Concerning the scattering of light by nematic liquid crystals

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We investigate the role of longitudinal and biaxial fluctuations of the order parameter in the scattering of electromagnetic waves in the nematic phase. It is shown that singular longitudinal scattering predominates in a definite range of angles, polarizations, and frequencies. At short wavelengths, $\lambda \leq 3\times 10^{-6}$ cm, however, biaxial fluctuations make an appreciable contribution to the scattering. The general conditions for thermodynamic equilibrium are analyzed.

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1. INTRODUCTION

Light scattering in liquid crystal is the subject of many theoretical and experimental studies. The present status of the question is described in the reviews of Stephen and Straley[1] and Chandrasekhar.[2] The main cause of the anomalously strong scattering in liquid crystals are the fluctuations of the director orientation. Excitation of homogeneous transverse fluctuations (i.e., of uniform rotations of the director in the entire space) does not call for overcoming an erngy barrier. The corresponding light scattering has therefore the character of critical opalescence. This situation is common to a large class of systems having a continuous symmetry group, the so-called degenerate systems.[3]

Simple analysis shows that the transverse fluctuations do not lead to scattering of light when the polarization satisfies certain conditions (see below). For example, there is no scattering of the vectors of the initial and final polarizations are in the equatorial plane, i.e., in the plane perpendicular to the director. More accurately speaking, the transverse scattering is small in a small interval of angles at which the polarization is close to the equatorial plane. In this region, the scattering of the light is determined by fluctuations of another type, namely longitudinal and biaxial fluctuations. Nor do transverse fluctuations lead to scattering for polarization along the director if the wave vectors of the incident and scattered light are in the equatorial plane. By longitudinal fluctuations mean fluctuations of the modulus of the order parameter. From the general theory of degenerate systems[3] it is known that longitudinal fluctuations are also anomalously strong, although much weaker than the transverse ones.

The biaxial fluctuation is defined in the following manner. It is known that in liquid crystal the order parameter is a second-rank tensor $S_{\alpha\beta}$ with zero trace. Such a quantity is determined in the general case by five independent components. But the tensor $S_{\alpha\beta}$ of all the known nematic liquid crystals (NLC) is uniaxial, and is therefore determined by one vector, i.e., by three quantities. Naturally, in long-wave fluctuations the local properties of a liquid crystal remain unchanged, i.e., the tensor $S_{\alpha\beta}$ is uniaxial at each point as before. However, with decreasing wavelength of the fluctuations, an ever increasing role is assumed by fluctuations that upset the uniaxiality of the tensor $S_{\alpha\beta}$. Even in the wavelength region where these fluctuations are small, they turn out to be influential in the scattering, for example in the equatorial plane (at certain polarizations).

We investigate in the present paper the influence of longitudinal and biaxial fluctuations on light scattering in NLC. In Sec. 2 we investigate the general conditions of thermodynamic equilibrium of NLC and discuss the reason why all NLC are uniaxial. It is shown that this is caused by the well known "weakness" of the first-order phase transitions from the isotropic phase in the NLC. In Sec. 3 we consider longitudinal scattering of light and show that in the parameter region of interest to us the multiple scattering can be neglected. Section 4 is devoted to a general examination of the order-parameter fluctuations, including biaxial ones. The problem reduces to diagonalization of a certain quadratic form that determines the fluctuation energy. We succeed in effecting this diagonalization in the most general case. An analogous problem was solved by de Gennes[4] for the isotropic phase. In Sec. 5 we obtain the intensity of the light scattering due to the biaxial fluctuations.

Within the framework of the Landau theory, longitudinal (nonsingular) scattering and biaxial fluctuations in NLC were considered by Stratonovich.[5] He, however, did not take into account the free-energy terms cubic in the order parameter, nor the presence of two correlation lengths. For sufficiently short wavelengths (see below), Stratonovich's results agree qualitatively with ours.

2. GENERAL CONDITIONS FOR THERMODYNAMIC EQUILIBRIUM OF NLC

We consider a homogeneous NLC. The thermodynamic potential Φ of this phase is a function of the invariants of the order parameter $S_{\alpha\beta}$. Likely any symmetrical real second-rank tensor, $S_{\alpha\beta}$ has three invariants. We can choose these invariants to be, for example, the three eigenvalues s_1, s_2, and s_3 of the matrix $\hat{S}=(S_{\alpha\beta})$. It is more convenient, however, to use a different system of invariants: $\mathrm{Tr}\,\hat{S}$, $\mathrm{Tr}\,\hat{S}^2$, and $\mathrm{Tr}\,\hat{S}^3$, which are re-

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lated to s_1, s_2, and s_3 in obvious fashion. As already stated, $\mathrm{Tr}\,\hat{S}=0$, and we are left with only two independent invariants, $x=\mathrm{Tr}\,\hat{S}^2$ and $y=\mathrm{Tr}\,\hat{S}^3$.

The thermodynamic potential Φ is in the general case an arbitrary function of the two variables x and y. Assume that this function has an absolute minimum at the point (x_0, y_0). By the same token, this determines completely, in the state of the thermodynamic equilibrium, the two invariants and consequently all the eigenvalues. Equality of two eigenvalues would in this case be rather improbable happenstance. It does not follow from the foregoing reasoning, however, that the biaxial situation is the most general one. The point is that even if the absolute minimum (x_0, y_0) of the thermodynamic potential Φ does exist, it may turn out to be unattainable This circumstance is connected with definite inequalities that restrict the value of y for a given x. It is easy to derive the rigorous inequality

$$y \leqslant x^{3/2}/\sqrt{6}. \tag{1}$$

Therefore, if it turns out that $y_0 > x_0^{3/2}/\sqrt{6}$ at the minimum, then the minimum cannot be attained.

Another possible situation is one in which $\Phi(x, y)$ has no absolute minimum at all. In both cases, minimization of the thermodynamic potential, given $\mathrm{Tr}\,\hat{S}=0$, leads to the equations

$$2\frac{\partial\Phi}{\partial x}S_{\alpha\beta}+3\frac{\partial\Phi}{\partial y}\left[(\hat{S}^2)_{\alpha\beta}-\frac{1}{3}\delta_{\alpha\beta}\,\mathrm{Sp}\,\hat{S}^2\right]=0, \tag{2}$$

with $\partial\Phi/\partial x$ and $\partial\Phi/\partial y$ different from zero. It is easy to verify that Eq. (2) is satisfied by the uniaxial tensor $S_{\alpha\beta}=s(n_\alpha n_\alpha-\frac{1}{3}\delta_{\alpha\beta})$, where $\mathbf{n}$ is an arbitrary unit vector. The modulus of the order parameter s satisfies the condition

$$2\frac{\partial\Phi}{\partial x}+\frac{\partial\Phi}{\partial y}s=0. \tag{3}$$

We shall show that Eq. (2) has no other solutions. In fact, we transform to a coordinate frame in which $S_{\alpha\beta}$ is diagonal. We write down Eqs. (2) for $\alpha=\beta=1$ and $\alpha=\beta=2$:

$$2\frac{\partial\Phi}{\partial x}s_1=-3\frac{\partial\Phi}{\partial y}\left[s_1^2-\frac{2}{3}(s_1^2+s_2^2+s_1s_2)\right], \tag{4}$$

$$2\frac{\partial\Phi}{\partial y}s_2=-3\frac{\partial\Phi}{\partial y}\left[s_2^2-\frac{2}{3}(s_2^2+s_2^2+s_1s_2)\right]. \tag{5}$$

We divide Eq. (4) and (5) and change over the variable $z=s_1/s_2$. We obtain for z a cubic equation that does not depend on the values of $\partial\Phi/\partial x$ and $\partial\Phi/\partial y$. Since the uniaxial tensor $S_{\alpha\beta}$ is a solution of Eq. (2), the cubic equation for z has the roots $z=1$, $z=-2$, and $z=-1/2$. Consequently this equation has no other roots. Thus, if the absolute minimum of the function $\Phi(x, y)$ is unattainable (or nonexistent), then the order parameter can be only uniaxial.

There are weighty arguments for stating that this is precisely the situation for all known NLC. In fact, measurements of the heats of transition and of the critical scattering in the isotropic phase, of birefringence in electric in magnetic fields, and others show that the phase transition from an isotropic liquid into an NLC is quite close to a second-order transition. From the point of view of Landau's theory of phase transitions this means that the thermodynamic potential can be expanded near the phase-transition point in the series

$$\Phi={}^1\!/_2 A\,\mathrm{Sp}\,\hat{S}^2-{}^1\!/_3 B\,\mathrm{Sp}\,\hat{S}^3+{}^1\!/_4 C(\mathrm{Sp}\,\hat{S}^2)^2. \tag{6}$$

The coefficient A vanishes at a certain temperature T^* close to the phase-transition temperature T_c,

$$A=a(T-T^*). \tag{7}$$

The coefficient B should be small enough. It is precisely the smallness of B which determines the quantity

$$T_c-T^*=\frac{2}{27}\frac{B^2}{aC}, \tag{8}$$

which in turn determines the intensities of the critical phenomena. It is known from the experimental data[1] that $(T_c-T^*)/T_c\sim 10^{-3}$. The characteristic value of the order parameter is relatively small ($s_c=2B/3C$). On the other hand, the region of the existence of the NLC is small in comparison with the transition temperature. There are grounds therefore for assuming that the Landau theory is a good approximation in the entire region where the NLC exist. In the Landau model, the derivative $\partial\Phi/\partial y=-B/3$ differs from zero). We are therefore justified in expecting the order parameter to be uniaxial in the entire region of the existence of the NLC.

The reason why the coefficient B is small for all NLC is still unknown. We are stating only that the smallness of B leads to the uniaxiality of the order parameter. It is therefore of interest to investigate the phenomena that occur in liquid crystals under pressure. Were it to turn out that the coefficient B (or the heat of transition) decreases substantially with increasing pressure and it is possible to come close enough to the critical point, where $B=0$, then biaxial static configurations would be on a par with the uniaxial ones.

If we put $B=0$ in the Landau thermodynamic potential (6), then this potential depends only on one invariant, $\mathrm{Tr}\,\hat{S}^2$. The value of $\mathrm{Tr}\,\hat{S}^2$ can be represented as the square of the modulus of a five-dimensional vector whose components are (apart from inessential numerical factors) the independent components of the tensor $S_{\alpha\beta}$. Thus, at $B=0$ the thermodynamic potential has the symmetry group O_5 of rotations in five-dimensional space, which is much higher than the usual symmetry O_3. It is clear that the number of static configuration is substantially increased thereby. In addition, the number of zero-gap fluctuations (Goldstone fluctuations) responsible for the anomalous scattering also increases. At $B\neq 0$ only two Goldstone fluctuations connected with the transverse dimensions of the director are possible. At $B=0$ the number of Goldstone fluctuations is four (corresponding to the number of components of the five-dimensional components that are orthogonal to the initial component). These phenomena would be observable were it possible to cause the coefficient B to vanish in one way or another. In the real situations, however, B is small enough, so that biaxial fluctuations in a certain frequency region play the principal role (see Secs. 4 and 5).

It is useful in this connection to investigate the variations of the thermodynamic potential in the case of transverse fluctuations of the most general form. We shall again regard the potential Φ as an arbitrary function of x and y, and assume the equilibrium configuration to be uniaxial:

$$S_{\alpha\beta}=s(n_\alpha n_\beta-{}^1/_3\delta_{\alpha\beta})+\delta S_{\alpha\beta}^{\perp}, \tag{9}$$

where $\delta S^{\perp}_{\alpha\beta}$ satisfies the conditions

$$n_\alpha n_\beta\delta S_{\alpha\beta}^{\perp}=0, \quad \delta S_{\alpha\alpha}^{\perp}=0. \tag{10}$$

It is convenient to introduce the new variables

$$\delta S_{\alpha\beta}^{\perp}=\xi_1(n_\alpha e_{1\beta}+n_\beta e_{1\alpha})+\xi_2(n_\alpha e_{2\beta}+n_\beta e_{2\alpha})+\xi_3(e_{1\alpha}e_{2\beta}+e_{1\beta}e_{2\alpha})+\xi_4(e_{1\alpha}e_{1\beta}-e_{2\alpha}e_{2\beta}), \tag{11}$$

where $\mathbf{n}$, $\mathbf{e}_1$, and $\mathbf{e}_2$ constitute a right-hand triad of unit vectors. It is easily seen that $\delta S^{\perp}_{\alpha\beta}$, which is defined by formula (11), satisfies the conditions (10) for any choice of ξ_i. Substituting (9) and (11) into the function $\Phi(x,y)$ and taking the condition (3) into account, we get

$$\delta\Phi=6\frac{\partial\Phi}{\partial x}(\xi_3^2+\xi_4^2). \tag{12}$$

Formula (12) is valid accurate to terms of cubic order in ξ_i. We note that, as expected, the energy increases only when biaxial fluctuations, to which the variables ξ_3 and ξ_4 correspond, set in. Thermodynamic stability calls for $\partial\Phi/\partial x>0$. It is easy to verify that this condition is satisfied in the Landau theory.

We point out that the value of s in the vicinity of the transition point need not be too small (experiment yields $s\sim0.3$ to 0.4), since the critical scattering is connected with quantities quadratic in s. We assume none the less that the Landau theory is a good approximation both above and below the transition point. The justification for this statement is the splendid agreement between the experimental data on scattering in the isotropic phase and the Curie law, as well as other critical phenomena.[1,2]

3. LONGITUDINAL SCATTERING

The longitudinal fluctuations of the order parameters are fluctuations of the quantity s:

$$\delta S_{\alpha\beta}^{\parallel}=\delta s(n_\alpha n_\beta-{}^1/_3\delta_{\alpha\beta}). \tag{13}$$

It is known from the general theory of degenerate systems[3] that by virtue of the principle of the conservation of the modulus, strong transverse fluctuations give rise to weaker longitudinal fluctuations:

$$2s\delta s=-(\delta S_{\alpha\beta}^{\perp})^2. \tag{14}$$

We consider long-wave fluctuations and neglect in this section biaxial fluctuations, the excitation of which requires that an energy barrier $\Delta\sim B^2/C$ be surmounted. It is then necessary to set ξ_3 and ξ_4 equal to zero in (11).

We use the known expression for the elastic energy of a liquid crystal[1] 1):

$$\delta\Phi=\frac{1}{2}K_1\left(\frac{\partial S_{\alpha\beta}}{\partial x_\gamma}\right)^2+\frac{1}{2}K_2\left(\frac{\partial S_{\alpha\beta}}{\partial x_\beta}\right)^2, \tag{15}$$

where K_1 and K_2 are phenomenological constants connected with the Frank moduli. Substituting formula (9) for $S_{\alpha\beta}$ in (15) and changing to the Fourier representation, we obtain

$$\delta\Phi={}^1/_2K_1q^2|\delta S_{\alpha\beta}^{\perp}|^2+{}^1/_2K_2|q_\beta\delta S_{\alpha\beta}^{\perp}|^2. \tag{16}$$

It is convenient to choose the vector $\mathbf{e}_1$ perpendicular to the plane defined by the vectors $\mathbf{n}$ and $\mathbf{q}$, and let $\mathbf{e}_1$ lie in this plane:

$$\mathbf{e}_1=\frac{[\mathbf{nq}]}{q\sin\theta}, \quad \mathbf{e}_2=[\mathbf{ne}_1], \tag{17}$$

where θ is the angle between the vectors $\mathbf{n}$ and $\mathbf{q}$. Changing over to the quantities $\xi_1(q)$ and $\xi_2(q)$ we obtain

$$\delta\Phi=K_1q^2(|\xi_1|^2+|\xi_2|^2)+{}^1/_2K_2q^2[|\xi_1|^2\cos^2\theta+|\xi_2|^2]. \tag{18}$$

From (18) we obtain the mean values $\langle|\xi_1(q)|^2\rangle$ and $\langle|\xi_2(q)|^2\rangle$:

$$\langle|\xi_1(q)|^2\rangle=\frac{T}{q^2(2K_1+K_2\cos^2\theta)}, \quad \langle|\xi_2(q)|^2\rangle=\frac{T}{q^2(2K_1+K_2)}. \tag{19}$$

The quantities $\langle|\xi_1|^2\rangle$ and $\langle|\xi_2|^2\rangle$ determine in turn nonzero mean values of the type $\langle\delta S^{\perp}_{\alpha\beta}(q)\delta S^{\perp}_{\gamma\delta}(-q)\rangle$:

$$\langle\delta S_{\alpha\beta}^{\perp}(q)\delta S_{\gamma\delta}^{\perp}(-q)\rangle=(n_\alpha e_{1\beta}+n_\beta e_{1\alpha})(n_\gamma e_{1\delta}+n_\delta e_{1\gamma})\langle|\xi_1|^2\rangle+(n_\alpha e_{2\beta}+n_\beta e_{2\alpha})(n_\gamma e_{2\delta}+n_\delta e_{2\gamma})\langle|\xi_2|^2\rangle. \tag{20}$$

To find the longitudinal correlator, we use the modulus-conservation principle (14):

$$\langle\delta s(\mathbf{r})\delta s(\mathbf{r}')\rangle=\frac{1}{2s^2}\langle\delta S_{\alpha\beta}^{\perp}(\mathbf{r})\delta S_{\alpha\beta}^{\perp}(\mathbf{r}')\rangle^2. \tag{21}$$

Changing over in (21) to the Fourier representation, we obtain

$$\langle|\delta s(q)|^2\rangle=\frac{1}{2s^2}\int\frac{d^3p}{(2\pi)^3}\times\langle\delta S_{\alpha\beta}^{\perp}(\mathbf{p})\delta S_{\gamma\delta}^{\perp}(-\mathbf{p})\rangle\langle\delta S_{\alpha\beta}^{\perp}(\mathbf{p}+\mathbf{q})\delta S_{\gamma\delta}^{\perp}(-\mathbf{p}-\mathbf{q})\rangle. \tag{22}$$

Substituting (20) and (19) in (22) after the integrations, we get

$$\langle|\delta s(q)|^2\rangle=\frac{T^2}{4s^2q}\left[\frac{1}{(2K_1+K_2)^2}+\frac{1}{\pi^2}\int_{-1}^{+1}\frac{du}{(2K_1+K_2u^2)}f(u)\right], \tag{23}$$

where the function $f(u)$ is an elliptic integral. The general expression for $f(u)$ is too unwieldy to be presented here. Several values of the integral in (23) in the equatorial plane are given below:

δ:	0	0.2	0.5	1.0
D:	0.25	0.20	0.17	0.15

Here

$$\frac{1}{\pi^2}\int_{-1}^{+1}\frac{du}{2K_1+K_2u^2}f(u)=\frac{D(\delta)}{K_1^2}, \quad \delta=\frac{K_2}{2K_1}.$$

The mean squared longitudinal fluctuation can be calculated directly within the framework of the Landau theory. To this end it is necessary to find the change of the thermodynamic potential (6) when s deviates from the equilibrium value. The result is

$$\langle \delta s^2 \rangle = \frac{81}{4} \frac{TC}{B^2}. \tag{24}$$

We note that for the isotropic phase an analogous expression was obtained by Stratonovich.[5] From a comparison of (24) and (23) we obtain the wave-vector region in which the singular longitudinal fluctuations (23) predominate:

$$q \leqslant \frac{T}{160 s^2} \frac{B^2}{K^2 C} \sim 10^{-4} a_0^{-1}, \tag{25}$$

where $a_0 \sim 3$ Å is the distance between the atoms. This upper bound corresponds in fact to wavelengths ~5000 Å.

We proceed to calculate the cross sections for light scattering. We use the known formula for the differential cross section in the frequency and solid-angle intervals $d\omega$ and $d\Omega$[6]:

$$\frac{d\sigma}{d\omega\, d\Omega} = \frac{\omega^4}{32\pi^3} \langle \delta\varepsilon_{\alpha\beta} \delta\varepsilon_{\gamma\delta} \rangle p_\alpha p_\gamma p_\beta' p_\delta', \tag{26}$$

where $\delta\varepsilon_{\alpha\beta}$ is the fluctuation of the dielectric tensor, $\mathbf{p}$ and $\mathbf{p}'$ are the polarization vectors of the incident and scattered light, and we use a system in which the speed of light $c=1$. By virtue of the symmetry, $\delta\varepsilon_{\alpha\beta}$ is connected with the fluctuation $\delta S^{\perp}_{\alpha\beta}$ of the order parameter by the relation

$$\delta\varepsilon_{\alpha\beta} = M \delta S_{\alpha\beta}^{\perp}, \tag{27}$$

where $M = \partial\varepsilon_a / \partial S$ and ε_a is the anisotropy of the dielectric constant. The value of M can be obtained from the experimental data on the temperature dependences of ε_a and s, namely, $M = (\partial\varepsilon_a/\partial T)/(\partial s/\partial T)$. Substituting (27) and (13) in (26) we get

$$\frac{d\sigma}{d\omega\, d\Omega} = \frac{\omega^4 M^2}{32\pi^3} \langle \delta s^2 \rangle \left[(\mathbf{pn})(\mathbf{p'n}) - \frac{1}{3} \mathbf{pp'} \right]^2. \tag{28}$$

Since we are interested in the longitudinal scattering in the equatorial plane only (this is the usual experimental situation), we shall examine this case in particular. Greatest interest attaches to two types of polarization: 1) the vectors $\mathbf{p}$ and $\mathbf{p}'$ lie in the equatorial plane; 3) the vectors $\mathbf{p}$ and $\mathbf{p}'$ are parallel to the director. In the former case the expression in the square brackets of (28) is equal to $-\frac{1}{3}\cos\chi$, where χ is the scattering angle. An additional angular dependence is contained in $\langle \delta s^2 \rangle$ in the case when singular longitudinal fluctuations predominate (see (23)). Thus, in this case the dependence of the cross section depends on the scattering angle is given by

$$\frac{d\sigma}{d\omega d\Omega} \sim \frac{\cos^2\chi}{\sin(\chi/2)}. \tag{29}$$

In the case of polarization along the director we have

$$\frac{d\sigma}{d\omega\, d\Omega} \sim 1 \Big/ \sin\frac{\chi}{2}. \tag{30}$$

When the polarization deviates from the equatorial plane, the rapidly growing transverse scattering suppresses the effects of the longitudinal fluctuations. Let us estimate the range of angles in which the longitudinal fluctuations are effective. The contribution of the transverse fluctuations to the scattering cross section is determined by formulas (26) and (19):

$$\frac{d\sigma}{d\omega\, d\Omega} = \frac{\omega^4}{32\pi^3} M^2 \{ \langle |\xi_1|^2 \rangle [(\mathbf{np})(\mathbf{e}_1\mathbf{p}') + (\mathbf{np}')(\mathbf{e}_1\mathbf{p})]^2 + \langle |\xi_2|^2 \rangle [(\mathbf{np})(\mathbf{e}_2\mathbf{p}') + (\mathbf{np}')(\mathbf{e}_2\mathbf{p})]^2 \}. \tag{31}$$

We denote the angle of inclination of the polarization from the equatorial plane by α. It is then seen from (31) that the cross section behaves like $\max[\alpha^2, (\theta-\pi/2)^2]$. Comparing (31) and (28), we find that the longitudinal scattering is significant in the angle region

$$\max\left(\alpha, \theta - \frac{\pi}{2}\right) \sim (TqM^2/Ks^2\varepsilon_a^2)^{1/4}. \tag{32}$$

Putting in (32) $M \sim \varepsilon_a$, $T \sim 300$ K, $K \sim 10^{-6}$ erg/cm, $s \sim 0.3$, and $q \sim 10^5$ cm^{-1}, we obtain $(\alpha, \theta - \pi/2) \sim 5$ to $10°$, a range perfectly accessible to experimental observation.

If the light is polarized along the director, an analogous estimate is valid for the angles $\theta - \pi/2$ and β, where β is the angle between the polarization and the director.

We note that the transverse fluctuations do not cause scattering also under other conditions, when the wave vectors $\mathbf{k}$ and $\mathbf{k}'$ of the incident and scattered light and the director $\mathbf{n}$ lie in the same plane, and the polarization vectors $\mathbf{p}$ and $\mathbf{p}'$ are perpendicular to this plane.

Longitudinal-scattering effects can be observed only if the secondary scattering due to transverse fluctuations is weaker than the latter. Let us estimate the secondary scattering. According to the general theory,[6] the field $\mathbf{E}''$ of the secondary scattered wave is expressed in terms of the field of the primary scattered wave $\mathbf{E}'$:

$$\mathbf{E}''(R) = -\frac{\exp\{ik_2R_0\}}{4\pi R_0 \varepsilon_0} \left[\mathbf{k}_2 \times \left[\mathbf{k}_2 \int \delta\hat{\varepsilon} \mathbf{E}'(r) \exp\{-i\mathbf{k}_2\mathbf{r}\} d^3r \right] \right], \tag{33}$$

where $\mathbf{k}_2$ is the wave vector of the secondary scattered wave. Similarly, $\mathbf{E}'$ is expressed in terms of the field of the incident wave $\mathbf{E}$.

As usual, it is required to calculate quadratic mean values of the type $\langle E'' E_j'' \rangle$. Analysis shows that the main contribution is made by terms of two types. Those of the first type are proportional to the sample volume (just as in primary scattering). Their contribution to the average energy is

$$\frac{E^2}{16\pi^2 R_0^2 \varepsilon_0^4} k_2^4 \sin^2\chi' \frac{V}{(2\pi)^3} I(q'), \tag{34}$$

where χ' is the secondary-scattering angle, $\mathbf{q}' = \mathbf{k}_2 - \mathbf{k}$, and $I(q')$ is determined by an integral of the product of two correlators of the transverse fluctuations. A rough estimate yields $I(q') \approx 25\, T^2 K^{-2} q^{-1}$.

The ratio of the intensity of this contribution of the secondary scattering to the primary one is of the order of

$$\frac{\langle|\mathbf{E}''|^2\rangle}{\langle|\mathbf{E}'|^2\rangle}\sim\frac{0{,}1}{\varepsilon_0^2}\frac{Tq}{K}\sim\frac{10^{-4}\div10^{-5}}{\varepsilon_0^2}.$$

Since $\varepsilon_0\sim10$, the contribution of the secondary scattering in the frequency region of us can be neglected in comparison with the longitudinal scattering, which amounts to $\sim10^{-2}\langle|\mathbf{E}'|^2\rangle$. The terms of the second type are proportional to $V^{4/3}$, and are therefore significant in the case of scattering by large samples. The coefficients depend on the shape of the scattering volume. An estimate for a spherical volume yields

$$\frac{\langle|\mathbf{E}''|^2\rangle}{\langle|\mathbf{E}'|^2\rangle}=\frac{1}{64\pi^2}\frac{Tq^2}{K\varepsilon_0^2}R,$$

where R is the radius of the scattering sphere. It is easy to estimate that at $R\sim1$ cm this ratio is $\sim10^{-2}/\varepsilon_0^2$, i.e., it is again small compared with the longitudinal one.

4. GENERAL INVESTIGATION OF THE FLUCTUATION OF THE ORDER PARAMETER

Our problem reduces to diagonalization of a quadratic form that constitutes the deviation $\delta\Phi$ of the thermodynamic potential from the equilibrium value in an arbitrary fluctuation. This problem was already solved in part in Secs. 2 and 3 (see (11), (12), (15), and (18)). It remains to diagonalize the quadratic form (16) without the assumption $\xi_3=\xi_4=0$. We use the variables ξ_i (see (11) in the unit-vector system (17). Substituting (11) in (16) and adding (12) we get

$$\delta\Phi=K_1q^2\sum_{i=1}^{4}|\xi_i|^2+\frac{1}{2}K_2q^2[(\xi_1\cos\theta+\xi_3\sin\theta)^2+\xi_2^2+\xi_4^2\sin^2\theta-\xi_2\xi_4\sin2\theta]+\frac{1}{2}\Delta(\xi_3^2+\xi_4^2),\qquad(35)$$

where $\Delta=12\,\partial\Phi/\partial x$.

We introduce in standard manner the new variation

$$\eta_1=\xi_1\cos\beta+\xi_3\sin\beta,\quad\eta_2=\xi_2\cos\gamma-\xi_4\sin\gamma,\qquad(36)$$

$$\eta_3=-\xi_1\sin\beta+\xi_3\cos\beta,\quad\eta_4=\xi_2\sin\gamma+\xi_4\cos\gamma,$$
$$\beta=\frac{1}{2}\operatorname{arctg}\frac{\sin2\theta}{\mu-\cos2\theta},\quad\gamma=\frac{1}{2}\operatorname{arctg}\frac{\sin2\theta}{-\mu+\cos^2\theta},\qquad(37)$$

where $\mu=\Delta/K_2q^2$. In terms of the variables η_i, the form (35) can be diagonalized:

$$\delta\Phi=\frac{1}{2}K_2q^2\sum_{i=1}^{4}Q_i|\eta_i|^2+K_1q^2\sum_{i=1}^{4}|\eta_i|^2;\qquad(38)$$

$$Q_1=\mu\sin^2\beta+\cos^2(\theta+\beta),$$
$$Q_2=\mu\sin^2\gamma+\cos^2\gamma+\sin^2\gamma\sin^2\theta+\cos\gamma\sin\gamma\sin2\theta,$$
$$Q_3=\mu\cos^2\beta+\sin^2(\theta+\beta),\qquad(39)$$
$$Q_4=\mu\cos^2\gamma+\sin^2\gamma+\cos^2\gamma\sin^2\theta-\cos\gamma\sin\gamma\sin2\theta.$$

From (38) it is easy to obtain the mean values

$$\langle|\eta_i|^2\rangle=T/[q^2(2K_1+K_2Q_i)].\qquad(40)$$

With the aid of (36) and (40) we can obtain all the nonzero mean values of the type $\langle\xi_i\xi_j^*\rangle$ (see the Appendix). Using formula (11), we can obtain the mean values $\langle\delta S_{\alpha\beta}^{\perp}\delta S_{\gamma\delta}^{\perp*}\rangle$, which are also given in the Appendix.

The difference between ξ_3 and ξ_4 becomes substantial when $Kq^2\sim\Delta$, i.e., at sufficiently short wavelengths. Let us estimate the corresponding wavelength for MBBA. We use the experimental data on the values of s_c, T_c-T^*, and the transition heat L,[7] namely $s_c=0.3$, $T_c-T^*\approx1$ K, and $L=381$ cal/mole. These data determine uniquely the coefficients $a=5\times10^{21}$ cm^{-3} and $B\approx C=2\times10^7$ erg/cm^3 (Boltzmann's constant is assumed equal to unity). In the Landau theory, the gap Δ is connected with the parameters B and C by the relation $\Delta=20B^2/9C$. Using the foregoing values, we obtain $\Delta\sim4\times10^7$ erg/cm^3. Recognizing that $K\sim10^{-6}$ erg/cm, we obtain the wavelength region in which the biaxial fluctuations are significant: $\lambda\lesssim3\times10^{-6}$ cm. We note also that the correlators of the order parameter were calculated under certain simplifying assumptions by Vigman, Larkin, and Filev.[8]

5. LIGHT SCATTERING BY BIAXIAL FLUCTUATIONS

The formulas derived in the preceding section (see also the Appendix) enable us to calculate the light-scattering intensity without neglecting the biaxial fluctuations. We use the general formula (26). In our case the connection between the tensor $\delta\varepsilon_{\alpha\beta}$ and the fluctuation $\delta S_{\alpha\beta}^{\perp}$ of the order parameter is more complicated than in the case of uniaxial fluctuations (see (27)). From symmetry considerations we can write in the general case

$$\delta\varepsilon_{\alpha\beta}=M\delta S_{\alpha\beta}^{\perp}+N(n_\alpha n_\gamma\delta S_{\beta\gamma}^{\perp}+n_\beta n_\gamma\delta S_{\alpha\gamma}^{\perp}).\qquad(41)$$

To obtain a general formula for the scattering cross section we must substitute (41) in (26) and use formulas (A.1)–(A.3). The resultant expressions are very cumbersome. We confine ourselves here only to scattering in the equatorial plane. We consider again the two types of polarization mentioned above: in the equatorial plane and along the director. In the former case the general formula is greatly simplified, so that the result takes the form

$$\frac{d\sigma}{d\omega\,d\Omega}=\frac{M^2}{32\pi^3}\omega^4\langle|\xi_4|^2\rangle,\qquad(42)$$

$\langle|\xi_4|^2\rangle$ is given by one of the formulas in (A.1). For the latter case, the scattering cross section is zero as before (and as in the uniaxial case).

An estimate shows that in the region of visible light the longitudinal scattering is of the same order as the biaxial scattering. To observe longitudinal scattering in the case of polarization in the equatorial plane, the measurements must therefore be made in the infrared region. It must be emphasized that if the polarization is along the director then the longitudinal fluctuations can be observed also in the optical band. In contrast to the longitudinal scattering, the cross section (42) for scattering by biaxial fluctuations is independent of the scattering angle in the optical region. The angular dependences become discernible only in the far ultraviolet region and in the soft x-ray region $\lambda\lesssim3\times10^{-6}$ cm. The effect manifests itself then in an additional frequency dependence of the scattering cross section (on top of the q^{-2} dependence).

6. CONCLUSION

Our main results are the following: There exists a region of wavelengths ($\lambda \lesssim 3\times 10^{-6}$ cm) that are long enough compared with interatomic distances, in which biaxial fluctuations are as strong as uniaxial ones. To this wavelength region electromagnetic waves are scattered by both uniaxial and biaxial fluctuations. Therefore the known formulas, which take into account only uniaxial fluctuations, no longer hold (see[1,2]). We have obtained the scattering cross section in the general case for arbitrary polarizations of the incident and scattered light and for arbitrary wavelengths (see the Appendix). However, even in the wavelength region where the biaxial fluctuations are negligibly small there exist geometric conditions under which transverse fluctuations do not lead to scattering of light (see Sec. 3). Under these conditions the entire scattering is determined by the biaxial and longitudinal fluctuations. These processes are in competition only when both polarization vectors (of the incident and scattered light) lie in the equatorial plane. In the optical band, the cross sections of these processes are of the same order of magnitude and amount to $\sim 10^{-2}$ of the characteristic scattering cross section. Longitudinal scattering predominates in the infrared, and biaxial in the far ultraviolet. On the other hand if the polarization vectors are parallel to the director, then there is no biaxial scattering at all.

A general analysis of the conditions for thermodynamic equilibrium of NLC has revealed a cause-and-effect connection between two heretofore known facts: uniaxiality of all the known NLC and "weakness" of the first-order phase transition to the isotropic phase.

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APPENDIX

We present here the formulas needed to calculate the correlation functions and the scattering cross section. Using formulas (36), we get

$$\begin{gathered}\langle|\xi_1|^2\rangle=\cos^2\beta\langle|\eta_1|^2\rangle+\sin^2\beta\langle|\eta_3|^2\rangle,\\ \langle|\xi_2|^2\rangle=\cos^2\gamma\langle|\eta_2|^2\rangle+\sin^2\gamma\langle|\eta_4|^2\rangle,\\ \langle\xi_2\xi_4^*\rangle=\langle\xi_4\xi_2^*\rangle=\sin\gamma\cos\gamma(\langle|\eta_2|^2\rangle-\langle|\eta_4|^2\rangle),\\ \langle|\xi_4|^2\rangle=\sin^2\gamma\langle|\eta_2|^2\rangle+\cos^2\gamma\langle|\eta_4|^2\rangle,\\ \langle\xi_1\xi_3^*\rangle=\langle\xi_3\xi_1^*\rangle=\sin\beta\cos\beta(\langle|\eta_1|^2\rangle-\langle|\eta_3|^2\rangle),\\ \langle\xi_2\xi_4^*\rangle=\langle\xi_4\xi_2^*\rangle=\sin\gamma\cos\gamma(\langle|\eta_2|^2\rangle-\langle|\eta_4|^2\rangle),\end{gathered}\tag{A.1}$$

where $\langle|\eta_i|^2\rangle$ are given by (40) and (39), and the angles β and γ by formulas (37).

To calculate mean values of the type $\langle\delta S^{\perp}_{\alpha\beta}\,\delta S^{\perp *}_{\alpha\beta}\rangle$ we use formulas (11) and (A.1):

$$\begin{gathered}\langle\delta S_{\alpha\beta}{}^{\perp}\delta S_{\gamma\delta}{}^{\perp *}\rangle=\langle|\xi_1|^2\rangle(n_\alpha e_{1\beta}+n_\beta e_{1\alpha})(n_\gamma e_{1\delta}+n_\delta e_{1\gamma})\\ +\langle|\xi_2|^2\rangle(n_\alpha e_{2\beta}+n_\beta e_{2\alpha})(n_\gamma e_{2\delta}+n_\delta e_{2\gamma})+\langle|\xi_3|^2\rangle(e_{1\alpha}e_{2\beta}+e_{2\alpha}e_{1\beta})(e_{1\gamma}e_{2\delta}+e_{2\gamma}e_{1\delta})\\ +\langle|\xi_4|^2\rangle(e_{1\alpha}e_{1\beta}-e_{2\alpha}e_{2\beta})(e_{1\gamma}e_{1\delta}-e_{2\gamma}e_{2\delta})\\ +\langle\xi_1\xi_3^*\rangle[(n_\alpha e_{1\beta}+n_\beta e_{1\alpha})(e_{1\gamma}e_{2\delta}+e_{2\gamma}e_{1\delta})+(\alpha\beta\rightleftarrows\gamma\delta)]\\ +\langle\xi_2\xi_4^*\rangle[(n_\alpha e_{2\beta}+n_\beta e_{2\alpha})(e_{1\gamma}e_{1\delta}-e_{2\gamma}e_{2\delta})+(\alpha\beta\rightleftarrows\gamma\delta)].\end{gathered}\tag{A.2}$$

The scattering cross section contains the correlators $\langle\delta\varepsilon_{\alpha\beta}\,\delta\varepsilon^*_{\gamma\delta}\rangle$, which are calculated with the aid of formulas (41), (11), (A.1), and (A.2). We obtain

$$\begin{gathered}\langle\delta\varepsilon_{\alpha\beta}\delta\varepsilon_{\gamma\delta}^*\rangle=M^2\langle\delta S_{\alpha\beta}{}^{\perp}\delta S_{\gamma\delta}{}^{\perp *}\rangle+N^2[T_{\alpha\gamma,\beta\delta}+T_{\beta\delta,\alpha\gamma}+T_{\alpha\delta,\beta\gamma}+T_{\beta\gamma,\alpha\delta}]\\ +MN[R_{\alpha\beta,\delta,\gamma}+R_{\alpha\beta,\gamma,\delta}+R_{\gamma\delta,\beta,\alpha}+R_{\gamma\delta,\alpha,\beta}],\end{gathered}\tag{A.3}$$

where

$$\begin{gathered}T_{\alpha\beta,\gamma\delta}=n_\alpha n_\beta[\langle|\xi_1|^2\rangle e_{1\gamma}e_{1\delta}+\langle|\xi_2|^2\rangle e_{2\gamma}e_{2\delta}],\\ R_{\alpha\beta,\gamma,\delta}=n_\delta[\langle|\xi_1|^2\rangle(n_\alpha e_{1\beta}+n_\beta e_{1\alpha})e_{1\gamma}+\langle|\xi_2|^2\rangle(n_\alpha e_{2\beta}+n_\beta e_{2\alpha})e_{2\gamma}\\ +\langle\xi_1\xi_3^*\rangle(e_{1\alpha}e_{2\beta}+e_{1\beta}e_{2\alpha})e_{1\gamma}+\langle\xi_2\xi_4^*\rangle(e_{1\alpha}e_{1\beta}-e_{2\alpha}e_{2\beta})e_{2\gamma}].\end{gathered}\tag{A.4}$$

[1)] Expression (15) is in fact the expansion of the elastic energy accurate to s^2. If s is not small it is necessary to take into account also higher invariants made up of the components of $\mathbf{n}$ and $\partial S_{\alpha\beta}/\partial x_\gamma$ (there are no invariants of degree higher than s^4 at all, because $\mathbf{n}^2=1$). For the questions of interest to us in the present paper (scattering in the equatorial plane), however this is of no importance.

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