Fluctuations and scattering of light in nematic liquid crystals

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(Submitted 17 May 1982)
Zh. Eksp. Teor. Fiz. **82**, 1777–1787 (November 1982)

We investigate longitudinal and transverse uniaxial and biaxial fluctuations in nematic liquid crystals. We show that the director fluctuations make a singular contribution not only to the longitudinal but also to the biaxial fluctuations. A general expression is constructed in the Gaussian approximation for the fluctuating contribution of the tensor order parameter to the thermodynamic potential of the liquid crystal. When account is taken of the spatial dispersion in the approximation quadratic in the wave vector, this expression contains twelve independent coefficients. In particular, for the difference $K_{33} - K_{11}$ of the Frank moduli it predicts a cubic dependence on the order parameter. The correlation function of the orientation fluctuation is calculated for both the nematic and the isotropic phase. A general analysis is presented of the conditions for the observation longitudinal and biaxial fluctuations in the usual light-scattering experimental geometry.

PACS numbers: 61.30.Gd, 61.30.Cz

One of the characteristic features of nematic liquid crystals (NLC) is the existence of strongly developed fluctuations of the director orientation. These fluctuations have in the absence of an external field the character of critical opalescence, and it is they which cause the strong light scattering in NLC.[1] At the same time, two other types of fluctuation should appear in nematics, namely, biaxial due to local disturbances of the uniaxiality of the NLC, and longitudinal due to changes in the degree of ordering of the system. The change of the ordering can take place spontaneously ("classical fluctuations") or on account of director fluctuations. The latter contribution to the longitudinal fluctuations is a property of all system with continuous symmetry, by virtue of the "modulus-conservation principle."[2] A simultaneous description of all three types of fluctuation was offered by Stratonovich,[3] who used the thermodynamic Maier-Saupe potential, and by Pokrovskiĭ and Kats[4] for a more general model of the potential.[1)] In the solution of this problem the ordering in the NLC was described by a tensor order parameter $S_{\alpha\beta}(\mathbf{r})$, and the thermodynamic-potential terms that took into account the spatial dispersion were taken to be the invariants $(\partial S_{\alpha\beta}/\partial x_\gamma)^2$ and $(\partial S_{\alpha\beta}/\partial x_\beta)^2$.

The fluctuation investigations in the cited papers, however, cannot be regarded as complete, since the terms with spatial dispersion were taken into account in the thermodynamic-potential expansion in Refs. 3 and 4 were taken into acount only in the lowest order in the degree of ordering. In particular, the two invariants cited above give only two independent orientational elastic moduli rather than the three obtained in the Oseen-Frank theory of NLC and actually observed in experiment.[1,5]

We derive here in a quadratic approximation a general expression for the fluctuation part of the free energy. This expression yields, when the fluctuations are described by the method of Ref. 4, an exact expression that generalizes the results of Refs. 3 and 4 for the correlation matrix in the Gaussian approximation. A unified description is presented for the fluctuations in both the nematic (N) and isotropic (I) plases of the NLQ. In the nematic phase are considered the classic and singular contributions to the longitudinal and biaxial fluctuations. The results are used to calculate the scattered-light intensity and to find the general conditions for observing the longitudinal and biaxial fluctuations.

1. TYPES OF FLUCTUATIONS IN NLC

The order parameter in NLC is a generally biaxial second-rank symmetric tensor $S_{\alpha\beta}(\mathbf{r})$ with zero trace.[1] Its equilibrium value in a uniaxial NLC is of the form

$$S_{\alpha\beta}^0 = S(n_\alpha^0 n_\beta^0 - {}^1/_3\delta_{\alpha\beta}), \tag{1}$$

where $\mathbf{n}^0$ is the equilibrium value of the director, S is a constant having the meaning of the degree of ordering of the long axes of the molecules along $\mathbf{n}^0$ ($S = 0$ in the isotropic phase). The fluctuations of the order parameter

$$\varphi_{\alpha\beta}(\mathbf{r}) = S_{\alpha\beta}(\mathbf{r}) - S_{\alpha\beta}^0 \tag{2}$$

are a symmetric tensor with zero trace. A general tensor of this type can be parametrized in the orthogonal coordinate frame $\mathbf{e}_1$, $\mathbf{e}_2$, $\mathbf{n}^0$ in the form[4]

$$\varphi_{\alpha\beta}(\mathbf{r}) = \varphi_{\alpha\beta}^{\perp(1)}(\mathbf{r}) + \varphi_{\alpha\beta}^{\perp(2)}(\mathbf{r}) + \varphi_{\alpha\beta}^{\parallel}(\mathbf{r}), \tag{3}$$

where

$$\varphi_{\alpha\beta}^{\perp(1)}(\mathbf{r}) = \xi_1(\mathbf{r})(n_\alpha^0 e_{1\beta} + n_\beta^0 e_{1\alpha}) + \xi_2(\mathbf{r})(n_\alpha^0 e_{2\beta} + n_\beta^0 e_{2\alpha}),$$

$$\varphi_{\alpha\beta}^{\perp(2)}(\mathbf{r}) = \xi_3(\mathbf{r})(e_{1\alpha}e_{2\beta} + e_{1\beta}e_{2\alpha}) + \xi_4(\mathbf{r})(e_{1\alpha}e_{1\beta} - e_{2\alpha}e_{2\beta}), \tag{4}$$

$$\varphi_{\alpha\beta}^{\parallel}(\mathbf{r}) = \sigma(\mathbf{r})(n_\alpha^0 n_\beta^0 - {}^1/_3\delta_{\alpha\beta}).$$

Here ξ_1, ξ_2, ξ_3, ξ_4, and σ are new variables. Each of the quantities $\varphi_{\alpha\beta}^{\perp(1)}$, $\varphi_{\alpha\beta}^{\perp(2)}$, and $\varphi_{\alpha\beta}^{\parallel}$ admits of a simple interpretation as a change of the equilibrium tensor $S_{\alpha\beta}^0$ following a definite transformation of the axes $\{\mathbf{e}_1, \mathbf{e}_2, \mathbf{n}^0\} \to \{\tilde{\mathbf{e}}_1, \tilde{\mathbf{e}}_2, \tilde{\mathbf{n}}\}$.

The fluctuations $\varphi_{\alpha\beta}^{\perp(1)}$ are determined by the transformation

$$\tilde{\mathbf{e}}_1 = \mathbf{e}_1 - \frac{\xi_1}{S}\mathbf{n}^0, \quad \tilde{\mathbf{e}}_2 = \mathbf{e}_2 - \frac{\xi_2}{S}\mathbf{n}^0, \quad \tilde{\mathbf{n}} = \mathbf{n}^0 + \frac{\xi_1}{S}\mathbf{e}_1 + \frac{\xi_2}{S}\mathbf{e}_2.$$

This transformation is an infinitely small rotation; the unit vector of the axis and the rotation angle are given by

$$(\xi_2/(\xi_1^2+\xi_2^2)^{1/2},\ -\xi_1/(\xi_1^2+\xi_2^2)^{1/2},\ 0),$$
$$\delta=(\xi_1^2+\xi_2^2)^{1/2}/S.$$

The fluctuations $\varphi^{\perp(1)}_{\alpha\beta}$ are determined by the transformations of the axes

$$\tilde{\mathbf{e}}_1=(\mathbf{e}_1\sin\psi+\mathbf{e}_2\cos\psi)(1+\zeta),$$
$$\tilde{\mathbf{e}}_2=(\mathbf{e}_1\cos\psi-\mathbf{e}_2\sin\psi)(1-\zeta),\quad \tilde{\mathbf{n}}=\mathbf{n}^0,$$

where

$$\operatorname{tg}2\psi=-\frac{\xi_3}{\xi_4},\quad \zeta=\frac{3}{2S}(\xi_3^2+\xi_4^2)^{1/2},$$

which constitutes dilatations in a plane perpendicular to $\mathbf{n}^0$ along the $\tilde{\mathbf{e}}_1$ and $\tilde{\mathbf{e}}_2$ directions, with respective coefficients $1+\zeta$ and $1-\zeta$, i.e., it is a biaxial transverse fluctuation.

Corresponding to the fluctuations $\varphi^{\parallel}_{\alpha\beta}$ is the transformation of the axes

$$\tilde{\mathbf{e}}_1=\mathbf{e}_1(1+\sigma/2S),\quad \tilde{\mathbf{e}}_2=\mathbf{e}_2(1+\sigma/2S),\quad \tilde{\mathbf{n}}=\mathbf{n}^0(1+\sigma/2S),$$

which determines the change of $S^0_{\alpha\beta}$ under a homogeneous scale transformation. This transformation corresponds in fact to a change of the coefficient S in (1), i.e., it is a longitudinal fluctuation.

The local oscillations of the director can contribute to the longitudinal[4] and biaxial fluctuations. To demonstrate this it suffices to consider the change of the tensor $S^0_{\alpha\beta}$ upon rotation of the vector $\mathbf{n}^0$, taking into account the conservation of its length

$$\mathbf{n}=\mathbf{n}^0+\delta\mathbf{n}=n^0+\delta n_\parallel\mathbf{n}^0+(\xi_1/S)\mathbf{e}_1+(\xi_2/S)\mathbf{e}_2.$$

Writing down the condition $n^2=n^{02}=1$ in the form

$$2\delta n_\parallel+\delta n_\parallel^2+(\xi_1/S)^2+(\xi_2/S)^2=0,$$

we find that the fluctuations of the order parameter are of the form

$$\varphi_{\alpha\beta}=S(n_\alpha n_\beta-{}^1/{}_3\delta_{\alpha\beta})-S_{\alpha\beta}{}^0=\varphi_{\alpha\beta}^{\perp(1)}(1+\delta n_\parallel)+\tilde{\xi}_3(e_{1\alpha}e_{2\beta}+e_{1\beta}e_{2\alpha})$$
$$+\tilde{\xi}_4(e_{1\alpha}e_{1\beta}-e_{2\alpha}e_{2\beta})+\tilde{\sigma}(n_\alpha{}^0n_\beta{}^0-{}^1/{}_3\delta_{\alpha\beta}),\tag{4a}$$

where

$$\tilde{\xi}_3=\frac{1}{S}\xi_1\xi_2,\quad \tilde{\xi}_4=\frac{1}{2S}(\xi_2^2-\xi_1^2),$$
$$\tilde{\sigma}=-\frac{3}{2S}(\xi_1^2+\xi_2^2),$$

i.e., in second order in ξ_1 and ξ_2 the director oscillation generate longitudinal ($\tilde{\sigma}$) and biaxial ($\tilde{\xi}_3$ and $\tilde{\xi}_4$) fluctuation. We neglect hereafter the term $\varphi^{\perp(1)}_{\alpha\beta}\delta n_\parallel$, which of fourth order of smallness in $\xi_{1,2}$. These fluctuations correspond to rotation of the coordinate system and do not change the independent invariants of the tensor $S_{\alpha\beta}$. The equations given above for $\tilde{\xi}_3$, $\tilde{\xi}_4$, and $\tilde{\sigma}$ can be obtained also from the vanishing of the variations of all the independent invariants of the order parameter. Such an approach was discussed in general form in Ref. 2. The onset of longitudinal fluctuations of this type is connected actually with the fact that the local deviations of the director decrease the degree of ordering of the system along $\mathbf{n}_0$, while the appearance of biaxial fluctuations can be easily understood with the uniaxial ellipsoid as the example: when its axis deviates from $\mathbf{n}^0$ the cross section in the plane perpendicular to $\mathbf{n}^0$ is no longer a circle.

The fluctuation tensor $\varphi'_{\alpha\beta}(\mathbf{r})$ in the isotropic phase, where there is no preferred direction $\mathbf{n}^0$, can be constructed in analogy with (3) and (4) by transforming to the spatial Fourier spectrum $\varphi_{\alpha\beta,\mathbf{q}}$ and be using for each Fourier component $m=\mathbf{q}/q$ as the preferred vector:

$$\varphi_{\alpha\beta,\mathbf{q}}=\xi'_{1,\mathbf{q}}(m_\alpha e_{1\beta}'+m_\beta e_{1\alpha}')+\xi'_{2,\mathbf{q}}(m_\alpha e_{2\beta}'+m_\beta e_{2\alpha}')$$
$$+\xi'_{3,\mathbf{q}}(e_{1\alpha}'e_{2\beta}'+e_{1\beta}'e_{2\alpha}')+\xi'_{4,\mathbf{q}}(e_{1\alpha}'e_{1\beta}'-e_{2\alpha}'e_{2\beta}')$$
$$+\sigma_{\mathbf{q}}'(m_\alpha m_\beta-{}^1/{}_3\delta_{\alpha\beta}).\tag{5}$$

2. ENERGY OF DISTORTION OF HOMOGENEOUS NLC

The thermodynamic potential of an NLC is a functional of the order parameter $S_{\alpha\beta}$. Since the potential must be invariant to homogenous rotations, it is a function of only the independent invariants of the tensor $S_{\alpha\beta}$. Following Refs. 2 and 4 we choose the invariants to be

$$x=S_{\alpha\beta}S_{\beta\alpha},\quad y=S_{\alpha\beta}S_{\beta\gamma}S_{\gamma\alpha},$$

i.e., $\Phi=\Phi(x,y)$. The condition $S_{\alpha\alpha}=0$ imposes[4] on x and y the restriction $x^3\geqslant 6y^2$, which is obvious from the identity

$$x^3-6y^2=2(s_1-s_2)^2(s_2-s_3)^2(s_3-s_1)^2,$$

where s_1, s_2, and s_3 are the eigenvalues of the matrix $\hat{S}_{\alpha\beta}$. It can be seen from this that the equation $x^3=6y^2$ is equivalent to the condition that $S_{\alpha\beta}$ be a uniaxial tensor. In this case x and y are expressed in terms of S as follows: $x=2S^2/3$, $y=2S^3/9$.

The condition for the extremum of the function $\Phi(x,y)$ at $x^3=6y^2$ is[4]

$$2S\partial\Phi/\partial x+S^2\partial\Phi/\partial y=0.\tag{6}$$

The solution $S=0$ corresponds to the isotropic phase. It is assumed here that the biaxial solution

$$\partial\Phi/\partial x=0,\quad \partial\Phi/\partial y=0,$$

which gives the unconditional extremum of $\Phi(x,y)$ is not realized physically.

To check whether the second variation is positive, we expand $\Phi(x,y)$ in the vicinity of the equilibrium point in a Taylor series accurate to terms of second order in δx and δy:

$$\delta\Phi_N=3\frac{\partial\Phi}{\partial x}\varphi_{\alpha\beta}\varphi_{\beta\alpha}-6\frac{\partial\Phi}{\partial x}n_\alpha{}^0n_\beta{}^0\varphi_{\alpha\gamma}\varphi_{\gamma\beta}$$
$$+\left(2S^2\frac{\partial^2\Phi}{\partial x^2}+2S^3\frac{\partial^2\Phi}{\partial x\,\partial y}+\frac{1}{2}S^4\frac{\partial^2\Phi}{\partial y^2}\right)(n_\alpha{}^0n_\beta{}^0\varphi_{\alpha\beta})^2.\tag{7}$$

We have used here Eq. (6) and the equalities

$$\delta x=2S_{\alpha\beta}{}^0\varphi_{\beta\alpha}+\varphi_{\alpha\beta}\varphi_{\beta\alpha},\quad \delta y=3S_{\alpha\beta}{}^0S_{\beta\gamma}{}^0\varphi_{\alpha\gamma}+3S_{\alpha\beta}{}^0\varphi_{\alpha\gamma}\varphi_{\gamma\beta},$$

which are valid accurate to terms of order $\hat{\varphi}^2$.

For the nematic phase we obtain from (4) and (7)

$$\delta\Phi_N={}^1/{}_2[A_1(\xi_3^2+\xi_4^2)+A_2\sigma^2],\tag{8}$$

where

$$A_1=12\frac{\partial\Phi}{\partial x},\quad A_2=\frac{4}{3}\left(-\frac{\partial\Phi}{\partial x}+\frac{4}{3}S^2\frac{\partial^2\Phi}{\partial x^2}+\frac{4}{3}S^3\frac{\partial^2\Phi}{\partial x\,\partial y}+\frac{1}{3}S^4\frac{\partial^2\Phi}{\partial y^2}\right)=\frac{\partial^2}{\partial S^2}[\Phi(x,y)],\tag{9}$$

with all the derivatives calculated under the condition $x^3 = 6y^2$. The coefficient A_1 was obtained in Ref. 4.

Since $S^0_{\alpha\beta} = 0$ in the isotropic phase, $\delta x = \varphi_{\alpha\beta}\varphi_{\beta\alpha}$ and $\delta y = 0$. We then have from (5)

$$\delta\Phi_I={}^1\!/_4A\varphi_{\alpha\beta}\varphi_{\beta\alpha}={}^1\!/_2A(\xi_1'^2+\xi_2'^2+\xi_3'^2+\xi_4'^2+{}^1\!/_3\sigma'^2),\tag{10}$$

where $A = 4\partial\Phi/\partial x$ at the point $x = y = 0$.

The conditions for the stability of the nematic phase are

$$A_1>0,\quad A_2>0.\tag{11}$$

The inequality $A > 0$ corresponds to the condition for the stability of the isotropic phase.

The temperature T_c of the first-order phase transition $I\leftrightarrow N$ is determined by the equality of the thermodynamic potentials and by the conditions for the stability of both phases

$$\begin{gathered}\Phi(x,y,P,T_c)|_{x^3=6y^2}=\Phi(0,0,P,T_c),\\ A_1(T_c)>0,\quad A_2(T_c)>0,\quad A(T_c)>0.\end{gathered}\tag{12}$$

Here P is the pressure.

The temperature T_1 at which the isotropic phase loses its stability is determined from the condition $A(T_1) = 0$, and that for the nematic phase is determined from (11) in which at least one of the coefficients A_1 or A_2 vanishes. If the derivatives

$$\frac{\partial^2\Phi}{\partial x^2}\quad\frac{\partial^2\Phi}{\partial x\,\partial y}\quad\frac{\partial^2\Phi}{\partial y^2}$$

have no singularities,[2)] A_1 and A_2 can vanish in the following cases.

1. $\partial\Phi/\partial y\neq 0$. Substituting (6) in (9) we see readily that A_2 always vanishes earlier than $A_1\sim\partial\Phi/\partial x$. In this case the relations $A_1\sim\partial\Phi/\partial x$, are satisfied at the stability-loss point T_2, and the degree of ordering $S(T)$ differs from zero in accord with (6).

2. $\partial\Phi/\partial y = 0$ at $T = T_3$. It follows from (6) that in this case $A_1(T_3) = 0$. If S also tends to zero in this case, A_2 vanishes according to (9) together with A_1, i.e., $T_3 = T_1 = T_2 = T_c$, which corresponds to the tricritical point of the isotropic, nematic, and biaxial phases.[6] If, however $S(T_3)\neq 0$, then either A_1 vanishes before A_2 (this case corresponds to a second-order transition into the biaxial phase[6]) or $\partial\Phi/\partial x$ and the sum of the terms containing S vanish in (9) simultaneously, i.e., $A_1 = A_2 = 0$, giving a tricritical point.[2]

When the vicinity of the $I\leftrightarrow N$ phase transition is described within the framework of the Landau–de Gennes model (see, e.g., Ref. 7), $\Phi(x, y, P, T)$ takes the form

$$\Phi(x,y)=\Phi(0,0)+{}^1\!/_2ax-{}^1\!/_3by+{}^1\!/_4cx^2,\tag{13}$$

where $a = a'(T - T^*)$, $a' > 0$, $c > 0$, $b > 0$; the last coefficient is assumed small. In this model

$$A_1=6a+4cS^2,\quad A_2={}^2\!/_3a-{}^4\!/_9bS+{}^4\!/_3cS^2,\quad A=2a.$$

Such a theory corresponds to our case 1. The first-order transition temperature is determined in it by the equality $T_c = T^* + b^2/27a'c$, and the temperatures T_1 and T_2 correspond to T^* and $T^{**} = T^* + b^2/24a'c$, which are seemingly the critical temperatures of the second-order phase transitions for the metastable isotropic and nematic phases. In this case $S(T^{**}) = b/4c > 0$. The temperature dependences of the coefficients A, A_1, and A_2 near the points T^* and T^{**} are given by (cf. Ref. 3)

$$A_1=\text{const},\quad A=2a'(T-T^*),$$

$$A_2=\frac{2}{9}b\left(\frac{3a'}{2c}\right)^{1/2}(T^{**}-T)^{1/2}+\frac{4}{3}a'(T^{**}-T).$$

3. FLUCTUATING CONTRIBUTION TO THE THERMODYNAMIC POTENTIAL

Whereas the order parameter is a function of a point, the thermodynamic potential depends not only on the values of the order parameter itself, but also on its gradients. Assuming the inhomogeneities to be smooth enough, we shall take into account spatial derivatives of order not higher than the second. The expansion of the thermodynamic potential includes terms of the form $S_{\alpha\beta}\ldots S_{\gamma\delta}$ and $S_{\alpha\beta}\ldots S_{\gamma\delta}\nabla_\rho S_{\mu\nu}\nabla_\varepsilon S_{\varphi\psi}$, contracted with respect to all pairs of indices. There are no terms linear in the gradients by virtue of the symmetry of nematics.[1] In the derivation of the general expression for the fluctuating part of the potential we confine ourselves to terms quadratic in $\varphi_{\alpha\beta}$. They exclude from consideration different terms that differ by the value of the surface energy, it is convenient to transform to the spatial Fourier spectrum $\varphi_{\alpha\beta,\mathbf{q}}$. (To simplify the notation we shall omit the subscript $\mathbf{q}$ hereafter.) The general expression for the fluctuation contribution to the potential will consist then of all the possible invariants obtainable by contracting the two tensors $\varphi_{\alpha\beta}$, an even number of vectors $\mathbf{q}$, and the tensors $S^0_{\alpha\beta}$. Taking into account the form of the tensor $S^0_{\alpha\beta}$ [see (1)], we can construct these invariants by contracting the two tensors $\varphi_{\alpha\beta}$, an even number of vectors $\mathbf{q}$ (0 or 2), as well as an even number of vectors $\mathbf{n}^0$. There are 14 such invariants:

$$\varphi_{\alpha\beta}\varphi_{\beta\alpha},\quad \varphi_{\alpha\beta}\varphi_{\beta\alpha}q_\gamma q_\gamma,\quad \varphi_{\alpha\beta}\varphi_{\beta\gamma}q_\alpha q_\gamma,\tag{14}$$

$$\begin{gathered}\varphi_{\alpha\beta}\varphi_{\beta\gamma}n_\alpha^0n_\gamma^0,\quad \varphi_{\alpha\beta}\varphi_{\gamma\delta}n_\alpha^0n_\beta^0n_\gamma^0n_\delta^0,\quad \varphi_{\alpha\beta}\varphi_{\beta\alpha}q_\gamma q_\delta n_\gamma^0n_\delta^0,\\ \varphi_{\alpha\beta}\varphi_{\beta\gamma}q_\delta q_\delta n_\alpha^0n_\gamma^0,\quad \varphi_{\alpha\beta}\varphi_{\beta\gamma}q_\alpha q_\delta n_\gamma^0n_\delta^0,\\ \varphi_{\alpha\beta}\varphi_{\gamma\delta}q_\alpha q_\beta n_\gamma^0n_\delta^0,\quad \varphi_{\alpha\beta}\varphi_{\gamma\delta}q_\alpha q_\gamma n_\beta^0n_\delta^0,\\ \varphi_{\alpha\beta}\varphi_{\beta\gamma}q_\delta q_\rho n_\alpha^0n_\gamma^0n_\delta^0n_\rho^0,\quad \varphi_{\alpha\beta}\varphi_{\gamma\delta}q_\alpha q_\rho n_\beta^0n_\gamma^0n_\delta^0n_\rho^0,\\ \varphi_{\alpha\beta}\varphi_{\gamma\delta}q_\rho q_\rho n_\alpha^0n_\beta^0n_\gamma^0n_\delta^0,\quad \varphi_{\alpha\beta}\varphi_{\gamma\delta}q_\rho q_\mu n_\alpha^0n_\beta^0n_\gamma^0n_\delta^0n_\rho^0n_\mu^0.\end{gathered}\tag{15}$$

In the isotropic phase, where there is no preferred direction $\mathbf{n}^0$, the first three invariants of (14) remain. We note that the invariants (14) and (15) stem from terms of different order of smallness in S. Thus, only 3 invariants (14) are preserved in second order in S, 9 invariants in the third, 13 in the fourth, and all 14 in the fifth. The expression for the thermodynamic potential should contain *a priori* all invariants with arbitrary coefficients that depend on S. It can be seen from (7), however, that the coefficients of $\varphi_{\alpha\beta}\varphi_{\beta\alpha}$ and $n_\alpha^0 n_\beta^0 \varphi_{\alpha\gamma}\varphi_{\gamma\beta}$ are actually dependent—their ratio is equal to -2. The reason for this connection is that the expansion (7) is carried at an extremum point of $\Phi(x, y)$, something not taken into account in the general derivation of the invariants.

For the calculations that follow it is convenient to choose

$$\mathbf{e}_2=[\mathbf{n}^0\times\mathbf{q}]/q\sin\theta,\quad \mathbf{e}_1=[\mathbf{e}_2\times\mathbf{n}^0]$$

where θ is the angle between the vectors $\mathbf{n}^0$ and $\mathbf{q}$ (Ref. 1). Using these unit vectors in Eqs. (4) and summing the invariants (14) and (15) with 13 arbitrary coefficients, we obtain

$$\delta\Phi_N=\tfrac{1}{2}[K_1\xi_1^2+K_2\xi_2^2+C_1(\xi_3^2+\xi_4^2)+C_2\sigma^2+2D(\xi_1\xi_4+\xi_2\xi_3)+2H\xi_1\sigma+2F\xi_4\sigma], \quad (16)$$

where

$$K_i=q^2[K_{ii}+(K_{33}-K_{ii})\cos^2\theta]/S^2,$$
$$C_i=A_i+q^2(b_i+c_i\cos^2\theta),\quad i=1,2; \quad (17)$$
$$D=q^2d\sin2\theta,\quad H=q^2h\sin2\theta,$$
$$F=q^2f\sin^2\theta.$$

Here $A_{1,2}, b_{1,2}, c_{1,2}, d, f, h, K_{ii}, i=1,2,3$ are independent coefficients. We point out that the modes ξ_1 and ξ_2 have not four but three independent coefficients, corresponding to the number of Frank elastic moduli in NLC [this decreases the total number of coefficients in (17) to 12]. We note that $1/2(K_1\xi_1^2+K_2\xi_2^2)$ in the $\mathbf{r}$-representation takes the form of the usual NLC energy

$$\tfrac{1}{2}K_{11}(\operatorname{div}\mathbf{n})^2+\tfrac{1}{2}K_{22}(\mathbf{n}^0\operatorname{rot}\mathbf{n})^2+\tfrac{1}{2}K_{33}[\mathbf{n}^0\times\operatorname{rot}\mathbf{n}]^2,$$

where $\mathbf{n}=\mathbf{n}^0+(\xi_1/S)\mathbf{e}_1+(\xi_2/S)\mathbf{e}_2$.

It can be seen from the foregoing construction that all these coefficients are made up of terms of different order in S. In particular, the Frank moduli can be represented in the form

$$K_{11}=k_1S^2+g_1S^3+\ldots,\quad K_{22}=k_2S^2+g_2S^3+\ldots,$$
$$K_{33}=k_1S^2+g_3S^3+\ldots, \quad (18)$$

where $k_{1,2}$ and $g_{1,2,3}$ are independent constants. It follows from this, in particular that $K_{11}-K_{33}\sim S^3$, a fact that lends itself to experimental verification.

Using (5) and (14) we obtain a similar equation for the fluctuation contribution to the thermodynamic potential in the isotropic phase

$$\delta\Phi_I=\tfrac{1}{2}[A+q^2(L_1+\tfrac{1}{2}L_2)](\xi_1'^2+\xi_2'^2)+\tfrac{1}{2}(A+q^2L_1)(\xi_3'^2+\xi_4'^2)+\tfrac{1}{6}[A+q^2(L_1+\tfrac{2}{3}L_2)]\sigma'^2, \quad (19)$$

where L_1 and L_2 are certain constants.

The condition that the quadratic form (16) be positive-definite are

$$K_1>0,\quad K_2>0,\quad K_1C_1-D^2>0,\quad K_2C_1-D^2>0,$$
$$(K_1C_1-D^2)(K_1C_2-H^2)>(FK_1-DH)^2. \quad (20)$$

From this it follows, in particular, that $C_1>0$ and $C_2>0$.

The analogous conditions for (19) are written as

$$A>0,\quad L_1>0,\quad L_1+\tfrac{2}{3}L_2>0. \quad (21)$$

4. CORRELATION FUNCTION OF THE ORIENTATION FLUCTUATIONS IN NLC

From Eqs. (4) and (4a), using the identity

$$\delta_{\alpha\beta}=e_{1\alpha}e_{1\beta}+e_{2\alpha}e_{2\beta}+n_\alpha^0n_\beta^0$$

and the equality

$$\mathbf{e}_1=(\mathbf{m}-\mathbf{n}^0\cos\theta)/\sin\theta,\quad \mathbf{m}=\mathbf{q}/q,$$

we obtain for the chosen system of unit vectors the correlation function of the orientation fluctuations

$$\begin{aligned}G_{\alpha\beta\gamma\delta,N}&\equiv\langle\varphi_{\alpha\beta}\varphi_{\gamma\delta}\rangle\\
&=\langle\xi_1^2\rangle(n_\alpha^0n_\gamma^0A_{\beta\delta}+n_\alpha^0n_\delta^0A_{\beta\gamma}+n_\beta^0n_\gamma^0A_{\alpha\delta}+n_\beta^0n_\delta^0A_{\alpha\gamma})\\
&+\langle\xi_2^2\rangle(n_\alpha^0n_\gamma^0B_{\beta\delta}+n_\alpha^0n_\delta^0B_{\beta\gamma}+n_\beta^0n_\gamma^0B_{\alpha\delta}+n_\beta^0n_\delta^0B_{\alpha\gamma})\\
&+\langle\bar\xi_3^2\rangle(A_{\alpha\gamma}B_{\beta\delta}+A_{\alpha\delta}B_{\beta\gamma}+A_{\beta\gamma}B_{\alpha\delta}+A_{\beta\delta}B_{\alpha\gamma})\\
&+\langle\bar\xi_4^2\rangle(A_{\alpha\beta}-B_{\alpha\beta})(A_{\gamma\delta}-B_{\gamma\delta})\\
&+\langle\bar\sigma^2\rangle D_{\alpha\beta}(\mathbf{n}^0)D_{\gamma\delta}(\mathbf{n}^0)+\langle\xi_2\bar\xi_3\rangle(B_{\alpha\gamma}C_{\beta\delta}+B_{\alpha\delta}C_{\gamma\beta}+B_{\beta\gamma}C_{\alpha\delta}+B_{\beta\delta}C_{\alpha\gamma})\\
&+\langle\xi_1\bar\xi_4\rangle[C_{\alpha\beta}(A_{\gamma\delta}-B_{\gamma\delta})+C_{\gamma\delta}(A_{\alpha\beta}-B_{\alpha\beta})]\\
&+\langle\xi_1\bar\sigma\rangle[D_{\alpha\beta}(\mathbf{n}^0)C_{\gamma\delta}+D_{\gamma\delta}(\mathbf{n}^0)C_{\alpha\beta}]\\
&+\langle\bar\xi_4\bar\sigma\rangle[D_{\alpha\beta}(\mathbf{n}^0)(A_{\gamma\delta}-B_{\gamma\delta})+D_{\gamma\delta}(\mathbf{n}^0)(A_{\alpha\beta}-B_{\alpha\beta})],\end{aligned} \quad (22)$$

where

$$A_{\alpha\beta}=\sin^{-2}\theta[m_\alpha m_\beta-\cos\theta(n_\alpha^0m_\beta+n_\beta^0m_\alpha)+n_\alpha^0n_\beta^0\cos^2\theta],$$
$$B_{\alpha\beta}=\delta_{\alpha\beta}-n_\alpha^0n_\beta^0-A_{\alpha\beta},$$
$$C_{\alpha\beta}=\sin^{-1}\theta(n_\alpha^0m_\beta+n_\beta^0m_\alpha-2n_\alpha^0n_\beta^0\cos\theta),$$
$$D_{\alpha\beta}(\mathbf{n}^0)=(n_\alpha n_\beta-\tfrac{1}{3}\delta_{\alpha\beta}),\quad \bar\xi_j=\xi_j+\tilde\xi_j,\quad \bar\sigma=\sigma+\tilde\sigma,\quad j=3,4.$$

To calculate the mean squared fluctuations in the nematic phase it suffices to invert the matrix of the quadratic form (16).[8] The problem is greatly simplified because this form is a sum of two independent forms of the variables ξ_2, ξ_3 and ξ_1, ξ_4, σ. Inverting the matrices of these quadratic forms we have

$$\langle\xi_1^2\rangle=T(C_1C_2-F^2)/\Delta_2,\quad \langle\xi_2^2\rangle=TC_1/\Delta_1,$$
$$\langle\xi_3^2\rangle=TK_2/\Delta_1,\quad \langle\xi_4^2\rangle=T(K_1C_2-H^2)/\Delta_2,$$
$$\langle\sigma^2\rangle=T(K_1C_1-D^2)/\Delta_2; \quad (23)$$
$$\langle\xi_2\xi_3\rangle=-TD/\Delta_1,\quad \langle\xi_1\xi_4\rangle=-T(DC_2-HF)/\Delta_2,$$
$$\langle\xi_1\sigma\rangle=-T(C_1H-DF)/\Delta_2,\quad \langle\xi_4\sigma\rangle=-T(K_1F-DH)/\Delta_2, \quad (24)$$

where

$$\Delta_1=K_2C_1-D^2,\quad \Delta_2=K_1C_1C_2+2DHF-D^2C_2-H^2C_1-F^2K_1.$$

If the terms containing $\mathbf{q}$ in (23) are assumed small, we can write accurate to terms of order q^2

$$\langle\xi_1^2\rangle = TS^2/q^2\mathcal{K}_1(\theta),\quad \langle\xi_2^2\rangle = TS^2/q^2\mathcal{K}_2(\theta), \tag{25}$$

$$\langle\xi_3^2\rangle = T\{A_1+q^2[b_1+c_1\cos^2\theta - S^2d^2\sin^2 2\theta/\mathcal{K}_2(\theta)]\}^{-1},$$

$$\langle\xi_4^2\rangle = T\{A_1+q^2[b_1+c_1\cos^2\theta - S^2d^2\sin^2 2\theta/\mathcal{K}_1(\theta)]\}^{-1}, \tag{26}$$

$$\langle\sigma^2\rangle = T\{A_2+q^2[b_2+c_2\cos^2\theta - S^2h^2\sin^2 2\theta/\mathcal{K}_1(\theta)]\}^{-1},$$

where

$$\mathcal{K}_i(\theta) = K_{ii} + (K_{33}-K_{ii})\cos^2\theta \quad (i=1,\,2).$$

We point out that the fluctuations $\langle\xi_1^2\rangle$ and $\langle\xi_2^2\rangle$ in (25) coincide in this approximation with de Gennes' known results.[1]

All the nonzero correlators of the nonclassical quantities $\tilde{\xi}_3$, $\tilde{\xi}_4$, and $\tilde{\sigma}$ can be represented with the aid of (4a) and (25) in the Gaussian approximation in the form

$$\langle\tilde{\xi}_3^2\rangle = \frac{2S^2T^2}{\pi^3 qK_{11}K_{22}}\int f_+(x_1)f_-(x_2)\,d\Gamma,$$

$$\langle\tilde{\xi}_4^2\rangle = \frac{1}{9}\langle\tilde{\sigma}^2\rangle$$

$$= \frac{S^2T^2}{\pi^3 q}\int\left[\frac{1}{K_{11}^2}f_+(x_1)f_-(x_1) + \frac{1}{K_{22}^2}f_+(x_2)f_-(x_2)\right]d\Gamma,$$

$$\langle\tilde{\xi}_4\tilde{\sigma}\rangle = \frac{3S^2T^2}{\pi^3 q}\int\left[\frac{1}{K_{11}^2}f_+(x_1)f_-(x_1) - \frac{1}{K_{22}^2}f_+(x_2)f_-(x_2)\right]d\Gamma,$$

where

$$\int d\Gamma = \int_0^\infty\int_{-1}^{1}\int_0^{2\pi} du\,dv\,dw,$$

$$f_\pm(x_j) = u[4u^2 \pm 4u\rho + 1 + (x_j-1)(2uv\pm\cos\theta)^2]^{-1},$$

$$\rho = v\cos\theta + (1-v^2)^{1/2}\sin\theta\cos w,\quad x_j = K_{33}/K_{jj}.$$

One of the inner integrals (with respect to u or w) can be easily calculated here.

All the cross correlators in (22), made up of classical and nonclassical quantities, are zero in the Gaussian approximation.

In the isotropic phase we have from (5) and (19)

$$G_{\alpha\beta\gamma\delta,I} = \frac{TE_{\alpha\beta\gamma\delta}(\mathbf{m})}{A+q^2(L_1+{}^1/_2L_2)} + \frac{3TD_{\alpha\beta}(\mathbf{m})D_{\gamma\delta}(\mathbf{m})}{A+q^2(L_1+{}^2/_3L_2)} + T\frac{2I_{\alpha\beta\gamma\delta} - 3D_{\alpha\beta}(\mathbf{m})D_{\gamma\delta}(\mathbf{m}) - E_{\alpha\beta\gamma\delta}(\mathbf{m})}{A+q^2L_1}, \tag{27}$$

where

$$E_{\alpha\beta\gamma\delta}(\mathbf{m}) = \delta_{\alpha\gamma}m_\beta m_\delta + \delta_{\alpha\delta}m_\gamma m_\beta + \delta_{\beta\gamma}m_\alpha m_\delta + \delta_{\beta\delta}m_\alpha m_\gamma - 4m_\alpha m_\beta m_\gamma m_\delta, \tag{28}$$

$$I_{\alpha\beta\gamma\delta} = {}^1/_2\delta_{\alpha\gamma}\delta_{\beta\delta} + {}^1/_2\delta_{\alpha\delta}\delta_{\beta\gamma} - {}^1/_3\delta_{\alpha\beta}\delta_{\gamma\delta}.$$

Equation (27) agrees with the result of Stratonovich.[3]

5. CONDITIONS FOR OBSERVING LIGHT SCATTERING BY BIAXIAL AND LONGITUDINAL FLUCTUATIONS

When light scattering in NLC is considered it is usually assumed[1] that the light propagates just as in an isotropic medium. In this case the intensity of the light scattering by the dielectric-tensor fluctuations $\delta\varepsilon_{\alpha\beta}$ can be written in the form[9]

$$I_\beta^\alpha(\mathbf{q}) \sim T_{\beta\gamma}(\mathbf{k}_p)T_{\beta\mu}^*(\mathbf{k}_p)\langle\delta\varepsilon_{\gamma\varphi,\,\mathbf{q}}\delta\varepsilon_{\mu\psi,\,-\mathbf{q}}\rangle E_\varphi E_\psi^*, \tag{29}$$

where $\mathbf{q} = \mathbf{k}_{\rm in} - \mathbf{k}_{\rm sc}$, $\mathbf{k}_{\rm in}$ and $\mathbf{k}_{\rm sc}$ are the wave vectors and α and β are the polarization vectors of the incident and scattered light, and $\mathbf{E} = \alpha E_0$, where E_0 is the amplitude of the incident light and

$$T_{ij}(\mathbf{k}) = \delta_{ij} - k_ik_j/k^2. \tag{30}$$

The Greek subscripts in the right-hand side of (29) are the unit vectors of the orthogonal coordinate system, one of which coincides with β, and there is no summation over β in (29).

In the light-scattering problem it is most convenient to use as the order parameter the anisotropic part of the dielectric tensor

$$S_{\alpha\beta}(\mathbf{r}) = M[\varepsilon_{\alpha\beta}(\mathbf{r}) - {}^1/_3\delta_{\alpha\beta}\varepsilon_{\gamma\gamma}(\mathbf{r})],$$

where M is a normalization constant. In this case

$$\langle\delta\varepsilon_{\alpha\beta,\,\mathbf{q}}\delta\varepsilon_{\gamma\delta,\,-\mathbf{q}}\rangle \propto G_{\alpha\beta\gamma\delta}(\mathbf{q}). \tag{31}$$

If we do not specify the order parameter,[4] the connection between $\langle\delta\varepsilon_{\alpha\beta,\mathbf{q}}\delta\varepsilon_{\gamma\delta,-\mathbf{q}}\rangle$ and $G_{\alpha\beta\gamma\delta}(\mathbf{q})$ differs from (31) in that the tensors $\varphi^{\perp(1)}_{\alpha\beta}, \varphi^{\perp(2)}_{\alpha\beta}, \varphi^{\parallel}_{\alpha\beta}$ of (3) are multiplied by inessential numerical coefficients.

In the nematic phase, the main contribution to the scattering is connected with the fluctuations of the director, i.e., with the modes $\langle\xi_1^2\rangle$ and $\langle\xi_2^2\rangle$. Therefore the biaxial and longitudinal fluctuations are easiest to observe in experimental geometries in which the director fluctuations make no contribution.

The condition for the absence of these contributions is the satisfaction of the equation

$$(\alpha\mathbf{e})[(\beta\mathbf{n}^0) - (\mathbf{p}\beta)(\mathbf{n}^0\mathbf{p})] + (\alpha\mathbf{n}^0)[(\mathbf{e}\beta) - (\mathbf{p}\mathbf{e})(\mathbf{p}\beta)] = 0 \tag{32}$$

for any $\mathbf{e}\perp\mathbf{n}^0$, $\mathbf{p} = \mathbf{k}_p/k_p$.

This condition can be easily obtained by substituting (4) in (29) and (39) and taking into account the statistical independence of the modes ξ_1 and ξ_2. Recognizing that the scattered wave is transverse, $(\mathbf{p}\cdot\beta) = 0$, we have from (32)

$$\mathbf{e}[\alpha(\beta\mathbf{n}^0) + \beta(\alpha\mathbf{n}^0)] = 0.$$

Since this equation should be satisfied for any $\mathbf{e}\perp n^0$, it is equivalent to the relation

$$\alpha(\beta\mathbf{n}^0) + \beta(\alpha\mathbf{n}^0) = l\mathbf{n}^0, \tag{33}$$

where $l = l(\alpha, \beta, \mathbf{n}^0)$ is a scalar function.

Considering the cases $l = 0$, $l \neq 0$; $\alpha = \beta$, $\alpha \neq \beta$, we find that (33) is satisfied only in the following cases:

$$(\alpha\mathbf{n}^0) = (\beta\mathbf{n}^0) = 0,\quad \mathbf{n}^0 = (\alpha\pm\beta)/[2(1\pm(\alpha\beta))]^{1/2}. \tag{34}$$

In the usual experimental geometry on light scattering[9] it is assumed that the incident light is directed along the x axis of the laboratory frame $\{x, y, z\}$, and the scattering is in the xy plane, the polarization α of the incident light taking on values z or y, and β of the scattered light is either z or lies in the xy plane.

Analyzing the conditions (34) in this coordinate system, we easily obtain experimental geometries in which there are

TABLE I. Light-scattering experimental geometries in which the director fluctuations make no contribution.

	1	2	3	4	5	6	7	8
α	z	z	z	z	y	y	y	y
β	z	z	xy	xy	z	z	xy	xy
$\mathbf{n}^0$	$\mathbf{z}$	$\mathbf{n}^0 \perp \mathbf{z}$	$\mathbf{p}$	$\boldsymbol{\alpha}\pm\boldsymbol{\beta}$	$\mathbf{x}$	$\boldsymbol{\alpha}\pm\boldsymbol{\beta}$	$\boldsymbol{\alpha}\pm\boldsymbol{\beta}$	$\mathbf{z}$

no contributions to the scattering from the modes $\langle \xi_1^2 \rangle$ and $\langle \xi_2^2 \rangle$. These geometries are listed in Table I. (In the table, α is the polarization of the incident light, β the polarization of the scattered light, and $\mathbf{n}^0$ the director direction.) In all the geometries, the scattering angle is φ, for which $\cos\varphi = (\mathbf{x}\cdot\mathbf{k}_p)/k_p$ is arbitrary. The geometries 1, 2, and 8 were cited earlier in Refs. 2 and 4, and the first condition of (34) in Ref. 3.

From Eqs. (22) and (31) we easily obtain the scattering intensities that correspond to these geometries:

$$1:\ I_z^z \sim {}^4/_9\langle \bar\sigma^2\rangle,\quad 2:\ I_z^z \sim \langle |\bar\xi_4 + {}^1/_3\bar\sigma|^2\rangle,\quad 3.5:\ I_{xy}^z = I_z^y \sim \langle \bar\xi_3^2\rangle,$$

$$4.6: I_{xy}^z = I_z^y \sim \frac{2\sin^2\varphi}{(3-\cos\varphi)^2}\langle \bar\xi_3^2\rangle + \frac{1}{4}\left\langle \left| \frac{1-3\cos\varphi}{3-\cos\varphi}\bar\xi_4 - \bar\sigma \right|^2 \right\rangle. \qquad (35)$$

$$7:\ I_{xy}^y \sim {}^1/_4\langle |(1\mp\cos\varphi)\bar\xi_4 \pm {}^1/_3(3\pm\cos\varphi)\bar\sigma|^2\rangle,$$

$$8:\ I_{xy}^y \sim \langle |\bar\xi_4 + {}^1/_3\bar\sigma\cos\varphi|^2\rangle.$$

The proportionality coefficient is the same in all these equations. The sign plus or minus in (35) for geometry 7 depends on whether the director is aligned with the vector $\boldsymbol{\alpha}+\boldsymbol{\beta}$ or $\boldsymbol{\alpha}-\boldsymbol{\beta}$. We point out that it follows from (17) and (24) that $\langle \xi_4^\sigma \rangle q^2$, and in the case of dispersion this cross correlator in (35) can be neglected. The classical and nonclassical contributions to (35) can be separated since they have different angular and temperature dependences.

For arbitrary polarization vectors $\boldsymbol{\alpha}$ and $\boldsymbol{\beta}$ satisfying only the condition of transversality of the electromagnetic waves, we can reconstruct from (34), using the values of $\boldsymbol{\alpha}$ and $\boldsymbol{\beta}$, the director orientations at which the modes $\langle \xi_1^2 \rangle$ and $\langle \xi_2^2 \rangle$ make no contribution to the light scattering. It is interesting to note that at $\boldsymbol{\alpha}\neq\boldsymbol{\beta}$ there exist three such directions of $\mathbf{n}^0$, which make up an orthogonal triad:

$$\mathbf{n}_1^0 \parallel \boldsymbol{\alpha}+\boldsymbol{\beta},\quad \mathbf{n}_2^0 \parallel \boldsymbol{\alpha}-\boldsymbol{\beta},\quad \mathbf{n}_3^0 \perp \boldsymbol{\alpha}, \boldsymbol{\beta}.$$

If the optical anisotropy is taken into account in the light scattering (see, e.g., Ref. 10), then Eqs. (29) and (30) cannot be used. It can be shown, however, that in the geometries 1–3, 5, and 8 the fluctuations of n make no contribution to the scattering even in the presence of optical anisotropy.

In conclusion, the author thanks L. Ts. Adzhemyan for interest in the work and for valuable advice, and E. I. Kats for a helpful discussion.

[1)] We note that the longitudinal fluctuations investigated in the cited papers differ in character, viz., classical fluctuations in Ref. 3 and those generated by the director fluctuations in Ref. 4.

[2)] Actually it suffices that the quantities $\partial^2\Phi/\partial x^2, S\partial^2\Phi/\partial x\partial y$, and $S^2\partial^2\Phi/\partial y^2$ have no singularities.

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Translated by J. G. Adashko