, ces amplitudes peuvent être exprimées en termes de trois constantes indéterminées.

Abstract. — The result, recently discovered by Forster, that the strength factors of the non-propagating modes in certain hydrodynamic correlation functions in nematic liquid crystals are not fully determined by the hydrodynamic matrix is reconsidered. Using time reversal and space inversion symmetry one finds that all the unspecified strength factors can be expressed in terms of three undetermined constants.

1. Introduction. — Spectral densities of fluctuations in nematic liquid crystals have been first calculated by the Orsay Liquid Crystal Group [1] and more recently by Forster [2, 3]. The latter author finds that the form of some of these spectral densities cannot be fully determined by hydrodynamic considerations. In this paper we reanalyse this problem. We find that if one uses pressure and entropy in the thermodynamic description of the system that the above mentioned undeterminedness is limited to cross correlations between entropy fluctuations and the longitudinal shear-director fluctuations and to correlations among the latter variables. Further we will show that the application of time reversal and space inversion symmetry leads to certain constraints on the unspecified factors in these spectral densities.

First we briefly consider the hydrodynamic calculation of spectral densities and we present some of their symmetry properties (section 2). Then we discuss those elements of degenerate perturbation theory that lie at the basis of the above mentioned indeterminacy of certain spectral densities (section 3). Subsequently in section 4 these hydrodynamically undetermined spectral densities in nematic liquid crystals are considered in detail leading to the results stated above. Finally we consider the practical implications of the problem of hydrodynamically undetermined spectral densities.

2. Calculation of spectral densities in the hydrodynamic limit. — The traditional procedure for the calculation of densities of fluctuations in the hydrodynamic limit (wavevector $\mathbf{k} \rightarrow 0$ and angular frequency $\omega \rightarrow 0$) is based upon Onsager's assumption that on the average fluctuations in the macroscopic variables of a system decay according to the macroscopic transport laws of that system. Suppose that A_i , $i = 1, 2, \dots, n$ are the variables specifying the hydrodynamic state of the system and that $\alpha_i(\mathbf{k}, t)$ are the spatial Fourier transforms of the fluctuations in these variables then according to Onsager's hypothesis

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

Here $M(\mathbf{k})$ is the so called hydrodynamic matrix and $\langle \dots \rangle_0$ denotes an average of the variable between the brackets subject to an initial condition at $t = 0$.

In hydrodynamic theory one assumes that the matrix M can be expanded in powers of k and one ordinarily only considers terms up to k^2 . Then assuming that there are no terms of order k^0 (i.e. excluding processes such as chemical reactions) one can write

$$M = kM^{(1)} + k^2M^{(2)}. \quad (2)$$

From the set of coupled differential equations (1) for the conditional averages of the fluctuations $\alpha_i(\mathbf{k}, t)$, together with the variances of these fluctuations

$$\chi_{ij} = \frac{1}{k_B T} \langle \alpha_i(\mathbf{k}) \alpha_j(\mathbf{k})^* \rangle \quad (3)$$

it is possible to calculate the spectral densities

$$S_{ij}(\mathbf{k}, \omega) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} \langle \alpha_i(\mathbf{k}, 0) \alpha_j(\mathbf{k}, t)^* \rangle e^{i\omega t} dt \quad (4)$$

of these fluctuations.

Using standard methods one obtains

$$S_{ij}(\mathbf{k}, \omega) = \frac{k_B T}{2\pi} \left[\{ [M + i\omega I]^{-1} \chi \}_{ji}^* + \varepsilon_i^T \varepsilon_j^T \{ [M - i\omega I]^{-1} \chi \}_{ji}^* \right] \quad (5)$$

where ε_i^T is the signature of the variable A_i under time reversal.

As written in equation (5) the spectral densities have a complicated form and are not directly suited for comparison with experimental results, such as light scattering spectra, which are determined by fluctuation spectra. Therefore one frequently undertakes a normal mode analysis. In order to facilitate such an analysis it is convenient to work with statistically independent and normalized fluctuations such that the variance matrix χ given by equation (3) is equal to the unit matrix. Using such variables the result of a normal mode analysis is that the spectral densities can be written as

$$S_{ij}(\mathbf{k}, \omega) = \frac{k_B T}{2\pi} \sum_{\mu} \left\{ \frac{Z_{ji}^{\mu*}}{\lambda_{\mu}^* - i\omega} + \frac{\varepsilon_i^T \varepsilon_j^T Z_{ji}^{\mu*}}{\lambda_{\mu}^* + i\omega} \right\} \quad (6)$$

where the summation runs over the eigenvalues $\lambda_1, \dots, \lambda_n$ of the hydrodynamic matrix.

The so called strength factors Z_{ji}^{μ} are elements of a matrix Z^{μ} that can be written as

$$Z^{\mu} = V_{\mu} W_{\mu} \quad (7)$$

where V_{μ} and W_{μ} are the right and left eigenvectors corresponding to λ_{μ} , normalized such that $W_{\mu} \cdot V_{\mu} = 1$.

The hydrodynamic matrix M in the form given by equation (2) determines the eigenvalues up to order k^2

$$\lambda_{\mu} = k\lambda_{\mu}^{(1)} + k^2 \lambda_{\mu}^{(2)} \quad (8)$$

where $\lambda_1^{(1)}, \dots, \lambda_n^{(1)}$ are the eigenvalues of $M^{(1)}$. Since we can write the hydrodynamic matrix in the form $M = kA$, its eigenvectors are ordinarily determined up to order k (and not k^2 as in the case of the eigenvalues)

$$V_{\mu} = V_{\mu}^{(0)} + kV_{\mu}^{(1)} \quad (9)$$

where $V_{\mu}^{(0)}$ is the eigenvector of $M^{(1)}$ corresponding to the eigenvalue $\lambda_{\mu}^{(1)}$. In case the eigenvectors are

determined to order k it follows from equation (7) that strength factors are also determined to order k

$$Z^{\mu} = Z^{(0)\mu} + kZ^{(1)\mu} \quad (10)$$

where

$$Z^{(0)\mu} = V_{\mu}^{(0)} W_{\mu}^{(0)} \quad (10a)$$

and

$$Z^{(1)\mu} = V_{\mu}^{(0)} W_{\mu}^{(1)} + V_{\mu}^{(1)} W_{\mu}^{(0)}. \quad (10b)$$

In the next section we shall see that in case $\lambda_{\mu}^{(1)}$ is a degenerate eigenvalue of $M^{(1)}$, the contribution of order k in the corresponding eigenvectors is not fully determined by the hydrodynamic matrix. In view of equation (10) this means that the terms of order k in the strength factors corresponding to the first order degenerate poles are hydrodynamically undetermined.

Due to the fact that the system is invariant to time and space translation, to time reversal and spatial inversion and that the fluctuations $\alpha_i(\mathbf{r}, t)$ are real, the spectral densities of these fluctuations have the following symmetry properties (see e.g. ref. [3], Chapter 3)

$$S_{ij}(\mathbf{k}, \omega) = S_{ij}(-\mathbf{k}, -\omega)^* = S_{ji}(-\mathbf{k}, -\omega) = \varepsilon_i^T \varepsilon_j^T S_{ij}(\mathbf{k}, -\omega) = \varepsilon_i^P \varepsilon_j^P S_{ij}(-\mathbf{k}, \omega) \quad (11)$$

where ε_i^P is the signature of variable A_i under space inversion. From the symmetry properties given in equation (11) it follows that the spectral density matrix is hermitian and that

$$S_{ij}(\mathbf{k}, \omega) = \varepsilon_i^T \varepsilon_j^T \varepsilon_i^P \varepsilon_j^P S_{ij}(\mathbf{k}, \omega)^*. \quad (12)$$

Applying these symmetry properties to the spectral densities in the hydrodynamic limit as given in the normal mode form, one finds that the strength factor matrices must satisfy certain symmetry relations. For the strength factor matrices corresponding to real roots λ_{μ} one obtains

$$Z_{ij}^{\mu} = \varepsilon_i^T \varepsilon_j^T Z_{ji}^{\mu*} = \varepsilon_i^P \varepsilon_j^P Z_{ij}^{\mu*} \quad (13a)$$

and for those corresponding to complex conjugated roots $\lambda_{\mu} = \lambda_{\sigma}^*$ one finds

$$Z_{ij}^{\mu} = \varepsilon_i^T \varepsilon_j^T Z_{ji}^{\sigma*} = \varepsilon_i^P \varepsilon_j^P Z_{ij}^{\sigma*}. \quad (13b)$$

In section 4 we shall see that these symmetry properties lead to certain constraints on the hydrodynamically undetermined strength factors.

3. Elements of degenerate perturbation theory. — Although, degenerate perturbation theory is treated in virtually every textbook on quantum mechanics [4], there are certain details that are not always presented correctly. As in the problem of the hydrodynamically undetermined strength factors a proper appreciation of the subtleties of degenerate perturbation theory is

indispensable we briefly review here some of these features.

As can be seen from equation (10), the strength factor matrices can be expressed in terms of the eigenvectors of the hydrodynamic matrix. These eigenvectors can be obtained using perturbation theory with the wavevector k playing the role of expansion parameter. The basic equation then is

$$(kM^{(1)} + k^2 M^{(2)}) (V_\mu^{(0)} + kV_\mu^{(1)}) = (k\lambda_\mu^{(1)} + k^2 \lambda_\mu^{(2)}) (V_\mu^{(0)} + kV_\mu^{(1)}) \quad (14)$$

For nematic liquid crystals, as we shall see in the next section, $M^{(1)}$ has a degenerate eigenvalue and thus to carry out the next step in perturbation theory one has to know the proper eigenvectors corresponding to the degenerate eigenvalue i.e. the eigenvectors that diagonalize the projection of $M^{(2)}$ on the space spanned by the degenerate eigenvalue.

Suppose $\lambda_1^{(1)} = \lambda_2^{(1)} = \dots = \lambda_r^{(1)}$ is the (r -fold) degenerate eigenvalue of $M^{(1)}$ and $\lambda_{r+1}^{(1)}, \dots, \lambda_n^{(1)}$ are the remaining non-degenerate eigenvalues of $M^{(1)}$ and further $V_1^{(0)}, \dots, V_n^{(0)}$ are the corresponding (proper) eigenvectors. Then the first order corrections to the eigenvectors can be written as

$$V_\mu^{(1)} = \sum_{\sigma=1}^n c_{\sigma\mu} V_\sigma^{(0)} \quad (15)$$

In the expansion of the first order correction, as given in equation (15), it is wellknown (4-6) that if V_μ corresponds to a non-degenerate eigenvalue (i.e. $\mu = r + 1, \dots, n$ in the present discussion), then the first order perturbation equation

$$(M^{(1)} - \lambda_\mu^{(1)} I) V_\mu^{(1)} + (M^{(2)} - \lambda_\mu^{(2)} I) V_\mu^{(0)} = 0 \quad (16)$$

determines the coefficients $c_{1\mu}, \dots, c_{n\mu}$ except $c_{\mu\mu}$. The latter coefficient remains arbitrary in so far as the perturbation equations are concerned and is conveniently taken to be zero, a practice we shall follow here as well. If V_μ corresponds to a degenerate eigenvalue (i.e. $\mu = 1, \dots, r$) one finds that the first order perturbation equation (16) now leaves undetermined the set coefficients $c_{\sigma\mu}$ where σ runs over the labels of the degenerate eigenvalues i.e. $\sigma = 1, \dots, r$. It is easy to show that [5, 6] of those coefficients that cannot be obtained from the first order perturbation equation only $c_{\mu\mu}$ remains arbitrary in so far as the higher order perturbation equations are concerned and can be taken to be zero whereas the remaining undetermined coefficients can be obtained from the second order perturbation equation [7].

That equation not only involves $M^{(1)}$ and $M^{(2)}$, but also the next higher order contribution in k in the hydrodynamic matrix [8]. However ordinarily in hydrodynamic theory one only considers $M^{(1)}$ and $M^{(2)}$ and thus to hydrodynamic order coefficients $c_{\sigma\mu}$, $\sigma \neq \mu = 1, \dots, r$ must be considered as hydrodynamically undetermined.

4. Hydrodynamically undetermined spectral densities in nematic crystals. — 4.1 SELECTION OF VARIABLES AND THE HYDRODYNAMIC MATRIX. — The hydrodynamic state of a nematic liquid crystal is specified by two thermodynamic variables, the velocity field \mathbf{v} and two components of the director perpendicular to \mathbf{n}^0 , the director in the equilibrium state.

We shall take \mathbf{n}^0 as directed along the z -axis. Then the system possesses axial symmetry around the z -axis and then, as discussed in reference [9], it is convenient to use as a specification for the velocity field the variables

$$d = \text{div } \mathbf{v}; \quad \psi = (\text{curl } \text{curl } \mathbf{v})_z; \quad \varphi = (\text{curl } \mathbf{v})_z \quad (17)$$

Applying the same notions about symmetry to the director variables it appears to be convenient to use

$$f = \frac{\partial n_x}{\partial x} + \frac{\partial n_y}{\partial y}; \quad g = \frac{\partial n_y}{\partial x} - \frac{\partial n_x}{\partial y} \quad (18)$$

We use as thermodynamic variables the specific entropy (s) and the pressure (p) as they lead to a simple mode structure for the spectral densities in normal fluids and have similar advantages in the calculation of the spectral densities for nematic liquid crystals.

Due to their different symmetry properties the longitudinal variables p, d, s, f and ψ are not coupled to the transverse variables g and φ .

The hydrodynamically undetermined spectral densities occur among the longitudinal variables. Therefore, in the following, we will only consider these variables. The fluctuations in these variables are already statistically independent but, as mentioned earlier, to carry out a normal mode analysis it has advantages to normalize them as well. This leads to the following spatially Fourier transformed variables

$$\begin{aligned} \alpha_1(\mathbf{k}, t) &= (\chi_s)^{1/2} p(\mathbf{k}, t) \\ \alpha_2(\mathbf{k}, t) &= \left(\frac{\rho}{k^2}\right)^{1/2} d(\mathbf{k}, t) \\ \alpha_3(\mathbf{k}, t) &= \left(\frac{\rho T}{c_p}\right)^{1/2} s(\mathbf{k}, t) \\ \alpha_4(\mathbf{k}, t) &= \left(\frac{\tilde{K}(\varphi)}{\sin^2 \varphi}\right)^{1/2} f(\mathbf{k}, t) \\ \alpha_5(\mathbf{k}, t) &= \left(\frac{\rho}{k^2 k_\perp^2}\right)^{1/2} \psi(\mathbf{k}, t) \end{aligned}$$

Here χ_s is the adiabatic compressibility, ρ is the mass density, c_p is the specific heat at constant pressure. Further

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

where K_{11} and K_{33} are the Frank elasticity constants

for splay and bend deformations respectively and φ is the angle between \mathbf{k} and \mathbf{n}^0 . Further $k_{\perp}^2 = k_x^2 + k_y^2$. The signatures of the variables used here under time reversal and spatial inversion are

$$\begin{aligned} \varepsilon_1^T &= \varepsilon_3^T = \varepsilon_4^T = +1, & \varepsilon_2^T &= \varepsilon_5^T = -1 \\ \varepsilon_1^P &= \varepsilon_2^P = \varepsilon_3^P = +1, & \varepsilon_4^P &= \varepsilon_5^P = -1. \end{aligned} \quad (20)$$

The hydrodynamic matrix describing the time

dependence of the variables $\alpha_i(\mathbf{k}, t)$ is obtained from the hydrodynamic equations given by Forster *et al.* [10] and is of the form $M = kM^{(1)} + k^2 M^{(2)}$. The only non-zero elements of $M^{(1)}$ are

$$M_{12}^{(1)} = -M_{21}^{(1)} = c \quad (21)$$

where c is the adiabatic sound velocity. The matrix $M^{(2)}$ is given by equation (22)

$$M^{(2)} = \begin{bmatrix} (c_p c_v^{-1} - 1) D_T(\varphi) & 0 & (c_p c_v^{-1} - 1)^{1/2} D_T(\varphi) & 0 & 0 \\ 0 & D_l(\varphi) & 0 & \frac{1}{2} i(\sin 2\varphi) \lambda \left(\frac{\tilde{K}(\varphi)}{\rho} \right)^{1/2} & i \frac{\tilde{v}(\varphi)}{\rho} \\ (c_p c_v^{-1} - 1)^{1/2} D_T(\varphi) & 0 & D_T(\varphi) & 0 & 0 \\ 0 & \frac{1}{2} i(\sin 2\varphi) \lambda \left(\frac{\tilde{K}(\varphi)}{\rho} \right)^{1/2} & 0 & \tilde{K}(\varphi) \xi & -\frac{1}{2} [1 + \lambda \cos 2\varphi] \left(\frac{\tilde{K}(\varphi)}{\rho} \right)^{1/2} \\ 0 & \frac{-i\tilde{v}(\varphi)}{\rho} & 0 & \frac{1}{2} [1 + \lambda \cos 2\varphi] \left(\frac{\tilde{K}(\varphi)}{\rho} \right)^{1/2} & \frac{\tilde{v}(\varphi)}{\rho} \end{bmatrix} \quad (22)$$

The transport coefficients appearing in equation (20) have the following meaning

$$\begin{aligned} c_p \rho D_T(\varphi) &= \kappa_{\perp} \sin^2 \varphi + \kappa_{\parallel} \cos^2 \varphi \\ \rho D_l(\varphi) &= (2v_1 + v_2 - v_4 + 2v_5) \cos^2 \varphi + \\ &+ (v_2 + v_4) \sin^2 \varphi - \frac{1}{2}(v_1 + v_2 - 2v_3) \sin^2 2\varphi \\ \tilde{v}(\varphi) &= \frac{1}{2}(v_4 - v_5 - v_1) \sin 2\varphi + \\ &+ \frac{1}{4}(2v_3 - v_1 - v_2) \sin 4\varphi \\ \tilde{v}_l(\varphi) &= v_3 \cos^2 2\varphi + \frac{1}{2}(v_1 + v_2) \sin^2 2\varphi \end{aligned}$$

where φ is the angle between \mathbf{k} and \mathbf{n}^0 , κ_{\parallel} and κ_{\perp} are the heat conductivities parallel and perpendicular to \mathbf{n}^0 and v_1, \dots, v_5 are the five independent viscosity coefficients of a nematic liquid crystal [10].

Further ξ is the director relaxation constant and λ is the coupling coefficient between shear flow and the director.

4.2 EIGENVALUES AND EIGENVECTORS. — The eigenvalues of the hydrodynamic matrix are of the form $\lambda_{\mu} = k\lambda_{\mu}^{(1)} + k^2\lambda_{\mu}^{(2)}$ where $\lambda_{\mu}^{(1)}$ are the eigenvalues of $M^{(1)}$. For nematic liquid crystals one obtains

$$\lambda_{1,2}^{(1)} = \pm ic, \quad \lambda_{3,4,5}^{(1)} = 0. \quad (23)$$

The corresponding matrix of zeroth order eigenvectors is

$$V^{(0)} = \begin{bmatrix} \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} & 0 & 0 & 0 \\ i & -i & 0 & 0 & 0 \\ \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & q & r \\ 0 & 0 & 0 & r & q \end{bmatrix}. \quad (24)$$

The lower right 3×3 block of $V^{(0)}$ diagonalizes the lower right 3×3 block of $M^{(2)}$ such that the third column of $V^{(0)}$ corresponds to the heat mode and the fourth and fifth column corresponds to the slow and fast longitudinal shear-director mode respectively. Since normally $\tilde{v}_l/\rho \gg \tilde{K}\xi$ it follows that $|q| \gg |r|$ and for later convenience we have normalized q and r such that $q^2 - r^2 = 1$.

Using perturbation theory to obtain $V_{\mu}^{(1)}$ one finds for reasons explained in section 3, that a number of elements in the eigenvectors corresponding to the degenerate eigenvalues are not fully determined by $M^{(1)}$ and $M^{(2)}$.

One can write

$$V^{(1)} = \begin{bmatrix} \times & \times & \times & \times & \times \\ \times & \times & \times & \times & \times \\ \times & \times & 0 & c_{34} & c_{35} \\ \times & \times & c_{43}q + c_{53}r & c_{54}r & c_{45}q \\ \times & \times & c_{43}r + c_{53}q & c_{54}q & c_{45}r \end{bmatrix} \quad (25)$$

where the elements that are completely specified by $M^{(1)}$ and $M^{(2)}$ are indicated by crosses. On the other hand the coefficients $c_{\sigma\mu}$ ($\sigma \neq \mu = 3, 4, 5$) are the coefficients that are not fully determined by the hydrodynamic matrix.

4.3 HYDRODYNAMICALLY UNDETERMINED STRENGTH FACTORS. — After calculating $W^{(0)} + kW^{(1)}$, the inverse of $V^{(0)} + kV^{(1)}$, one can obtain the strength factor matrices to order k using equation (10). The undetermined elements that occur in the first order

eigenvectors only introduce indeterminacies in the first order strength factor matrices corresponding to modes 3 to 5. These strength factors matrices can be written as

$$Z^{(1)3} = \begin{bmatrix} 0 & 0 & \times & 0 & 0 \\ 0 & 0 & \times & 0 & 0 \\ \times & \times & 0 & (-c_{34}q + c_{35}r) & (c_{34}r - c_{35}q) \\ 0 & 0 & (c_{43}q + c_{53}r) & 0 & 0 \\ 0 & 0 & (c_{43}r + c_{53}q) & 0 & 0 \end{bmatrix} \quad (26)$$

$$Z^{(1)4} = \begin{bmatrix} 0 & 0 & 0 & \times & \times \\ 0 & 0 & 0 & \times & \times \\ 0 & 0 & 0 & c_{34}q & -c_{34}r \\ \times & \times & -c_{43}q & qr(c_{45} + c_{54}) & -(c_{45}q^2 + c_{54}r^2) \\ \times & \times & -c_{43}r & (c_{45}r^2 + c_{54}q^2) & -qr(c_{45} + c_{54}) \end{bmatrix} \quad (27)$$

$$Z^{(1)5} = \begin{bmatrix} 0 & 0 & 0 & \times & \times \\ 0 & 0 & 0 & \times & \times \\ 0 & 0 & 0 & -c_{35}r & c_{35}q \\ \times & \times & -c_{53}r & -qr(c_{54} + c_{45}) & (c_{45}q^2 + c_{54}r^2) \\ \times & \times & -c_{53}q & -(c_{45}r^2 + c_{54}q^2) & qr(c_{45} + c_{54}) \end{bmatrix} \quad (28)$$

Here the non-zero elements of $Z^{(1)3-5}$ that are completely determined by the hydrodynamic matrix are again indicated by crosses. From equations (26)-(28) it is clear that the undetermined strength factors occur only in $S_{ij}(\mathbf{k}, \omega)$ $i, j = 3, 4, 5$ for the modes $\mu = 3, 4, 5$.

So far the undetermined coefficients $c_{\sigma\mu}$ $\sigma \neq \mu = 3, 4, 5$ are completely unspecified. They could be real, imaginary or complex. Applying the symmetry relations given by equation (13) to the strength factor matrices $Z^{(1)3-5}$ one obtains the following results for the undetermined coefficients c

$$\begin{aligned} c_{34} &= c_{43} = -c_{34}^* \\ c_{35} &= -c_{53} = -c_{35}^* \\ c_{45} &= c_{54} = c_{45}^* \end{aligned} \quad (29)$$

From the above relations it follows that c_{34} and c_{35} are imaginary and that c_{45} is real.

5. Concluding remarks. — The object of the present paper has been a reexamination of the problem of the hydrodynamically undetermined spectral densities in nematic liquid crystals, a problem first recognized by Forster [2]. We have shown that if one uses entropy and pressure as thermodynamic variables in the description of the nematic liquid crystal that the undetermined strength factors occur in the cross correlations of entropy fluctuations and the longitudinal shear-director fluctuations and in correlations

among the latter fluctuations. Actually, that the spectral densities of the longitudinal shear-director fluctuations do contain hydrodynamically undetermined strength factors has not been recognized before.

One of the principal reasons for calculating hydrodynamic spectral densities is their connection with the spectrum of scattered light. In liquid crystals the central peak of the lightscattering spectrum is primarily due to director fluctuations and thus the indeterminacy in the spectral density linking entropy and director fluctuations will be of little consequence and the effect of the undetermined strength factors in the spectral density of the director fluctuations is small compared to the zeroth order strength factors. Thus we may conclude that the problem of the hydrodynamically undetermined spectral densities will be of little consequence for the analysis of light-scattering-spectra.

Finally we wish to point out that the case that $M^{(1)}$ has a degenerate eigenvalue is not restricted to the case of nematic liquid crystals. For multicomponent fluids $M^{(1)}$ will also have a degenerate eigenvalue. This also leads to undetermined strength factors in the spectral densities. This problem will be treated elsewhere.

Acknowledgments. — This work has been supported by the award of a NATO grant. (806) and by the award of a NRC of Canada Studentship to DLC.

References

- [1] Groupe d'Etude des Cristaux Liquides (Orsay), *J. Chem. Phys.* **51** (1969) 816.
- [2] FORSTER, D., *Ann. Phys.* (N.Y.) **85** (1974) 505.
- [3] FORSTER, D., *Hydrodynamic Fluctuations, Broken Symmetry and Correlation Functions* (W. A. Benjamin) 1975, Ch. 11.
- [4] See e.g. SCHIFF, L. I., *Quantum Mechanics*, Third Edition (Mc Graw-Hill) 1968, section 31.
- [5] LANDAU, L. D. and LIFSHITZ, E. M., *Quantum Mechanics* (Addison Wesley) 1965, section 39 (Problem 2).
- [6] HAMEKA, H., *Advanced Quantum Chemistry* (Addison Wesley) 1965, section 4-3.
- [7] In some treatments of degenerate perturbation theory these remain coefficients are also set equal to zero (see e.g. ref. [4]). Such a procedure is incorrect as becomes clear when one considers the second order perturbation equation.
- [8] There is evidence that the first term with $k > 2$ in the expansion of the hydrodynamic matrix need not to be of order k^3 . See e.g. ERNST and DORFMAN, J. R., *J. Stat. Phys.* **12** (1975) 311. However such a feature does not alter our analysis or conclusions as we do not use the explicit form of the contributions to the hydrodynamic matrix with $k > 2$.
- [9] LEKKERKERKER, H. N. W. and BOON, J. P., *Phys. Rev. A* **10** (1974) 1355.
- [10] FORSTER, D. *et al.*, *Phys. Rev. Lett.* **26** (1971) 1016. For a more detailed exposition see MARTIN, P. C., PARODI, O. and PERSHAN, P. J., *Phys. Rev. A* **6** (1972) 2401.
-