Spatial correlation function of thermal fluctuations in cholesteric liquid crystals

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The spectral density of spatial fluctuations in the low-temperature phase of cholesteric liquid crystals is calculated without assuming uniaxiality of the fluctuation orientation tensor. The results are applied to calculation of the scattering of light by fluctuation inhomogeneities.

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1. INTRODUCTION

The correlation function of spatial thermal fluctuations in the high-temperature phase of cholesteric liquid crystals has been found by de Gennes[1] and by Brazovskiĭ and Dmitriev.[2] In the second of these papers, the results are presented in tensorially covariant form. In the case of the low-temperature phase, where a spontaneous spiral anisotropy is present, such comprehensive results have so far not been obtained. In papers of Lubensky[3] and in the review by Stephen and Straley,[4] the correlation function was found under the additional limiting assumption that not only for the mean orientation tensor, but also for the fluctuational part, the uniaxiality condition

$$S_{\alpha\beta}=S(n_\alpha n_\beta-{}^1/_3\delta_{\alpha\beta}), \tag{1.1}$$

is satisfied, where n_α is the director (directing vector). Then the fluctuations $\delta S_{\alpha\beta}$ reduced to the fluctuations δn_α. Furthermore, fluctuating angles of rotation of the director were introduced, and additional assumptions were made about slowness of variation of these angles in comparison with the period of the helix. This was stated with especial clarity in the review of Stephen and Straley.[4] In the present paper we shall free ourselves from these limitations.

Tensorially covariant methods[2,5] will be applied. As in Ref. 2, we shall use an expansion of the tensor $S_{\alpha\beta}$ in terms of the basis

$$\begin{gathered}\sigma_{\alpha\beta}{}^2={}^1/_2(l_\alpha+im_\alpha)(l_\beta+im_\beta),\\ \sigma_{\alpha\beta}{}^1={}^1/_2[(l_\alpha+im_\alpha)s_\beta+s_\alpha(l_\beta+im_\beta)],\\ \sigma_{\alpha\beta}{}^0=({}^3/_2)^{1/2}(s_\alpha s_\beta-\delta_{\alpha\beta}/3),\qquad \sigma_{\alpha\beta}{}^{-k}=(\sigma_{\alpha\beta}{}^k)^*.\end{gathered} \tag{1.2}$$

Here **s**, **l**, and **m** are unit vectors forming a right-handed system. In contrast to Ref. 2, however, it is for some purposes convenient, in the presence of a spontaneous spirality, to direct the unit vector **s** along the axis of the helix. The medium is assumed to be homogeneous and infinite in all three directions.

Cholesteric liquid crystals have been investigated experimentally in a number of papers.[6–8] In them attention was paid primarily to the high-temperature phase. By using the results of these papers, one can estimate the width of the temperature interval, near the critical point, in which the correlation radius r_c is comparable with the period l of the spiral or larger than it. It is found that the relation $r_c\gtrsim l$ is valid over a range of thousandths of a degree. The relation between the correlation radius and the pitch of the helix is important for the theory, because different variants of the theory are valid for the different inequalities $r_c\gg l$ and $r_c\ll l$. Both variants will be expounded below. In Refs. 3 and 4 it was implicitly assumed that $r_c\gg l$. In Sec. 4 the results of these papers will be compared with our results relating to that case. The contrary case $r_c\ll l$ is treated in Sec. 5. This is, as far as we know, the first calculation of the correlation function of the fluctuations in this case.

The results found can be applied primarily to the calculation of the differential cross section for scattering of light by fluctuation inhomogeneities (Sec. 6). Here it is possible to test the predictions of the theory experimentally.

2. THE FIELD THAT MINIMIZES THE FREE ENERGY, AND THE SPECTRAL LINE CORRESPONDING TO IT.

We shall start from the following expression for the free energy of a cholesteric liquid crystal:

$$\begin{aligned}F[S_{\alpha\beta}]=\frac{1}{2}\int d\mathbf{r}[b(\partial_\gamma S_{\alpha\beta})^2+2c(\partial_\alpha S_{\alpha\beta})(\partial_\gamma S_{\gamma\beta})\\ +2d\varepsilon_{\alpha\rho\gamma}S_{\alpha\beta}\partial_\gamma S_{\rho\beta}]+\frac{9}{8}\int d\mathbf{r}f(S).\end{aligned} \tag{2.1}$$

where $\varepsilon_{\alpha\rho\gamma}$ is the completely antisymmetric tensor. The terms containing derivatives are taken the same as in Refs. 1 and 2. The function $f(S)$ in Landau's approximation is approximated by a polynomial: $f(S)=aS^2+\mu S^3+\lambda S^4$ (for a more complete form of it, see Ref. 5). The value of S in the case of a uniaxial field is determined by (1.1). In the more general biaxial case, we have $S=\theta\,|(\frac{3}{2}S_{\alpha\beta})^{1/2}|$, where $\theta=\operatorname{sign}\lambda_0$, the sign of the characteristic value of the matrix $S_{\alpha\beta}$ that is largest in absolute value. It is important that the usefulness of expression (2.1) is not limited to the immediate vicinity of the critical point.

The field $S^0_{\alpha\beta}(\mathbf{r})$ that minimizes the free energy (2.1) is found by means of the equation

$$\frac{\delta F}{\delta S_{\alpha\beta}}=0. \tag{2.2}$$

By calculating the variational derivative and carrying out the analysis of this equation, it is easy to show that its

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solution has the form (1.1), where S is determined by the equation

$$f'(S)=0, \tag{2.3}$$

and

$$n_\alpha(\mathbf{r})=l_\alpha\cos(\varkappa\mathbf{sr}+\psi)-m_\alpha\sin(\varkappa\mathbf{sr}+\psi), \tag{2.4}$$

$\varkappa=d/b$, ψ is a constant, and **s**, **l**, and **m** are unit vectors. All directions of **s** are of course equally possible; we suppose that the direction of the axis of the spiral is prescribed. The period of the spiral thus obtained is $l=2\pi b/d$.

By substituting (2.4) in (1.1) it is easy to represent $S^0_{\alpha\beta}$ in the form of an expansion in terms of the basis (1.2):

$$S_{\alpha\beta}{}^0=S\sum_j e^{ij(\varkappa r+\psi)}g_j\sigma_{\alpha\beta}{}^j=S\sum_j \tilde{g}_j\sigma_{\alpha\beta}{}^j, \tag{2.5}$$

where

$$\boldsymbol{\varkappa}=\varkappa\mathbf{s},\quad g_2=g_{-2}={}^1/_2,\quad g_1=g_{-1}=0,\quad g_0=-6^{-1/2}. \tag{2.6}$$

Under the usual experimental conditions, the initial phase ψ of the spiral is randomly and uniformly distributed. Thus in the usual experiments on light scattering in a liquid crystal, there is no relation between the phase of the incident light and the phase of the spiral. Therefore they may be considered independent and completely random. It is not difficult to calculate the spectral density of the field (2.5) for random initial phase,

$$\bar{G}^0_{\alpha\beta\gamma\delta}(\mathbf{k})=2\pi^3S^2[\delta(\mathbf{k}+2\boldsymbol{\varkappa})\overline{\sigma_{\alpha\beta}}^{2}\sigma_{\gamma\delta}{}^2+\delta(\mathbf{k}-2\boldsymbol{\varkappa})\sigma_{\alpha\beta}{}^2\overline{\sigma_{\gamma\delta}}^{2}] \tag{2.7}$$

$(\delta(\mathbf{k})=\delta(k_1)\delta(k_2)\delta(k_3))$. Naturally the delta function that enters here is in actuality only an idealization. Under real conditions the delta function is smeared out (replaced by a certain approximation) for two reasons. The first reason is that the medium is spatially bounded. Thus if it fills a parallelopiped with dimensions $L_1\times L_2\times L_3$, the delta function must be replaced by an approximation $\delta_\varepsilon(k_1)\delta_\mu(k_2)\delta_\nu(k_3)$, where $\varepsilon=1/L_1$, $\mu=1/L_2$, $\nu=1/L_3$, and $\delta_\varepsilon(x)$ is an approximation of width ε. The second reason is the variability and diffusion of phase that in principle is always present. This leads to spreading of the delta function even if the medium is supposed infinite in several directions.

We shall estimate the spreading of the delta function that results from diffusion of phase. Instead of carrying out a detailed multidimensional treatment, we shall replace the problem by a one-dimensional one. We shall first consider diffusion of phase along the axis of the spiral. We shall suppose that ψ depends only on $\mathbf{rs}\equiv r_\parallel$. Using (2.1), we then get

$$F[\psi]=bS^2A_\perp\int(\psi')^2\,dr_\parallel+\text{const}, \tag{2.8}$$

where $A_\perp$ is the area of the cross section of the spiral wave. On substituting (2.8) in the expression const $\cdot\exp[-F/k_BT]$, we find the probability functional for $\psi(r_\parallel)$ and hence obtain the longitudinal diffusion coefficient

$$D_\parallel=k_BT/2bS^2A_\perp. \tag{2.9a}$$

Similarly we find the transverse diffusion coefficient

$$D_\perp=k_BT/2(b+c)S^2A_\parallel. \tag{2.9b}$$

As is well known in the theory of self-excited oscillators, phase diffusion leads to a Lorentz shape of a spectral line. Thus on the assumption of longitudinal unboundedness of the medium, we get for $\mathbf{k}\parallel\boldsymbol{\varkappa}$, instead of (2.7),

$$\bar{G}^0_{\alpha\beta\gamma\delta}(\mathbf{k})=S^2A_\perp D_\parallel\left[\frac{\overline{\sigma_{\alpha\beta}}^{2}\sigma_{\gamma\delta}{}^2}{(k_\parallel+2\varkappa)^2+4D_\parallel{}^2}+\frac{\sigma_{\alpha\beta}{}^2\overline{\sigma_{\gamma\delta}}^{2}}{(k_\parallel-2\varkappa)^2+4D_\parallel{}^2}\right]. \tag{2.10}$$

Numerical calculation shows that the spread of the spectral line resulting from diffusion is much smaller than the spread resulting from spatial boundedness. When the dimensions of the region filled by the liquid crystal are of the order of a few millimeters, the diffusive broadening is smaller by a factor ~10^6 than the broadening caused by spatial boundedness. Therefore we shall hereafter disregard phase diffusion.

We shall consider deviations $\delta S_{\alpha\beta}=S_{\alpha\beta}-S^0_{\alpha\beta}$ from the unperturbed field, assuming them to be sufficiently small. Field changes caused by small deviations of phase are incorporated in $\delta S_{\alpha\beta}$; large deviations of phase are impossible in consequence of the spatial boundedness discussed earlier. As in (2.5), we represent these deviations in the form of an expansion

$$\delta S_{\alpha\beta}=\sum_j\varphi_j\sigma_{\alpha\beta}{}^j.$$

If we substitute $S_{\alpha\beta}=S^0_{\alpha\beta}+\delta S_{\alpha\beta}$ in (2.1), the terms linear in $\delta S_{\alpha\beta}$ drop out because of (2.2). Taking into account the smallness of the deviations $\delta S_{\alpha\beta}$, we retain in the expression obtained only the terms quadratic in $\delta S_{\alpha\beta}$ or φ_j.

We write the resulting expression in matrix form:

$$F={}^1/_2\boldsymbol{\varphi}^+[\mathbf{L}(\nabla)+f''\tilde{\mathbf{g}}\tilde{\mathbf{g}}^+\mathbf{J}]\boldsymbol{\varphi}, \tag{2.11}$$

where φ denotes the column vector $\|\varphi_j(\mathbf{r})\|$, $\mathbf{J}=\|\delta(\mathbf{r}_1-\mathbf{r}_2)\|$, and $\mathbf{L}(\nabla)=\|L_{jk}(\nabla)\|$ is the matrix corresponding to the terms containing derivatives in (2.1), taken in the basis (1.2). It was shown in Ref. 2 that the matrix $\mathbf{L}(-i\mathbf{k})$ assumes diagonal form in the basis $\{\tilde{\sigma}^j_{\alpha\beta}\}$, where $\tilde{\sigma}^j_{\alpha\beta}$ are constructed like (1.2) but on the unit vectors $\tilde{\mathbf{s}}$, $\tilde{\mathbf{l}}$, and $\tilde{\mathbf{m}}$, where $\tilde{\mathbf{s}}\parallel\mathbf{k}$ and $\tilde{\mathbf{s}}\mathbf{s}\geqslant 0$. In this representation we have[2]

$$\begin{gathered}L_{jl}(-i\mathbf{k})=\tau_j(k)\delta_{jl},\\ \tau_{\pm2}(\mathbf{k})=bk^2\pm2dk_\parallel,\quad \tau_{\pm1}(\mathbf{k})=(b+c)k^2\pm dk_\parallel,\\ \tau_0(\mathbf{k})=(b+{}^4/_3c)k^2\quad(k_\parallel=\mathbf{k}\tilde{\mathbf{s}}).\end{gathered} \tag{2.12}$$

The basis vectors $\tilde{\sigma}^j_{\alpha\beta}$ and $\sigma^j_{\alpha\beta}$ are interrelated by the unitary transformation

$$\tilde{\sigma}_{\alpha\beta}{}^j=u_l{}^j\sigma_{\alpha\beta}{}^l, \tag{2.13}$$

where the u^j_i depend on the angle γ between $\tilde{\mathbf{s}}$ and $\mathbf{s}$ (see (A.4)). Therefore in the basis $\sigma^j_{\alpha\beta}$, the matrix in question has the form

$$L_{jl}(-i\mathbf{k})=(u_j^s)^*\tau_s(\mathbf{k})u_l^s. \qquad (2.14)$$

It is important that, in contrast to the cases considered earlier,[1,2,5] the matrix inside the square brackets in (2.11) depends not only on the difference $\mathbf{r}_1-\mathbf{r}_2$ but also on the sum $\mathbf{r}_1+\mathbf{r}_2$. This indicates a periodic inhomogeneity of the random field $\delta S_{\alpha\beta}$ or φ_j for fixed initial phase ψ.

3. SPECTRAL DENSITY OF THE FLUCTUATIONS FOR RELATIVELY LARGE CORRELATION RADII

The free energy (2.11) determines the density functional of the probability distribution of the random field $\varphi_j(\mathbf{r})$. In consequence of the quadratic character of the free energy, the field is Gaussian. In accordance with the theory of Gaussian fluctuations, the correlation matrix is obtained by inversion of the matrix that occurs in (2.11):

$$\mathbf{G}^1\equiv\langle\boldsymbol{\varphi}\boldsymbol{\varphi}^+\rangle=k_BT[\mathbf{L}(\nabla)+f''\tilde{\mathbf{g}}\tilde{\mathbf{g}}^+\mathbf{J}]^{-1}. \qquad (3.1)$$

In the case under consideration, the low-temperature phase, the situation is complicated by the fact that the fluctuation field is periodically inhomogeneous, so that the correlation matrix (3.1) not only depends on $\mathbf{r}_1-\mathbf{r}_2$ but also is a periodic function of $\mathbf{r}_1+\mathbf{r}_2$. In the usual experiments, there is no coherence between the spiral and the incident light beam. Then the experimentally measurable quantities are influenced only by the correlation function averaged over a period. We shall denote by $\overline{\mathbf{G}}$ the value of the correlation function averaged over $\mathbf{r}_1+\mathbf{r}_2$ or over a random initial phase. We must of course not suppose that it is impossible to perform special experiments in which the coherence between the incident beam and the spiral is significant, but they are at present unknown. For the analysis of such experiments, it would not be permissible to carry out the averaging described.

An averaging similar to the averaging over $\mathbf{r}_1+\mathbf{r}_2$ has been carried out also by other authors.[3,4] Thus in Lubensky's first paper,[3] formula (17) was obtained as the result of averaging over $z+z'$, although this fact was not explicitly stated there. In the review[4] of Stephen and Straley, it is stated on page 661: "Terms which vary like $\exp[\pm it_0(z_1+z_2)]$ have been neglected because they average to zero." In Lubensky's second paper,[3] this averaging is not carried out, because the final formulas (3.26) and (6.25) are left in a form that is not simplified or definitive.

We shall find the inverse matrix in (3.1) by representing it by a matrix series in powers of the second matrix term:

$$\mathbf{G}^1=k_BT\sum_{n=0}^{\infty}\mathbf{L}^{-1}(\nabla)[-f''\tilde{\mathbf{g}}\tilde{\mathbf{g}}^+\mathbf{J}\mathbf{L}^{-1}(\nabla)]^n. \qquad (3.2)$$

It is shown in the Appendix that this series in fact converges as a series in powers of the parameter l/r_c. At a given point this parameter is by hypothesis small ($\varkappa r_c \ll 1$), and therefore the series converges rapidly.

In the Appendix it is also shown that one can without difficulty find also the correlation function $\overline{\mathbf{G}}$ averaged over $\mathbf{r}_1+\mathbf{r}_2$ and the corresponding spectral density $\overline{\mathbf{G}}^1(k)$. By use of (2.14), one obtains for this spectral density formula (A.2). We write the first few terms of this series:

$$\overline{G}^1_{\alpha\beta\gamma\delta}(\mathbf{k})=k_BT\tau_s^{-1}(\mathbf{k})\Big[\delta_{sr}-f''\overset{sr}{v_{00}}\tau_r^{-1}(\mathbf{k}) + \sum_{\nu}f''^2\overset{st}{v_{0\nu}}\tau_t^{-1}(\mathbf{k}-\varkappa s)\overset{tr}{v}_{-\nu,0}\tau_r^{-1}\Big]\overset{-s}{\bar{\sigma}_{\alpha\beta}}\bar{\sigma}_{\gamma\delta}{}^r. \qquad (3.3)$$

Here we have returned to tensor notation and have used (2.13). The quantities $v^{st}_{\mu\nu}$ that occur here are determined by formulas (A.3) and (A.4). To obtain the whole spectral density $\overline{G}_{\alpha\beta\gamma\delta}(\mathbf{k})$, it is necessary to add (3.3) to (2.7).

The first term on the right side of (3.3) is of isotropic character. It insures the continuity of the changes of spectral density with change of temperature and with transition through a critical point. In fact, on approach to the critical point from below the expression (2.7) vanishes, since $S\to 0$. The higher-order terms in (3.3) also vanish. There is only a weakly expressed jumpiness in this vanishing, because the phase transition is a weakly expressed transition of first order. On approach to the critical point from above, i.e., from the high-temperature-phase region, as was shown in Ref. 2, the spectral density becomes equal to an expression corresponding to the first term in (3.3) with the values (2.12) of $\tau_j(\mathbf{k})$.

The following question is interesting: what sort of expression is obtained if one first averages the matrix in (2.11) over $\mathbf{r}_1+\mathbf{r}_2$ and then calculate the inverse matrix; how much will this result differ from the true one? It is easily seen that then in the expansion (A.1) only those terms will occur for which $a_\alpha=b_\alpha$, i.e., $\nu_\alpha=0$. Then in the expression (3.3) those terms disappear that are quadratic in f''/τ_j and in which $\nu\neq 0$. Consequently, not only the first term on the right side of (3.3) but also the second term is taken into account in this simplified calculation procedure. But in terms of the next and higher orders of smallness, discrepancies arise.

The spectral density (3.3) obtained has a band character; that is, it increases noticeably in definite frequency bands. By taking account of the form (2.12) of the functions $\tau_j(\mathbf{k})$, one easily sees that the first term in (3.3) describes fluctuations in bands near the frequencies $k_\parallel=0$, $k_\parallel=\pm 2\varkappa$, and $k_\parallel=\pm d/(b+c)$.

The second term in (3.3) describes less intense fluctuations whose frequencies lie in bands near the frequencies

$$k_\parallel=\pm 4\varkappa$$

(these bands come from the product $\tau_{\mp}^{-1}\tau_{\mp 2}^{-1}$) and

$$k_\parallel=\pm 2d/(b+c), \quad k_\parallel=\pm 2\varkappa\pm d/(b+c)$$

(these come from products $\tau_{\mp 1}^{-1}\tau_{\mp 1}^{-1}$ and $\tau_{\mp 2}^{-1}\tau_{\mp 1}^{-1}$), and also the bands indicated earlier for the first term. Higher terms describe still less intense fluctuations whose frequencies lie in more distant side bands. On lowering of the temperature from the critical and decrease of the correlation radius, the bands mentioned broaden, the intensity of the side bands increases, and for $\varkappa r_c \sim 1$ the approximation (3.3) loses its validity.

Formulas (3.3) and (2.7) can be tested experimentally by observation of the scattering of light by fluctuation inhomogeneities in cholesteric liquid crystals. As is well known, the differential scattering cross section per unit solid angle and per unit scattering volume is given by the formula

$$\frac{d\sigma}{d\Omega}=\frac{k_0^4}{32\pi^3}(N\Delta\varepsilon)^2\tilde{G}_{\alpha\beta\gamma\delta}(\mathbf{q})e_\alpha e_\beta' e_\gamma e_\delta', \tag{3.4}$$

where $\mathbf{q}=\mathbf{k}-\mathbf{k}'$; $\mathbf{k}$ and $\mathbf{e}$ are the wave vector and the unit polarization vector of the incident wave, $\mathbf{k}'$ and $\mathbf{e}'$ of the scattered; N is the number of molecules in unit volume; and $\Delta\varepsilon=\varepsilon_\parallel-\varepsilon_\perp$.

It is of interest to test experimentally the above-described band structure of the fluctuation spectrum by measuring, say, the dependence of the cross section (3.4) on $q=|\mathbf{k}-\mathbf{k}'|$. True, experiments under the condition $\varkappa r_c \gg 1$ present a well-known difficulty, because the temperature range near the critical point in which this condition is satisfied is, as was mentioned in the Introduction, usually very narrow. Under actual experimental conditions, especially near the critical point, there may be in the liquid crystal a violation of the condition of homogeneity with respect to the orientation of the helix, and specifically domains may appear with different spontaneous orientations of the helix. In this case, in order to find the resultant spectral density it is necessary to carry out an averaging over the orientation of the spiral, assuming, say, that the distribution over orientations is uniform. In such an averaging, the isotropic first term in (3.3) does not change; but the other terms, and also (2.7), undergo a change. We shall write the result of the averaging of the largest of these terms, the expression (2.7):

$$\tilde{G}^{0}_{\alpha\beta\gamma\delta}(\mathbf{k})=\frac{2\pi^3S^2}{k^2}[\delta(k_\parallel+2\varkappa)\tilde{\sigma}_{\alpha\beta}^{-2}\tilde{\sigma}_{\gamma\delta}^{2}+\delta(k_\parallel-2\varkappa)\tilde{\sigma}_{\alpha\beta}^{2}\tilde{\sigma}_{\gamma\delta}^{-2}].\quad k_\parallel=k\tilde{s}.$$

Finally, we note that in application of these formulas to a real case of a spatially bounded medium, it is necessary to carry out a smoothing of the spectral density (that is, to take a convolution integral) with the function $\delta_\varepsilon(k_1)\delta_\mu(k_2)\delta_\nu(k_3)$ discussed in Sec. 2.

4. COMPARISON WITH RESULTS OF PREVIOUS PAPERS

We shall compare the results obtained with the formulas of the review by Stephen and Straley,[4] where the results are presented in a more definitive form than that of Lubensky.[3] We shall write formula (10.17) of Ref. 4 (see also Ref. 9), derived for the case in which $c=0$ in (2.1). In consequence of equation (8.5) of Ref. 4, this formula in our notation has the form

$$\frac{d\sigma}{d\Omega}=\frac{1}{32\pi^3}k_0^4(SN\Delta\varepsilon)^2J(\mathbf{q}).$$

Here

$$J(\mathbf{q})=A[I_\varphi(\mathbf{q}+2\varkappa)+I_\varphi(\mathbf{q}-2\varkappa)]+B[I_z(\mathbf{q}+\varkappa)+I_z(\mathbf{q}-\varkappa)], \tag{4.1}$$

where

$$4A=[(\mathbf{el})^2+(\mathbf{em})^2][(\mathbf{e'l})^2+(\mathbf{e'm})^2],$$
$$4B=[(\mathbf{el})(\mathbf{e's})+(\mathbf{es})(\mathbf{e'l})]^2+[(\mathbf{em})(\mathbf{e's})+(\mathbf{es})(\mathbf{e'l})]^2.$$

The functions I_z and I_φ are determined by formulas (10.9) and (10.10) of Ref. 4; that is,

$$I_z(\mathbf{q})=\frac{k_BT}{k_0(q^2+\varkappa^2)},\quad I_\varphi(\mathbf{q})=\frac{k_BT}{k_0q_\parallel^2} \tag{4.2}$$

($k_0=2bS^2$, $q_\parallel=\mathbf{qs}$). In the expression for I_φ we have neglected terms that are small because $q^2/\varkappa^2\ll 1$ when $q\sim r_c^{-1}$, by virtue of the inequality $\varkappa r_c\gg 1$.

We note that the terms containing I_φ in (4.1) give the same expression as does formula (2.10) if, on the right side of the latter formula, we omit the small terms $4D_\parallel^2$ in the denominator.

According to formula (4.1), the differential scattering cross section is influenced only by those fluctuations of the orientation tensor whose frequencies lie in the bands $\mathbf{k}\approx\pm 2\varkappa$, $\pm\varkappa$. It was shown in Sec. 3, however, that in the spectral density there are also present fluctuations with frequencies that lie in other bands. Failure to take into account the fluctuations in other frequency bands is a shortcoming of the methods of previous papers.[3,4]

Besides this, discrepancies of the bands $\pm 2\varkappa$ and $\pm\varkappa$ also occur. In fact, if in (3.3) we retain only the first term and in it take account only of $\tau_{\pm 2}$ and $\tau_{\pm 1}$, we shall have

$$J(\mathbf{q})=k_BTS^{-2}\{\tilde{A}[\tau_2^{-1}(\mathbf{q})+\tau_{-2}^{-1}(\mathbf{q})]+\tilde{B}[\tau_1^{-1}(\mathbf{q})+\tau_{-1}^{-1}(\mathbf{q})]\}, \tag{4.3}$$

where $\tilde{A}$ and $\tilde{B}$ are analogous to A and B but are constructed on the vectors $\tilde{\mathbf{s}}$, $\tilde{\mathbf{l}}$, and $\mathbf{m}$. The last expression is similar in form to (4.1), but there are also some obvious differences. Formula (4.3) must be regarded as a refinement of the result (4.1), which was derived by a less general and less rigorous method. One can also write in (4.3) the additional corrective terms that occur in (3.3).

In a comparison of (4.3) with (4.1), it is necessary to remember the following important fact. The point is that the characteristic values $\tau_\pm(\mathbf{k})$ and $\tau_{\pm 1}(\mathbf{k})$ indicated in (2.12) are not nonnegative functions. This means that the matrix $\mathbf{L}(\nabla)$ in the expression (2.11) for the free energy and, consequently, also the corresponding matrix in (2.1) are not nonnegative definite. This is not permissible, since it leads to thermodynamic instability of the field (2.5) (as well as of the field $S^0_{\alpha\beta}=0$ in the high-temperature phase) in a range adjacent to the critical point, and also to nonpositiveness of the expression for the spectral density of certain linear combinations of the compounds of $\mathbf{S}_{\alpha\beta}(\mathbf{r})$. In order to deal with a nonnegative definite operator $\mathbf{L}(\nabla)$, it is expedient to change the original expression (2.1). We replace, say, the term $2d\varepsilon_{\alpha\rho\gamma}S_{\alpha\beta}\partial_\gamma S_{\rho\beta}$ in (2.1) by the expression

$$4d\varepsilon_{\alpha\rho\gamma}S_{\alpha\beta}\partial_\gamma S_{\rho\beta}+4d^2b^{-1}[S_{\alpha\beta}^2-{}^3/_2(\partial_\alpha S_{\alpha\beta})(\nabla^{-2}\partial_\gamma S_{\gamma\beta})].$$

Here the principal term is the last term. The other terms are less important; terms of this form were already contained in (2.1). These terms are introduced for redetermination of the coefficients of $S_{\alpha\beta}^2$ and $\varepsilon_{\alpha\rho\gamma} S_{\alpha\beta} \partial_\gamma S_{\rho\beta}$ so that the period of the spiral and the critical temperature may remain unchanged.

After this substitution, the characteristic values (2.12) are replaced by the nonnegative functions

$$\tau_{\pm 2}(\mathbf{k}) = b(k_\parallel \pm 2\varkappa)^2, \quad \tau_{\pm 1}(\mathbf{k}) = b(k_\parallel \pm \varkappa)^2 + ck^2 \tag{4.4}$$

($\tau_0(\mathbf{k})$ is unchanged), which indicate nonnegative definiteness of the new matrix $\mathbf{L}(\nabla)$. No other changes result in the theory expounded above. With the values (4.4), the expression (4.3) becomes still more like (4.1) and (4.2). An especially great similarity occurs for $\mathbf{k} \parallel \mathbf{s}$. It will be interesting to test experimentally which of these two expressions, which differ most from each other when $\mathbf{k} \perp \mathbf{s}$, is actually correct.

5. SPECTRAL DENSITY FOR RELATIVELY SMALL CORRELATION RADII

We turn to consideration of the opposite case, in which $\varkappa r_c \ll 1$. Because of the narrowness of the temperature interval in which $r_c \gtrsim \varkappa^{-1}$, as was discussed in the Introduction, this situation is more typical. We shall start from formula (3.1), where

$$\tilde{g}_j = e^{ij\Psi} g_j, \quad \Psi = \varkappa r + \psi. \tag{5.1}$$

The functions (5.1) change appreciably over a distance $\Delta r \sim \varkappa^{-1}$, while the correlation function changes appreciably over a distance r_c. Since $r_c \ll \varkappa^{-1}$, the function $\tilde{g}_j$ undergoes no substantial change over a distance r_c. Therefore in a calculation of the correlation function near a point that corresponds to a certain value of Ψ, Ψ (and therefore also $\tilde{g}_j$) may be considered constant.

The constancy of $\tilde{g}_j$ makes the inversion of the matrix (3.1) simple:

$$G^1(\mathbf{k}, \Psi) = k_B T[\mathbf{L}^{-1}(-i\mathbf{k}) - f'' h(\mathbf{k}, \Psi) \mathbf{L}^{-1} \tilde{\mathbf{g}} \tilde{\mathbf{g}}^+ \mathbf{L}^{-1}], \tag{5.2}$$

where

$$h(\mathbf{k}, \Psi) = [1 + f'' \tilde{\mathbf{g}}^+ \mathbf{L}^{-1}(-i\mathbf{k}) \tilde{\mathbf{g}}]^{-1}. \tag{5.3}$$

One can show the validity of this matrix inversion by direct multiplication by the original matrix. It is convenient to use formulas (5.2) and (5.3) on the basis $\tilde{\sigma}_{\alpha\beta}^j$, because then the matrix $\mathbf{L}(-i\mathbf{k})$ has the diagonal form. With use of (2.14), we have in this basis

$$G_{jl}^1(\mathbf{k}, \Psi) = k_B T \tau_j^{-1}(\mathbf{k}) \left[\delta_{jl} - f'' h(\mathbf{k}, \Psi) \sum_\nu v_\nu^{jl} e^{i\nu\Psi} \tau_l^{-1}(\mathbf{k}) \right]; \tag{5.4}$$

$$h^{-1}(\mathbf{k}, \Psi) = 1 + f'' \sum_{\nu, m} v_\nu^{mm} e^{i\nu\Psi} \tau_m^{-1}(\mathbf{k}) \equiv a + b \cos 2\Psi. \tag{5.5}$$

Here

$$v_\nu^{jl} = \sum_b u_{b+\nu}^j g_{b+\nu} g_b (u_b^l)^*$$

(only the values for $\nu = \pm 2, 0$ are nonzero); u_b^j are determined by formulas (A.4) and depend only on the angle between $\tilde{\mathbf{s}}$ and $\mathbf{s}$.

Analysis shows that h^{-1} loses its dependence on Ψ if we set $c = 0$ and neglect the term $dk = b\varkappa k$, which is small in comparison with bk^2 when $k \sim r_c^{-1}$. In general, $h^{-1}(\Psi)$ has a constant component a and a cosinusoidal component $b \cos 2\Psi$. We represent $h(\Psi)$ by the expansion

$$h(\Psi) = \sum_\nu A_\nu e^{-i\nu\Psi} \tag{5.6}$$

(sum over even ν), where

$$A_0 = (a^2 - b^2)^{-1/2}, \quad A_2 = A_{-2} = b^{-1}[1 - a(a^2 - b^2)^{-1/2}].$$

By substituting (5.6) in (5.4), one can easily carry out the averaging of the spectral density $G_{jl}^1(\mathbf{k}, \Psi)$ with respect to Ψ over a period, which corresponds to averaging of the correlation function with respect to $\mathbf{r}_1 + \mathbf{r}_2$, as was discussed in Sec. 3. As a result we finally get

$$\bar{G}_{\alpha\beta\gamma\delta}^1(\mathbf{k}) = k_B T \tau_j^{-1}(\mathbf{k}) \left[\delta_{jl} - f'' \sum_{\nu=-2} A_\nu v_\nu^{jl} \tau_l^{-1}(\mathbf{k}) \right] \tilde{\sigma}_{\alpha\beta}^{-j} \tilde{\sigma}_{\gamma\delta}^l. \tag{5.7}$$

The second term is now not small, in contrast to the way it was in (3.3). When $k \sim r_c^{-1}$, where $r_c = (b/f'')^{1/2}$, it has the same order of magnitude as the first term.

The method used in this section may be called quasistatic, since in the calculation of the local correlation function the direction of the director was assumed to be static (constant). If in the expressions for $\tau_{\pm 1}$ and $\tau_{\pm 2}$ we discard the terms containing $dk_\parallel$, the medium thereby is replaced by a nematic. The difference from the usual case of a nematic medium will be only in the fact that in the calculation of the local correlation function, an additional averaging is carried out over the various possible directions of the director perpendicular to the axis of the spiral. When the product $\varkappa r_c$ is not too small, it is of course better not to neglect the terms in τ_j containing dk.

Formula (5.7) is applicable also to the case of a spatially bounded medium, provided only that the spiral of spontaneous anisotropy succeeds in executing a large number of revolutions. A condition for applicability of this formula is also invariability of the direction of the axis of the spiral over the whole volume. In the case of large inconstancy of the direction of the axis, an additional averaging should be carried out over these directions, as was done at the end of Sec. 3. Allowance for spatial boundedness of the medium is made, as has already been indicated, by a supplementary smoothing of the spectral density with weight $\delta_\varepsilon(k_1)\delta_\mu(k_2)\delta_\nu(k_3)$.

We note that the results of Refs. 3 and 4 are not valid when $k \sim r_c^{-1} \gtrsim \varkappa$. In fact, in this case the spectral density is influenced by a large number of terms of the expansion (A.1). But in the expression (4.1) no allowance has been made for spectral components of the fluctuations, in other frequency bands, given by these terms; that is, the higher terms have not been taken into account. It was shown in Ref. 4 (p. 661) that the case $k_z \gg \varkappa$, when the liquid crystal is nearly nematic, falls outside the framework of the treatment. But we consider the results of this paper inapplicable also when $k \sim r_c^{-1} \sim \varkappa$.

6. APPLICATION TO SCATTERING THEORY

1. As has already been indicated, the expressions found for the spectral density of fluctuations can be applied to the calculation of the differential cross section for scattering of light by fluctuation inhomogeneities (see (3.4)). Here we shall consider only the special case in which the unit vectors $\mathbf{e}$ and $\mathbf{e}'$ are perpendicular to the scattering plane and the vector $\mathbf{q}=\mathbf{k}-\mathbf{k}'$ is parallel to the axis of the helix. In this case, $\gamma=0$, and the matrix u_j^l is the unit matrix; furthermore $\mathbf{e}=\mathbf{e}'=\mathbf{m}$. The function (5.5) in this case loses its dependence on Ψ (that is, $b=0$).

If $\varkappa r_c \ll 1$, (5.7) may be used. Substitution of (5.7) in (3.4) in this case leads to the result

$$\frac{d\sigma}{d\Omega}=\frac{k_BT}{128\pi^3}k_0^4(N\Delta\varepsilon)^2\Big\{\tau_2^{-1}(\mathbf{q})\,[1-(2r_c)^{-2}hb\tau_2^{-1}(\mathbf{q})]$$
$$+\frac{2}{3}\tau_0^{-1}(\mathbf{q})\left[1-\frac{2}{3}(2r_c)^{-2}hb\tau_0^{-1}\right]+\tau_{-2}^{-1}(\mathbf{q})\,[1-(2r_c)^{-2}hb\tau_{-2}^{-1}]\Big\} \tag{6.1}$$

where $r_c=(f''S^2/b)^{-1/2}$. This formula is applicable when $q\sim r_c^{-1}\gg\varkappa$ and when the other conditions indicated in Sec. 5, under which formula (5.7) is valid, are satisfied.

The second terms in the square brackets describe the effect of the spontaneous anisotropy. They are absent in the high-temperature phase. Formula (6.1) indicates that the dependence of the differential cross section on the dimensionless argument qr_c in the low-temperature phase differs significantly from the corresponding dependence in the high-temperature phase. It would be interesting to verify this difference experimentally.

The other important difference in the scattering in the low-temperature phase is that the differential cross section depends significantly on the angle γ between q and the direction of the axis of the spiral. It would be interesting to investigate experimentally, say, the difference between the cross section for $\mathbf{q}\parallel\mathbf{s}$ and the cross section for $\mathbf{q}\perp\mathbf{s}$ at fixed qr_c. Analytically, it is easy to obtain the value of the cross section for $\mathbf{q}\perp\mathbf{s}$ by use of (5.7) and to find its difference from (6.1).

2. In closing, we shall consider one effect of scattering that is specific to cholesteric liquid crystals. It consists in the fact that a linearly polarized wave gives a scattered wave in which different rotations of the polarization are differently represented. As before, we shall suppose that the incident beam is linearly polarized ($\mathbf{e}=\mathbf{m}$). We shall take the scattered beam to be elliptically polarized:

$$\mathbf{e}'=\mathbf{m}\cos\chi+i(\tilde{\mathbf{l}}\cos\vartheta+\tilde{\mathbf{s}}\sin\vartheta)\sin\chi, \tag{6.2}$$

where ϑ is the half-angle of scattering; χ determines the degree of ellipticity. In order to calculate the corresponding differential cross section, it is necessary to substitute (6.2) in (3.4) in the role of e'_β, and the complex-conjugate vector in the role of e'_δ. We shall denote this cross section by $(d\sigma/d\Omega)_1$.

We consider further still another cross section $(d\sigma/d\Omega)_2$, for a scattered beam with the opposite polarization,

$$\mathbf{e}'=\mathbf{m}\cos\chi-i(\tilde{\mathbf{l}}\cos\vartheta+\tilde{\mathbf{s}}\sin\vartheta)\sin\chi$$

and take the difference of these two cross sections. A nonvanishing value of this difference is also a specific cholesteric effect, due to the inversion-noninvariant term containing d in (2.1). In the same approximation as in (6.1), we obtain the formula

$$\left(\frac{d\sigma}{d\Omega}\right)_1-\left(\frac{d\sigma}{d\Omega}\right)_2=\frac{k_BT}{64\pi^3}k_0^4(N\Delta\varepsilon)^2\{\tau_2^{-1}(\mathbf{q})\,[1-(2r_c)^{-2}hb\tau_2^{-1}]$$
$$-\tau_{-2}^{-1}(\mathbf{q})\,[1-(2r_c)^{-2}hb\tau_{-2}^{-1}]\}\cos\vartheta\sin 2\chi.$$

It is also possible to calculate how scattering of an elliptically polarized beam occurs. The general rule is: in a cholesteric liquid crystal, as distinguished from a nematic, the mean rotation of the polarization vector changes on scattering.

APPENDIX

Analysis of the expansion (3.2)

By use of the well-known formula

$$e^{i\mathbf{z}\mathbf{r}}\Phi(\nabla)=\Phi(\nabla-i\mathbf{z})e^{i\mathbf{z}\mathbf{r}},$$

we shift all the exponential factors $\exp(\pm ij\varkappa\mathbf{r})$ that occur in (3.2) in $\tilde{\mathbf{g}}$ and $\tilde{\mathbf{g}}^+$ to the right. We then perform the averaging over $\mathbf{r}$. After the averaging, only those terms remain for which the product of these exponential factors gives unity. This leads to the expression

$$\bar{G}_{jl}{}^1=k_BT\sum_{n=0}^{\infty}\sum_{a,b}(-f'')^nL^{-1}(\nabla)_{ja_1}\prod_{\alpha=1}^{\infty}g_{a_\alpha}g_{b_\alpha}L^{-1}(\nabla+i\varkappa\nu_\alpha)_{b_\alpha a_{\alpha+1}}, \tag{A.1}$$

where

$$a_{n+1}=l,\quad \nu_\alpha=b_1-a_1+\ldots+b_\alpha-a_\alpha.$$

In the sum (A.1), only those terms occur for which $\nu_n=0$. On going over to a spectral representation, we replace ∇ by $-i\mathbf{k}$ in (A.1). On using (2.14) and substituting

$$L^{-1}(-i\mathbf{k})_{ba}=(u_b^l)^*\tau_l^{-1}u_a^l$$

in (A.1), we get

$$\bar{G}_{jl}{}^1(\mathbf{k})=k_BT\sum_{n=0}^{\infty}\sum_{t,c}(-f'')^n(u_j^{t_0})^*\tau_{t_0}^{-1}(\mathbf{k})$$
$$\times\prod_{\alpha=1}^{n}v(t_{\alpha-1},t_\alpha;\nu_{\alpha-1},\nu_\alpha)\tau_{t_\alpha}^{-1}((\mathbf{k}-\varkappa\nu_\alpha)\mathbf{s}_{\nu_\alpha})u_l^{t_n} \tag{A.2}$$
$$(\nu_\alpha=c_1+\ldots+c_\alpha),$$

where the notation is

$$v(s,r;\nu,\mu)\equiv v_{\nu\mu}^{sr}=\sum_a u_a^s(\gamma_\nu)g_ag_{a+\mu-\nu}u_{a+\mu-\nu}^{r*}(\gamma_\mu); \tag{A.3}$$

$$\gamma_\mu=\arcsin\mathbf{l}\tilde{\mathbf{s}}_\nu,\quad \tilde{\mathbf{s}}_\nu\parallel\mathbf{k}-\varkappa\nu,\quad \mathbf{s}_\nu\mathbf{s}\geqslant0,\quad |\mathbf{s}_\nu|=1.$$

In the sum (A.2), as before, only terms with $\nu_n=0$ occur. The values of $v_{\nu\mu}^{sr}$, as well as of u_j^l, depend only on the angles between $\mathbf{s}$ and $\tilde{\mathbf{s}}_\nu$. The calculation gives for $u_j^l(\gamma)$ the following values:

$$\|u_0^j(\gamma)\| = \frac{1}{2}\left\| \left(\frac{3}{2}\right)^{1/2} \sin^2\gamma,\ -6^{1/2}\sin\gamma\cos\gamma,\ 3\cos^2\gamma-1,\right.$$
$$\left. -6^{1/2}\sin\gamma\cos\gamma,\ \left(\frac{3}{2}\right)^{1/2}\sin^2\gamma \right\|,$$
$$\|u_{\pm 2}^j(\gamma)\| = \frac{1}{4}\left\| (\cos\gamma\pm1)^2,\ 2\sin\gamma(\cos\gamma\pm1),\right. \tag{A.4}$$
$$\left. 6^{1/2}\sin^2\gamma,\ 2\sin\gamma(\cos\gamma\mp1),\ (\cos\gamma\mp1)^2 \right\|.$$

We consider the relative values of the terms that occur in (A.1) and (A.2). The following estimate is valid:

$$\mathrm{L}^{-1}(-i\mathbf{k})f''\mathbf{g}\mathbf{g}^{\tau} \sim (k^2 r_c^2 + k\varkappa r_c^2)^{-1}. \tag{A.5}$$

We shall assume that $\varkappa r_c \gg 1$. From (A.5) we have

$$\mathrm{L}^{-1}(-i\mathbf{k})f''\mathbf{g}\mathbf{g}^{\tau} \sim (\varkappa r_c)^{-1}$$

for $k \sim r_c^{-1}$,

$$\mathrm{L}^{-1}(-i\mathbf{k})f''\mathbf{g}\mathbf{g}^{\tau} \sim (\varkappa r_c)^{-2}$$

for $k \sim \varkappa$.

Each of these values is much less than unity. From these estimates it is evident that in the case of relatively large correlation radii, the terms of the series (A.1) or (A.2) decrease rapidly.

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