Fluctuations in liquid crystals near the liquid-nematic phase transition

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With neglect of dissipation effects, the space-time correlation function of the thermal fluctuations of the complete orientation tensor $S_{\alpha\beta}$ is found in both the isotropic phase and the nematic phase of a liquid crystal. It is shown that in the nematic phase the correlation function consists of three parts: longitudinal, uniaxial transverse and biaxial transverse. Ways of observing these parts are discussed.

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1. INTRODUCTION

In a number of papers (cf., e.g., [1]) it has been noted that the fluctuations in the isotropic phase of a liquid crystal can be described approximately by a formula of the Ornstein-Zernike type,

$$K(r)=\text{const}\cdot r^{-1}\exp(-r/r_c), \tag{1.1}$$

where $K(r)$ is the spatial correlation function of the fluctuations; r_c is the correlation length, which, near the phase-transition temperature T_c, increases without limit like $(T-T_c)^{-\nu}$, $\nu>0$.

In the present paper we seek the space-time correlation function of the thermal fluctuations in the liquid phase, in the linear approximation. From this we can obtain both the spatial correlation function, of the form (1.1), and also the purely temporal correlation function. The fluctuations in the nematic phase are treated by the same method.

In the existing literature [1–4] the fluctuations in the nematic phase of a liquid crystal have been studied on the basis of the phenomenological elasticity-hydrodynamical theory of Ericksen and Leslie. In the latter theory the behavior of the liquid crystal is described by the direction vector $\mathbf{n}(\mathbf{x}, t)$, and only the fluctuations of this vector are taken into account. In a liquid crystal the components of the traceless tensor $S_{\alpha\beta}(\mathbf{x}) = \overline{\nu_\alpha\nu_\beta} - \frac{1}{3}\delta_{\alpha\beta}$, where ν_α is the unit vector directed along the long axis of the molecule, serve as the internal thermodynamic parameters. This tensor has five independent components. In the case of a uniaxial medium the number of independent components is reduced to three, and the tensor can be expressed in terms of the unit vector n_α (the director) by the formula

$$S_{\alpha\beta}=S(n_\alpha n_\beta-\delta_{\alpha\beta}/3), \tag{1.2}$$

where $S=1-3\langle\sin^2\vartheta\rangle/2$ is a scalar indicating the degree of anisotropy.

In the papers mentioned the fluctuations of the tensor $S_{\alpha\beta}$ were reduced to fluctuations of the director n_α by the formula

$$\delta S_{\alpha\beta}=S(n_\alpha\delta n_\beta+n_\beta\delta n_\alpha).$$

Here two errors are committed. First, fluctuations of the coefficient S in (1.2) are neglected. Secondly, formula (1.2) for the fluctuating tensor $S_{\alpha\beta}$ has itself been taken without justification. The well-known uniaxiality (on the average) of the nematic phase leads only to an equality of the type (1.2) for the averages:

$$\bar{S}_{\alpha\beta}=S^0(\bar{n}_\alpha\bar{n}_\beta-\delta_{\alpha\beta}/3), \tag{1.2a}$$

and there is no reason for (1.2) to be fulfilled for fluctuational micro-inhomogeneities. The theory developed in this paper does not require these assumptions, since in it the fluctuations of the orientation tensor are treated directly. In this respect the present paper borders upon the work of Cheng and Meyer, [5] who also consider the complete tensor $S_{\alpha\beta}$.

In this paper we shall not take into account volume fluctuations or fluctuations of the velocities v_α of different parts of the medium. This approximation is permissible when the velocity fluctuations are relatively small because of the high density of the medium or because of its high viscosity, and also when the cross viscosity connecting the translational and orientational motions is small.

In the article, we consider, in essence, a simple model of a liquid crystal: the molecules are fixed at the sites of a cubic lattice, and interaction occurs with the Maier-Saupe Hamiltonian[6]

$$\mathscr{H}_{\text{int}}=-\frac{1}{2}\sum_{i\neq j}\varepsilon(\mathbf{r}_{ij})\,s^{(i)}_{\alpha\beta}\,s^{(j)}_{\beta\alpha}, \tag{1.3}$$

where $s^{(i)}_{\alpha\beta}=\nu^{(i)}_\alpha\nu^{(i)}_\beta-\delta_{\alpha\beta}/3$. The mean-field method is applied to this system and the linear approximation is considered. Of course, a more complicated variant of the theory can also be developed.

2. SPACE-TIME CORRELATION FUNCTION OF THE ISOTROPIC PHASE

We shall take the free-energy density in the form

$$F_0={}^1/_2A_1S_{\alpha\beta}^2+{}^1/_2L(\nabla S_{\alpha\beta})^2. \tag{2.1}$$

Here $A_1=a_1(T-T^*)$; this coefficient is positive in the liquid phase. A term of the form $\partial_\alpha S_{\alpha\gamma}\partial_\beta S_{\beta\gamma}$ has been omitted in the expression (2.1), since application of the mean-field method to the Hamiltonian (1.3) does not lead to its appearance. The mean-field method gives

$$L=\frac{N}{4}\sum_j \varepsilon(\mathbf{r}_{ij})(r_{ij})_1^2,\quad a_1T^*=N\sum_j \varepsilon(\mathbf{r}_{ij}).$$

We shall use (2.1) in writing the relaxation-fluctuation equations. It is known (e.g., [7,8]) that, if the free energy F is given as a function of the internal parameters A_1, A_2, ..., then, in the linear approximation, we have the equations

$$\dot{A}_i=-L_{ij}\partial F/\partial A_j+\xi_i, \tag{2.2}$$

where L_{ij} is the Onsager matrix, which satisfies (if the A_i are all time-even or all time-odd) the Onsager relations $L_{ij}=L_{ji}$, and the ξ_i are delta-correlated random functions with zero average and with the correlation function

$$\langle\xi_i(t_1)\xi_j(t_2)\rangle=2TL_{ij}\delta(t_{12}). \tag{2.3}$$

As applied to our case, when the $S_{\alpha\beta}(\mathbf{x})$ take the role of the A_i, formulas (2.2) and (2.3) have the form

$$\dot{S}_{\alpha\beta}(\mathbf{x})=-\int L_{\alpha\beta\gamma\rho}(\mathbf{x},\mathbf{x}')\frac{\delta F}{\delta S_{\gamma\rho}(\mathbf{x}')}d\mathbf{x}'+\xi_{\alpha\beta}(\mathbf{x},t), \tag{2.4}$$

$$\langle\xi_{\alpha\beta}(\mathbf{x}_1,t_1)\xi_{\gamma\rho}(\mathbf{x}_2,t_2)\rangle=2TL_{\alpha\beta\gamma\rho}(\mathbf{x}_1,\mathbf{x}_2)\delta(t_{12}). \tag{2.5}$$

Because of the short-range character of the interaction forces between the molecules (it is assumed that the interaction range r_{int} is much shorter than the correlation length r_c), it is natural to put

$$L_{\alpha\beta\gamma\rho}(\mathbf{x}_1,\mathbf{x}_2)=L_{\alpha\beta\gamma\rho}\delta(\mathbf{r}_{12}). \tag{2.6}$$

We shall assume that the possible additional terms with derivatives with respect to $\mathbf{r}_{12}$ (say, of the form $\partial_\alpha^2\delta(\mathbf{r}_{12})$) are absent. In the isotropic case the tensor can be constructed from the tensor $\delta_{\alpha\beta}$ alone. Because of the symmetry under interchange of α and β (and also of γ and ρ) and the zero trace ($L_{\alpha\alpha\gamma\rho}=0$), there remains only one possible combination

$$L_{\alpha\beta\gamma\rho}=\zeta^{-1}[{}^1/_2(\delta_{\alpha\gamma}\delta_{\beta\rho}+\delta_{\alpha\rho}\delta_{\beta\gamma})-{}^1/_3\delta_{\alpha\beta}\delta_{\gamma\rho}]\equiv\zeta^{-1}I_{\alpha\beta\gamma\rho}. \tag{2.7}$$

The expression $I_{\alpha\beta\gamma\rho}$, for the given symmetry, plays the role of the unit matrix δ_{ij}. In (2.7) ζ is a phenomenological constant having the meaning of a viscosity coefficient. By virtue of (2.6) and (2.7), formulas (2.4) and (2.5) take the form

$$\zeta S_{\alpha\beta}=-\frac{\delta F}{\delta S_{\alpha\beta}(\mathbf{x})}+\zeta\xi_{\alpha\beta},\quad \langle\xi_{\alpha\beta}\xi_{\gamma\rho}\rangle=\frac{2T}{\zeta}I_{\alpha\beta\gamma\rho}\delta(\mathbf{r}_{12})\delta(t_{12}). \tag{2.8}$$

Using (2.1), from this we have

$$\zeta\dot{S}_{\alpha\beta}=-A_1S_{\alpha\beta}+L\nabla^2S_{\alpha\beta}+\zeta\xi_{\alpha\beta}. \tag{2.9}$$

If we go over to the spectral representation

$$S_{\alpha\beta}(\mathbf{k},\omega)=\frac{1}{(2\pi)^2}\int e^{-i\omega t+i\mathbf{k}\mathbf{x}}S_{\alpha\beta}(\mathbf{x},t)\,d\mathbf{x}\,dt \tag{2.10}$$

and analogously for $\xi_{\alpha\beta}$, from (2.9) we shall have

$$S_{\alpha\beta}(\mathbf{k},\omega)=\zeta[i\omega\zeta+A_1+Lk^2]^{-1}\xi_{\alpha\beta}(\mathbf{k},\omega). \tag{2.11}$$

Hence we find the spectral density of the fluctuations:

$$G_{\alpha\beta\gamma\rho}(\mathbf{k},\omega)=\int\exp(i\mathbf{k}\mathbf{r}_{12}-i\omega t_{12})\langle S_{\alpha\beta}(\mathbf{x}_1,t)S_{\gamma\rho}(\mathbf{x}_2,t)\rangle\,d\mathbf{r}_{12}\,dt_{12}. \tag{2.12}$$

Taking into account also the second equality (2.8), we obtain

$$G_{\alpha\beta\gamma\rho}(\mathbf{k},\omega)=\frac{2T\zeta I_{\alpha\beta\gamma\rho}}{(\omega\zeta)^2+(A_1+Lk^2)^2}=\frac{2T\zeta}{A_1^2}\frac{I_{\alpha\beta\gamma\rho}}{(\omega t_c)^2+(1+r_c^2k^2)^2}, \tag{2.13}$$

where $t_c=\zeta/A_1$ and $r_c=(L/A_1)^{1/2}$ are respectively the correlation time and correlation length. Since $A_1=a_1(T-T^*)$, near the critical point the time t_c has a singularity of the type $(T-T^*)^{-1}$ and r_c has a singularity of the type $(T-T^*)^{-1/2}$.

Fourier transformation of formula (2.13) gives

$$K_{\alpha\beta\gamma\rho}(\mathbf{r}_{12},t_{12})=2TA_1^{1/2}L^{-3/2}f_1\left(\frac{r_{12}}{r_c},\frac{t_{12}}{t_c}\right)I_{\alpha\beta\gamma\rho}, \tag{2.14}$$

where

$$f(r,t)=\frac{1}{16\pi r}\left\{\left[1-\Phi\left(\left(1-\frac{r}{2t}\right)\sqrt{t}\right)\right]e^{-r}-\left[1-\Phi\left(\left(1+\frac{r}{2t}\right)\sqrt{t}\right)\right]e^{r}\right\} \tag{2.15}$$

($\Phi(y)$ is the error function).

If we perform the Fourier transformation over ω only, we shall have

$$G_{\alpha\beta\gamma\rho}(\mathbf{k},t_{12})=\frac{T}{A_1}\frac{I_{\alpha\beta\gamma\rho}}{1+k^2a^2}\exp\left[-\frac{(1+r_c^2k^2)|t_{12}|}{t_c}\right].$$

In particular,

$$G_{\alpha\beta\gamma\rho}(\mathbf{k},0)=\frac{T}{A_1}\frac{1}{1+k^2r_c^2}I_{\alpha\beta\gamma\rho}. \tag{2.16}$$

The original for this expression is well known—this is a formula of the Ornstein-Zernike type (1.1). Now, however, there is a tensor factor $I_{\alpha\beta\gamma\rho}$ in it.

Another particular result following from (2.13) and (2.14) is the formula for the temporal correlation function for $r_{12}=0$:

$$K_{\alpha\beta\gamma\rho}(0,t_{12})=TA_1^{1/2}L^{-3/2}\frac{1}{8\pi}\left[\Phi(\sqrt{t})-1+\frac{1}{\sqrt{\pi t}}e^{-t}\right]I_{\alpha\beta\gamma\rho} \tag{2.17}$$

($t=t_{12}/t_c$). At the point $T=T_c$, when $r_c=\infty$, from (2.13) and (2.14) we have the following correlation function:

$$K_{\alpha\beta\gamma\rho}(\mathbf{r}_{12},t_{12})=\frac{T}{4\pi r_{12}L}\Phi\left(\frac{\sqrt{t_{12}}}{r_{12}}\sqrt{\frac{L}{\zeta}}\right)I_{\alpha\beta\gamma\rho},$$
$$G_{\alpha\beta\gamma\rho}(\mathbf{k},\omega)=\frac{2T\zeta}{(\omega\zeta)^2+L^2k^4}I_{\alpha\beta\gamma\rho}. \tag{2.18}$$

These formulas describe the orientational "critical opalescence."

3. SPATIAL CORRELATION FUNCTION IN THE NEMATIC PHASE

In treating the nematic phase we must replace (2.1) by the more complete expression

$$F_0 = -{}^1/{}_2 a_1 T^* S_{\alpha\beta}^2 - TS_0(S) + {}^1/{}_2 L(\nabla S_{\alpha\beta})^2, \qquad (3.1)$$

where $S_0(S)$ is the entropy density. Mean-field theory gives the following parametric representation of the function $S_0(S)$:

$$S_0/N = \varphi - \lambda d\varphi/d\lambda, \quad d\varphi/d\lambda = (2S+1)/3, \qquad (3.2)$$

where

$$\varphi(\lambda) = \ln[\Psi(\sqrt{\lambda})/\sqrt{\lambda}], \quad \Psi(z) = \int_0^z e^{x^2}\,dx.$$

For a fixed temperature the magnitude of the spontaneous anisotropy $S = S^0$ is determined by minimizing the expression

$$F_0(S, T) = -{}^1/{}_3 a_1 T^* S^2 - TS_0(S), \qquad (3.3)$$

which is obtained from (3.1), with $\nabla S_{\alpha\beta} = 0$, taking into account the relation

$$S_{\alpha\beta}^2 = {}^2/{}_3 S^2, \qquad (3.4)$$

which follows from (1.2a).

We shall denote by T_c the temperature at which a minimum of the expression (3.3) that does not lie at the coordinate origin appears, and by S_c the position at which it appears (concerning the two critical temperatures T^* and T_c, see[4]). These values are determined from the equations

$$\frac{\partial F_0}{\partial S}(S_c, T_c) = 0, \quad \frac{\partial^2 F_0}{\partial S^2}(S_c, T_c) = 0.$$

Therefore,

$$F_0(S, T_c) = -{}^1/{}_6 T_c S_0'''(S_c)(S-S_c)^3 + \dots \qquad (3.5)$$

In (3.3) we put $T = T_c - \Delta T$ and take (3.5) into account. This gives

$$\begin{aligned} F_0(S, T) &= -{}^1/{}_6 T_c S_0'''(S_c)(S-S_c)^3 + \Delta T S_0(S) + \dots \\ &= -{}^1/{}_6 T_c S_0\ (S-S_c)^3 + \Delta T[S_0(S_c) + S_0'(S_c)(S-S_c) + {}^1/{}_2 S_0''(S-S_c)^2] + \dots \end{aligned} \qquad (3.6)$$

Differentiating this expression and equating the derivative to zero, we find the equation

$$-{}^1/{}_2 T_s S_0'''(S^0-S_s)^2 + \Delta T S_0'(S_c) = -\Delta T S_0''(S_0 - S_c) + \dots,$$

which determines the position S^0 of the minimum. Hence,

$$S^0 - S_c = [2\Delta T S_0'/(T_c S_0''')]^{1/2} + O(\Delta T). \qquad (3.7)$$

Here $\Delta T > 0$ and $S_0'/S_0''' > 0$.

We now find the coefficient of the expansion at the minimum:

$$\begin{aligned} F_0(S, T) &= F_0(S^0, T) + {}^1/{}_3 A_2 (S-S^0)^2 \\ &= F_0(S^0, T) + {}^1/{}_2 A_2 (S_{\alpha\beta} - S_{\alpha\beta}^0)^2. \end{aligned} \qquad (3.8)$$

According to (3.6) and (3.7), we have

$$\begin{aligned} A_2 &= \frac{3}{2}\frac{\partial^2 F_0}{\partial S^2}(S^0, T) = -\frac{3}{2} T_c S_0'''(S^0 - S_c) + O(\Delta T) \\ &= \frac{3}{2} T_c |S_0'''| \left(\frac{2S_0'}{TS_0'''}\right)^{1/2} (T_c - T)^{1/2} + O(\Delta T). \end{aligned} \qquad (3.9)$$

Let the spontaneous anisotropy at a temperature $T < T_c$ be described by the tensor (cf. (1.2a))

$$S_{\alpha\beta}^0 = S^0(n_\alpha^0 n_\beta^0 - \delta_{\alpha\beta}/3),$$

where S^0 is defined above and n^0 is the direction vector of the preferred orientation. We denote $\delta S_{\alpha\beta} = S_{\alpha\beta} - S_{\alpha\beta}^0$. By virtue of (3.4), we have

$$S = [{}^3/{}_2(S_{\alpha\beta}^{0\,2} + 2S_{\alpha\beta}^0 \delta S_{\alpha\beta} + \delta S_{\alpha\beta}^2)]^{1/2} = S^0\left(1 + \frac{3}{2S^{0\,2}} S_{\alpha\beta}^0 \delta S_{\beta\alpha} + \dots\right). \qquad (3.10)$$

Taking (3.8) and (3.10) into account and returning to the case of a nonuniform tensor field, when terms with gradients are present (cf. (3.1)), we obtain

$$F_0 = {}^1/{}_2 A_2 (n_{\alpha\beta}^0 \delta S_{\alpha\beta})^2 + {}^1/{}_2 L(\nabla \delta S_{\alpha\beta})^2. \qquad (3.11)$$

Here we have omitted the unimportant term $F_0(S_{\alpha\beta}^0)$ and introduced the notation

$$n_{\alpha\beta}^0 = \sqrt{{}^3/{}_2}(n_\alpha^0 n_\beta^0 - \delta_{\alpha\beta}/3), \qquad (3.12)$$

so that $(n_{\alpha\beta}^0)^2 = 1$.

The expression (3.11) is the analog for the nematic phase of formula (2.1). It determines the probability-distribution density functional for spatial fluctuations, by the formula

$$p[S_{\alpha\beta}(\mathbf{x})] = \text{const}\cdot\exp\left\{-T^{-1}\int F_0(S_{\alpha\beta}(\mathbf{x}))\,d\mathbf{x}\right\}. \qquad (3.13)$$

It is convenient to go over to the spatial spectral representation, using formula (2.10) but without the temporal transformation. In this representation (3.11) takes the form

$$\begin{aligned} \int F_0\,d\mathbf{x} &= \frac{1}{2} A_2 \int \delta S_{\alpha\beta}^*(\mathbf{k}) n_{\beta\alpha}^0 n_{\gamma\rho}^0 \delta S_{\rho\gamma}(\mathbf{k})\,d\mathbf{k} \\ &+ \frac{1}{2} L \int k^2 \delta S_{\alpha\beta}^*(\mathbf{k}) \delta S_{\beta\alpha}(\mathbf{k})\,d\mathbf{k}. \end{aligned} \qquad (3.14)$$

We substitute (3.14) into (3.13) and use the fact that it follows from the Gaussian distribution

$$p(y) = \text{const}\cdot\exp\{-{}^1/{}_2 \mathbf{y}^T \mathbf{D} \mathbf{y}\}$$

that the form of the correlation function is

$$\langle \mathbf{y}\mathbf{y}^T \rangle = \mathbf{D}^{-1}. \qquad (3.15)$$

In our case the matrix $\mathbf{D}$ has the form

$$\mathbf{D} = T^{-1} \| [(A_2 + Lk^2) n_{\alpha\beta}^0 n_{\gamma\rho}^0 + Lk^2 (I_{\alpha\beta\gamma\rho} - n_{\alpha\beta}^0 n_{\gamma\rho}^0)] \delta(\mathbf{k}_{12}) \|. \qquad (3.16)$$

The matrices $n_{\alpha\beta}^0 n_{\gamma\rho}^0$ and $I_{\alpha\beta\gamma\rho} - n_{\alpha\beta}^0 n_{\gamma\rho}^0$ are projection operators on to orthogonal subspaces, and therefore

$$\begin{aligned} &\| (A_2 + Lk^2) n_{\alpha\beta}^0 n_{\gamma\rho}^0 + Lk^2 (I_{\alpha\beta\gamma\rho} - n_{\alpha\beta}^0 n_{\gamma\rho}^0) \|^{-1} \\ &= \| (A_2 + Lk^2)^{-1} n_{\alpha\beta}^0 n_{\gamma\rho}^0 + (Lk^2)^{-1} (I_{\alpha\beta\gamma\rho} - n_{\alpha\beta}^0 n_{\gamma\rho}^0) \|. \end{aligned} \qquad (3.17)$$

Because of this, application of (3.15) gives

$$\langle \delta S_{\alpha\beta}^{*}(\mathbf{k}_1)\,\delta S_{\gamma\rho}(\mathbf{k}_2)\rangle = G_{\alpha\beta\gamma\rho}(\mathbf{k}_1)\,\delta(\mathbf{k}_{12}),$$

where

$$G_{\alpha\beta\gamma\rho}(\mathbf{k}) = \frac{T n_{\alpha\beta}{}^{0} n_{\gamma\rho}{}^{0}}{A_2 + Lk^2} + T\,\frac{I_{\alpha\beta\gamma\rho} - n_{\alpha\beta}{}^{0} n_{\gamma\rho}{}^{0}}{Lk^2} \qquad (3.18)$$

is the spectral density of the spatial fluctuations.

Fourier transformation of (3.18) gives the correlation function

$$K_{\alpha\beta\gamma\rho}(\mathbf{r}_{12}) = \frac{T}{4\pi r_{12} L}\left[n_{\alpha\beta}{}^{0} n_{\gamma\rho}{}^{0} \exp\left\{-\frac{r_{12}}{r_c}\right\} + I_{\alpha\beta\gamma\rho} - n_{\alpha\beta}{}^{0} n_{\gamma\rho}{}^{0}\right], \qquad (3.19)$$

where $r_c = (L/A_2)^{1/2}$ is the correlation length, which, because of (3.9), has a singularity of the type $(T_c - T)^{1/4}$ near T_c.

The first term in (3.18), (3.19) describes the "longitudinal" fluctuations and the second the "transverse" fluctuations. The slow decrease of the second term with increase of r_{12} reflects the presence of "rotational critical opalescence" for all $T < T_c$. If we let $T \to T_c - 0$ for fixed r_{12}, then $\exp\{-r_{12}/r_c\}$ will tend to unity and the nonisotropic terms associated with $n^0_{\alpha\beta} n^0_{\gamma\rho}$ will vanish. A continuous transition to the isotropic phase is thereby realized.

4. SPACE-TIME CORRELATION FUNCTION FOR THE NEMATIC PHASE

We shall write the relaxation-fluctuation equations (2.2), (2.4) for the nematic phase. As in Sec. 2, they have the form

$$\delta S_{\alpha\beta} = -L_{\alpha\beta\gamma\rho}\frac{\delta F}{\delta(\delta S_{\gamma\rho})} + \xi_{\alpha\beta}, \quad (\langle \xi_{\alpha\beta}\xi_{\gamma\rho}\rangle = 2TL_{\alpha\beta\gamma\rho}\delta(\mathbf{r}_{12})\,\delta(t_{12})), \qquad (4.1)$$

but now the tensor $L_{\alpha\beta\gamma\rho}$ is not necessarily constructed, generally speaking, from $\delta_{\alpha\beta}$ alone. Now there is also the vector n^0_α, and this increases the number of possible combinations. The necessary zero-trace and symmetry conditions are satisfied by only the following independent combinations:

$$I_{\alpha\beta\gamma\rho}, \quad B^{2}_{\alpha\beta\gamma\rho} = n_{\alpha\beta}{}^{0} n_{\gamma\rho}{}^{0},$$
$$B^{3}_{\alpha\beta\gamma\rho} = {}^1\!/_2(\delta_{\alpha\gamma} n_\beta{}^0 n_\rho{}^0 + \delta_{\alpha\rho} n_\beta{}^0 n_\gamma{}^0 + \delta_{\beta\gamma} n_\alpha{}^0 n_\rho{}^0 + \delta_{\beta\rho} n_\alpha{}^0 n_\gamma{}^0 - 4 n_\alpha{}^0 n_\beta{}^0 n_\gamma{}^0 n_\rho{}^0). \qquad (4.2)$$

We denote $B^1_{\alpha\beta\gamma\rho} = I_{\alpha\beta\gamma\rho} - B^2_{\alpha\beta\gamma\rho} - B^3_{\alpha\beta\gamma\rho}$. It is not difficult to convince oneself that the matrices $B^1_{\alpha\beta\gamma\rho}$, $B^2_{\alpha\beta\gamma\rho}$ and $B^3_{\alpha\beta\gamma\rho}$ are idempotent and orthogonal with respect to the matrix multiplication $B^i_{\alpha\beta\gamma\rho} B^j_{\gamma\rho\mu\nu}$, i.e., they are projection operators on to mutually orthogonal subspaces. This makes the determination of the inverse matrix and multiplication easier.

The general form of the tensor L is

$$L_{\alpha\beta\gamma\rho} = \sum_{n=1} c_n B^{n}_{\alpha\beta\gamma\rho}, \qquad (4.3)$$

where the c_n are phenomenological constants. Substituting (4.3) into the equation

$$i\omega\,\delta S_{\alpha\beta} + (A_2 L_{\alpha\beta\gamma\rho} n_{\gamma\rho}{}^{0} n_{\sigma\tau}{}^{0} + Lk^2 L_{\alpha\beta\sigma\tau})\,\delta S_{\sigma\tau} = \xi_{\alpha\beta},$$

which follows from (4.1) and (3.11), we obtain

$$[(i\omega + c_1 Lk^2) B^{1}_{\alpha\beta\gamma\rho} + (i\omega + (A_2 + Lk^2) c_2) B^{2}_{\alpha\beta\gamma\rho}$$
$$+ (i\omega + c_3 Lk^2) B^{3}_{\alpha\beta\gamma\rho}]\,\delta S_{\gamma\rho} = \xi_{\alpha\beta}. \qquad (4.4)$$

These equations are trivially solved:

$$\delta S_{\alpha\beta}(\mathbf{k}, \omega) = [(i\omega + c_1 Lk^2)^{-1} B^{1}_{\alpha\beta\gamma\rho} + (i\omega + c_2(A_2 + Lk^2))^{-1} B^{2}_{\alpha\beta\gamma\rho}$$
$$+ (i\omega + c_3 Lk^2)^{-1} B^{3}_{\alpha\beta\gamma\rho}]\,\xi_{\gamma\rho}.$$

Taking into account the form of the correlation function (4.1) for $\xi_{\alpha\beta}$ and using the orthogonality of the matrices B^n, from this we easily find the spectral density of the fluctuations of $S_{\alpha\beta}$:

$$G_{\alpha\beta\gamma\rho}(\mathbf{k}, \omega) = \frac{2Tc_1 B^{1}_{\alpha\beta\gamma\rho}}{\omega^2 + c_1{}^2 L^2 k^4} + \frac{2Tc_2 B^{2}_{\alpha\beta\gamma\rho}}{\omega^2 + c_2{}^2 (A_2 + Lk^2)^2} + \frac{2Tc_3 B^{3}_{\alpha\beta\gamma\rho}}{\omega^2 + c_3 L^2 k^4}. \qquad (4.5)$$

We can also write down the Fourier transformation of these expressions. The first and third terms give an expression of the type (2.18), and the second gives one of the type (2.14). If we put $t_{12} = 0$, i.e., integrate (4.5) over ω, the first and third terms combine into one and give in the sum the second term in the right-hand side of (3.18), while the second term of (4.5) gives the first term of (3.18).

The second term in (4.5) and the first term in (3.18) describe the longitudinal fluctuations, which can be explained by the fluctuations of the coefficient S in (1.2). In addition to the longitudinal term in (4.5) there are also two transverse terms, describing fluctuations of the critical-opalescence type. The third term in (4.5) can be explained by the fluctuations of the director $\mathbf{n}_\alpha$ in (1.2). In fact, the theory of nematic fluctuations expounded in[1–4], which considers only director fluctuations, leads to the appearance of precisely the tensor factor $B^3_{\alpha\beta\gamma\delta}$. But the first term in (4.5) requires a more complicated explanation.

We shall show that it cannot be explained in the framework of the theory of uniaxial fluctuations. If the uniaxiality condition (1.2) is fulfilled, then, denoting $b_\alpha = S^{1/2} n_\alpha$ and varying, we have

$$\delta S_{\alpha\beta} = b_\alpha{}^0 \delta b_\beta + b_\beta{}^0 \delta b_\alpha - {}^2\!/_3 b_\gamma{}^0 \delta b_\gamma \delta_{\alpha\beta}. \qquad (4.6)$$

In the general case δb_α has the following correlation function:

$$\langle \delta b_\alpha \delta b_\beta \rangle = a_\parallel n_\alpha{}^0 n_\beta{}^0 + a_\perp(\delta_{\alpha\beta} - n_\alpha{}^0 n_\beta{}^0), \qquad (4.7)$$

where $a_\parallel$ and $a_\perp$ are certain functions of r_{12} and t_{12}. After a series of computations, from (4.6) and (4.7) we shall have

$$\langle \delta S_{\alpha\beta} \delta S_{\gamma\rho} \rangle = {}^8\!/_3\, a_\parallel S^0 B^{2}_{\alpha\beta\gamma\rho} + 2a_\perp S^0 B^{3}_{\alpha\beta\gamma\rho}.$$

Here the term with $B^1_{\alpha\beta\gamma\rho}$ is absent, and so the assumption of local biaxiality of the fluctuations is necessary for its appearance.

5. IMPROVED CORRELATION FUNCTION FOR THE FLUCTUATIONS IN THE ISOTROPIC PHASE

From general considerations, a term $\frac{1}{2}L_2\partial_\alpha S_{\alpha\gamma}\partial_\beta S_{\beta\gamma}$ can be added to the free-energy density (2.1), (3.1). In the preceding treatment we did not take this into account. For the example of the isotropic phase we shall examine what kind of changes arise if this term is taken into account.

Introducing a symmetric matrix with zero trace, we can write this term in the form

$$\begin{aligned}{}^1/_2L_2(\partial_\alpha S_{\alpha\gamma})^2={}^1/_8L_2S_{\alpha\beta}[\partial_\alpha{}^\tau\partial_\gamma\delta_{\beta\rho}+\partial_\beta{}^\tau\partial_\gamma\delta_{\alpha\rho}+\partial_\alpha{}^\tau\partial_\rho\delta_{\beta\gamma}\\+\partial_\beta{}^\tau\partial_\rho\delta_{\alpha\gamma}-{}^4/_3\partial_\alpha{}^\tau\partial_\beta\delta_{\gamma\rho}-{}^4/_3\partial_\gamma{}^\tau\partial_\rho\delta_{\alpha\beta}+{}^4/_9\partial_\sigma{}^\tau\partial_\sigma\delta_{\alpha\beta}\delta_{\gamma\rho}]S_{\gamma\rho}.\end{aligned} \tag{5.1}$$

When we go over to the spectral representation ∂_α is replaced by $-ik_\alpha$. In this case it is convenient to express the matrix in the square brackets in terms of matrices $\tilde{B}^2_{\alpha\beta\gamma\rho}$ and $\tilde{B}^3_{\alpha\beta\gamma\rho}$ analogous to the matrices (4.2) but, unlike the latter, constructed not from n^0_α but from the vector $m_\alpha=k_\alpha/k$. Obviously, they possess the same algebraic properties.

Thus, we have

$$\begin{aligned}k_\alpha k_\gamma\delta_{\beta\rho}+k_\beta k_\gamma\delta_{\alpha\rho}+k_\alpha k_\rho\delta_{\beta\gamma}+k_\beta k_\rho\delta_{\alpha\gamma}-{}^4/_3\,k_\alpha k_\beta\delta_{\gamma\rho}\\-{}^4/_3k_\gamma k_\rho\delta_{\alpha\beta}+{}^4/_9k^2\delta_{\alpha\beta}\delta_{\gamma\rho}={}^5/_3k^2\overset{2}{\tilde{B}}_{\alpha\beta\gamma\rho}+2k^2\overset{3}{\tilde{B}}_{\alpha\beta\gamma\rho}.\end{aligned} \tag{5.2}$$

Because of (5.1), (5.2), Eq. (2.9) will now have the form

$$[(i\omega\zeta+A_1+L_1k^2)I_{\alpha\beta\gamma\rho}+{}^2/_3L_2k^2\overset{2}{\tilde{B}}_{\alpha\beta\gamma\rho}+{}^1/_2L_2k^2\overset{3}{\tilde{B}}_{\alpha\beta\gamma\rho}]S_{\gamma\rho}=\zeta\xi_{\alpha\beta}\quad(L_1\equiv L).$$

This equation is solved for $S_{\alpha\beta}$ in exactly the same way as was (4.4); this gives

$$\begin{aligned}S_{\alpha\beta}=[(i\omega\zeta+A_1+L_1k^2)^{-1}\overset{1}{\tilde{B}}_{\alpha\beta\gamma\rho}+(i\omega\zeta+A_1\\+(L_1+{}^2/_3L_2)k^2)^{-1}\,\overset{2}{\tilde{B}}_{\alpha\beta\gamma\rho}+(i\omega\zeta+A_1+(L_1+{}^1/_2L_2)k^2)\overset{3}{\tilde{B}}_{\alpha\beta\gamma\rho}]\zeta\xi_{\gamma\rho}.\end{aligned} \tag{5.3}$$

Hence, by analogy with (4.5), we obtain the spectral density

$$\begin{aligned}G_{\alpha\beta\gamma\rho}(\mathbf{k},\omega)=2T\zeta[(\omega\zeta)^2+(A_1+L_1k^2)^2]^{-1}(I_{\alpha\beta\gamma\rho}-\overset{2}{\tilde{B}}_{\alpha\beta\gamma\rho}-\overset{3}{\tilde{B}}_{\alpha\beta\gamma\rho})\\+2T\zeta[(\omega\zeta)^2+(A_1+L_1k^2+{}^2/_3\,L_2k^2)^2]^{-1}\,\overset{2}{\tilde{B}}_{\alpha\beta\gamma\rho}\\+2T\zeta[(\omega\zeta)^2+(A_1+L_1k^2+{}^1/_2L_2k^2)^2]^{-1}\,\overset{3}{\tilde{B}}_{\alpha\beta\gamma\rho}.\end{aligned} \tag{5.4}$$

We see that in (5.4), as compared with (2.13), additional nonisotropic terms proportional to $\tilde{B}^2_{\alpha\beta\gamma\rho}$ and $\tilde{B}^3_{\alpha\beta\gamma\rho}$ have appeared.

It is somewhat more complicated to refine formula (4.5). However, the situation is simplified if the vector $\mathbf{n}^0$ is parallel to the wave-vector $\mathbf{k}$. Then allowance for the term (5.1) leads only to replacement of L by $L_1+\frac{2}{3}L_2$ in the second term of (4.5) and to replacement of L by $L_1+\frac{1}{2}L_2$ in the third term.

6. SOME CONSEQUENCES OF THE RESULTS OBTAINED

Fluctuations in a liquid crystal are conveniently investigated experimentally by observing light scattering by the fluctuational inhomogeneities. As is well known, the differential scattering cross-section per unit volume, unit solid angle and unit angular frequency is given by the formula

$$\frac{d\sigma}{d\Omega\,d\omega}=\frac{1}{32\pi^3}k_0{}^4J_{\alpha\beta\gamma\rho}(\mathbf{k}-\mathbf{k}',\omega)\,e_\alpha e_\gamma e_\beta{}'e_\rho{}'. \tag{6.1}$$

Here $\mathbf{k}$, $\mathbf{e}$ are the wave-vector and polarization vector of the incident wave and $\mathbf{k}'$, $\mathbf{e}'$ are those of the scattered wave. Furthermore,

$$J_{\alpha\beta\gamma\rho}(\mathbf{q},\omega)=\int\exp(i\mathbf{q}\mathbf{r}_{12}-i\omega t_{12})\langle\delta\varepsilon_{\alpha\beta}(\mathbf{x}_1,t_1)\,\delta\varepsilon_{\gamma\rho}(\mathbf{x}_2,t_2)\rangle\,d\mathbf{r}_{12}\,dt_{12}. \tag{6.2}$$

Since the dielectric-permittivity tensor $\varepsilon_{\alpha\beta}$ (and, analogously, the magnetic tensor) is related to $S_{\alpha\beta}$ by the formula

$$\varepsilon_{\alpha\beta}-{}^1/_3\varepsilon_{\gamma\gamma}\delta_{\alpha\beta}=N\Delta\varepsilon S_{\alpha\beta}$$

($\Delta\varepsilon=\varepsilon_{\parallel}-\varepsilon_{\perp}$, N is the number of particles in unit volume), (6.2) can be expressed directly in terms of the spectral density $G_{\alpha\beta\gamma\rho}(\mathbf{q},\omega)$:

$$J_{\alpha\beta\gamma\rho}(\mathbf{q},\omega)=(N\Delta\varepsilon)^2G_{\alpha\beta\gamma\rho}(\mathbf{q},\omega). \tag{6.3}$$

Substituting (6.3) into (6.1), it is not difficult to examine the influence exerted on the scattering by the individual terms of the expressions (2.13), (4.5) and (5.4). Thus, (2.13) gives ($\mathbf{q}=\mathbf{k}-\mathbf{k}'$)

$$\frac{d\sigma}{d\Omega\,d\omega}=\frac{1}{32\pi^3}k_0{}^4(N\Delta\varepsilon)^2T\zeta\frac{1+(\mathbf{e}\mathbf{e}')^2/3}{(\omega\zeta)^2+(A_1+Lq^2)^2}\,.$$

Passing to formula (4.5), corresponding to the nematic phase, we see that the differential scattering cross-section is equal to the sum of three terms, which are respectively proportional to the following factors:

$$\begin{aligned}\overset{1}{B}_{\alpha\beta\gamma\rho}e_\alpha e_\gamma e_\beta{}'e_\rho{}'&={}^1/_2+{}^1/_2(\mathbf{e}\mathbf{n}^0)^2(\mathbf{e}'\mathbf{n}^0)^2-{}^1/_2(\mathbf{e}\mathbf{n}^0)^2-{}^1/_2(\mathbf{e}'\mathbf{n}^0)^2,\\\overset{2}{B}_{\alpha\beta\gamma\rho}e_\alpha e_\gamma e_\beta{}'e_\rho{}'&={}^3/_2(\mathbf{e}\mathbf{n}^0)^2(\mathbf{e}'\mathbf{n}^0)^2-(\mathbf{e}\mathbf{n}^0)(\mathbf{e}'\mathbf{n}^0)(\mathbf{e}\mathbf{e}')+{}^1/_6(\mathbf{e}\mathbf{e}')^2,\\\overset{3}{B}_{\alpha\beta\gamma\rho}e_\alpha e_\gamma e_\beta{}'e_\rho{}'&=(\mathbf{e}\mathbf{n}^0)(\mathbf{e}'\mathbf{n}^0)(\mathbf{e}\mathbf{e}')+{}^1/_2(\mathbf{e}\mathbf{n}^0)^2+{}^1/_2(\mathbf{e}'\mathbf{n}^0)^2-2(\mathbf{e}\mathbf{n}^0)^2(\mathbf{e}'\mathbf{n}^0)^2.\end{aligned} \tag{6.4}$$

The extent to which the terms in the refined formula (5.4) manifest themselves is determined by the same factors, but with $\mathbf{n}^0$ replaced by $\mathbf{m}=\mathbf{k}/k$.

If we change the mutual orientation of the vectors $\mathbf{e}$, $\mathbf{e}'$ and $\mathbf{n}^0$, then, according to (6.4), the different terms of (4.5) will manifest themselves to different extents. Thus, if $\mathbf{e}$ and $\mathbf{e}'$ are perpendicular to $\mathbf{n}^0$, the third term, describing the usual (director) transverse fluctuations, drops out, and there remain only a term describing biaxial transverse fluctuations and a term corresponding to longitudinal fluctuations:

$$\frac{d\sigma}{d\Omega\,d\omega}=\frac{1}{32\pi^3}k_0{}^4(N\Delta\varepsilon)^2T\left[\frac{c_1}{\omega^2+c_1{}^2L^2q^4}+\frac{c_2(\mathbf{e}\mathbf{e}')/3}{\omega^2+c_2{}^2(A_2+Lq^2)^2}\right].$$

These terms can be distinguished by taking into account the different dependence on ω and q or the different dependence on $\mathbf{e}\cdot\mathbf{e}'$.

If we put $\mathbf{e}\perp\mathbf{e}'$ and $\mathbf{e}\perp\mathbf{n}^0$, on the other hand, the second term drops out. If, however, all three vectors $\mathbf{e}$, $\mathbf{e}'$ and $\mathbf{n}^0$ are made almost mutually orthogonal, the first term will be the most important.

By the methods described it is possible to investigate experimentally whether there are locally-biaxial fluctuations, i.e., whether the constant c_1 is nonzero. In order to eliminate the effect of complicating terms such as the additional terms in (5.4), it is appropriate to make $\mathbf{k}-\mathbf{k}'$ parallel to $\mathbf{n}^0$. These terms then disappear.

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Magnetic resonance of an isotropic superparamagnet[1)]

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Magnetic resonance induced by a circularly or linearly polarized high-frequency field **h** in an isotropic superparamagnet located in a stationary field **H** is investigated. It is shown that orientational diffusion of the magnetic moment, leading to superparamagnetism of small particles of the ferromagnet, deforms the absorption line. The line shape is defined by the Langevin parameter $\sigma = MVH/kT$ (M is the magnetization, V the particle volume). The resonance line at $\sigma \gg 1$ changes into a purely relaxation line at $\sigma \ll 1$. Thermal fluctuations are taken into account by replacing the dynamic description of motion of the magnetic moment (Landau-Lifshitz equation) by a statistical description (Fokker-Planck equation). Two methods of solving the problem are presented. One is based on a direct solution of the Fokker-Planck equation for a circularly polarized field **h**. This method involves a search for a rotating coordinate system whose axis of rotation coincides with the direction of precession of the mean magnetization. The other method of calculating the dynamic susceptibility is based on the use of the equation of motion of the magnetization of the superparamagnet. The equation is derived from the Fokker-Planck equation by the method of moments.

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INTRODUCTION

A superparamagnet is an ensemble of non-interacting ferromagnetic particles, the dimensions of which are so small that the formation of a domain structure in them is energywise unfavored; thus, each particle is magnetized to saturation even in the absence of an external magnetic field, although the total magnetic moment of the ensemble is equal to zero. Under the influence of a magnetic field H, a system of such particles becomes magnetized like a classical Langevin paramagnet

$$\langle m_z\rangle=\langle M_z/M\rangle=\operatorname{cth}\sigma-\sigma^{-1}\equiv L(\sigma),$$

where $\sigma=MVH/kT$, M is the magnetization per unit volume at $T=0$, and V is the volume of the particle.

At sufficiently small V and not too large H, the characteristic paramagnetic-disorder temperatures can lie much lower than the Curie temperature T_c; greatest interest attaches then to the temperature region $T \ll T_c$, where the temperature dependence of M can be neglected.

The theoretical study of the dynamics of superparamagnets was initiated by Brown,[1] who wrote down the Fokker–Planck equation for such a system and investigated the processes of relaxation in anisotropic particles. The magnetic resonance of an anisotropic superparamagnet under the influence of a weak high-frequency field at $H=0$ (resonance in the effective field of uniaxial magnetic anisotropy) was investigated in[2]. Dynamic magnetic hysteresis of an isotropic superparamagnet under the influence of an alternating magnetic field of arbitrary amplitude was investigated in [3].

The present paper is devoted to the dynamic susceptibility of an isotropic superparamagnet placed in a constant field H and in a weak high-frequency field **h**. In this situation, size effects typical of ultrasmall particles of a ferromagnet should appear. We note that a particle with diameter on the order of 100 Å contains only 10^4–10^5 atoms. This number is not large enough to be able to neglect the thermal fluctuations of the field. The amplitude of the fluctuating field is of the order of kT/MV, so that for microcrystals with volume $V \lesssim 10^{-18}$ cm^3 at a