mechanism responsible for the effect of superconductivity stimulation by microwave radiation is the mechanism proposed by Éliashberg.<sup>[5,6]</sup> Let us briefly enumerate the main results supporting such a conclusion. 1) The existence of the effect of critical-current growth not only in short, but also in long, bridges. 2) The existence of a lower frequency limit consistent with the Eliashberg theory. 3) The existence of the growth effect in a temperature region fairly far below  $T_c$ , where the influence of the fluctuations is insignificant. 4) The fact that the theoretical value of the Ginzburg-Landau pairbreaking critical current is exceeded by the values of the critical current under the influence of radiation. 5) The agreement between the experimental power dependences of  $I_c$  and the theoretical dependences obtained from the Éliashberg equation with allowance for the thermal effects.

The Éliashberg mechanism is also attested by the discovery of the growth of  $I_c$  in bridges and point contacts under the influence of phonons, and not photons.<sup>[17]</sup> In fact, the stimulation of superconductivity can occur as a result of the heating of the quasiparticles relative to the state of thermodynamic equilibrium either by microwave radiation, or by phonons. The factor limiting this effect may be the heating of the film lattice by the phonons emitted during the energy relaxation.

The authors are very grateful to G. M. Éliashberg, I. K. Yanson, B. I. Ivlev, A. F. Volkov, and S. N. Artemenko for useful advice and comments.

<sup>1)</sup>As can be shown on the basis of<sup>[6]</sup>, the mean excess energy given away by the quasiparticles during relaxation is of the order  $\Delta$ . For  $T_c - T \approx 0.1$  K, i.e., in the temperature region where we compared experiment with theory,  $\Delta \sim kT$ , and the processes of relaxation of the excess energy are close to

being equilibrium processes. In this case we can use the heat-transfer coefficients measured under equilibrium conditions.  $^{[15]}$ 

<sup>2)</sup>The authors are grateful to A. D. Malov for carrying out the computer calculations.

<sup>1</sup>A. F. G. Wyatt, V. M. Dmitriev, W. S. Moore, and F. W. Sheard, Phys. Rev. Lett. **16**, 1166 (1966).

- <sup>2</sup>A. H. Dayem and J. J. Wiegand, Phys. Rev. **155**, 419 (1967).
- <sup>3</sup>V. M. Dmitriev, E. V. Khristenko, and S. Shapiro, Trudy FTINT **28**, 3 (1973).
- <sup>4</sup>Yu. I. Latyshev and F. Ya. Nad', Pis'ma Zh. Eksp. Teor. Fiz. **19**, 737 (1974) [JETP Lett. **19**, 380 (1974)]; IEEE Trans. Magn. **11**, 877 (1975).
- <sup>5</sup>G. M. Éliashberg, Pis'ma Zh. Eksp. Teor. Fiz. **11**, 186 (1970) [JETP Lett. **11**, 114 (1970)].
- <sup>6</sup>B. I. Ivlev, S. G. Lisitsyn, and G. M. Éliashberg, J. Low Temp. Phys. **10**, 449 (1973).
- <sup>7</sup>F. E. Harper and M. Tinkham, Phys. Rev. 172, 441 (1970).
- <sup>8</sup>J. Clarke and J. L. Paterson, J. Low Temp. Phys. **15**, 491 (1974).
- <sup>9</sup>F. Ya. Nad' and O. Yu. Polyanskii, Manuscript deposited in Central Res. Inst., "Élektronika," No. 764, 1973; Radiotekh. Élektron. 18, 2445 (1973).
- <sup>10</sup>W. J. Skocpol, M. R. Beasley, and M. Tinkham, J. Appl. Phys. **45**, 4054 (1974).
- <sup>11</sup>T. K. Hunt and J. E. Mercereau, Phys. Rev. Lett. 18, 551 (1967).
- <sup>12</sup>K. W. Shepard, Physica **55**, 786 (1971).
- <sup>13</sup>L. P. Gor'kov, Zh. Eksp. Teor. Fiz. **37**, 1407 (1959) [Sov. Phys. JETP **10**, 998 (1960)].

<sup>14</sup>V. P. Andratskii, L. M. Grundel', V. N. Gubankov, and N. B. Pavlov, Zh. Eksp. Teor. Fiz. **65**, 1591 (1973) [Sov. Phys. JETP **38**, 794 (1974)].

- <sup>15</sup>V. E. Holt, J. Appl. Phys. **37**, 798 (1966); I. Ames and H. Seki, J. Appl. Phys. **35**, 2069 (1964).
- <sup>16</sup>V. P. Andratskii, V. N. Gubankov, K. K. Likharev, and N. B. Pavlov, Zh. Eksp. Teor. Fiz. **70**, 292 (1976) [Sov. Phys. JETP **43**, 151 (1976)].
- <sup>17</sup>T. J. Tredwell and E. H. Jacobsen, Phys. Rev. Lett. **35**, 244 (1975).

Translated by A. K. Agyei

## Van der Waals forces in liquid crystals with a large dielectric anisotropy

B. G. Kamenskii and E. I. Kats

L. D. Landau Institute of Theoretical Physics, USSR Academy of Sciences (Submitted April 26, 1976) Zh. Eksp. Teor. Fiz. **71**, 2168–2177 (December 1976)

Methods are proposed for the calculation of Van der Waals forces in liquid crystals whose dielectric anisotropy is not small. An expansion in terms of the deviation of the director from the equilibrium orientation or of its derivative is employed. Examples are considered. It is shown that the Van der Waals forces can induce instability of the plane disclination. Biaxial effects, which are appreciable near the point of a phase transition to an isotropic phase, are taken into account in the intensity of the light scattering.

PACS numbers: 61.30.+w

1. In recent years, the general theory of Van der Waals forces in condensed systems<sup>[1]</sup> has been applied to various problems of the physics of liquid crystals.<sup>[2-4]</sup> This interest is due mainly to the fact that the magnitude

of the short-range forces, which assure the stability of the liquid crystal, is not large. Therefore, the longrange forces, which are usually not very significant, can lead to appreciable effects. In the work of Dzyaloshinskii, Dmitriev and one of the present authors, [2] the method of expansion in powers of the anisotropy of the dielectric permittivity tensor  $\varepsilon_a$  was used for the calculation of the Van der Waals forces. Smallness of  $\varepsilon_a$  in comparison with the isotropic part of  $\varepsilon_0$  is required for the validity of such an expansion:  $\varepsilon_a \ll \varepsilon_0$ . Here (in lowest order) the magnitude of the Van der Waals energy turns out to be roughly ~  $(\varepsilon_a/\varepsilon_0)^2$ . Therefore, the long-range forces are more important in systems with  $\varepsilon_a \sim \varepsilon_0$ . However, under such conditions, the method of<sup>[2]</sup> is inapplicable. The problem of the calculation of the Van der Waals energy at  $\varepsilon_a \sim \varepsilon_0$  is not merely methodological, since such liquid crystals do exist. For example, in di-n-heptyl-azoxybenzene we have  $\varepsilon_a/$  $\varepsilon_0 \approx 0.7$  near the temperature of transition from the nematic to the smectic A phase.<sup>[5]</sup>

In this connection, we calculate the Van der Waals energy by a method that does not make use of the smallness of  $\varepsilon_a/\varepsilon_0$ . The essence of the method is briefly as follows. As is well known, <sup>[1,2]</sup> the problem of the calculation of the energy of longwave fluctuations reduces to the determination of the Green's function of radiation in the medium. In a liquid crystal far from the transition temperature we have a dielectric permittivity tensor that depends, generally speaking, on the coordinates:

$$\varepsilon_{ik}(\mathbf{r}) = \varepsilon_0 \delta_{ik} + \varepsilon_a n_i(\mathbf{r}) n_k(\mathbf{r})$$
(1)

(n is the director). Therefore, the equation for the Green's function

$$[\varepsilon_{ik}(\mathbf{r})\omega^{2} + \operatorname{rot}_{im}\operatorname{rot}_{mk}]D_{kl} = 4\pi\omega^{2}\delta_{il}\delta(\mathbf{r}-\mathbf{r}')$$
(2)

cannot be solved in general form. Since we wish to determine the liquid-crystal part of the Van der Waals energy, which is connected with the fluctuations of the orientation, we must separate out the part in (1) corresponding to the equilibrium orientation of the direction  $n^{0}(\mathbf{r})$ ;

$$\varepsilon_{ik}^{0}(\mathbf{r}) = \varepsilon_{0} \delta_{ik} + \varepsilon_{a} n_{i}^{0}(\mathbf{r}) n_{k}^{0}(\mathbf{r}).$$
(3)

If Eq. (2) can be solved in general form in the case of the dielectric permittivity (3), then its solution is found in the form of an expansion in the deviations of the director from the equilibrium value:

$$\mathbf{n}(\mathbf{r}) = \mathbf{n}^{\circ}(\mathbf{r}) + \mathbf{v}(\mathbf{r}), \quad \mathbf{n}^{\circ}(\mathbf{r})\mathbf{v}(\mathbf{r}) = 0.$$
(4)

The expression for the free energy thus obtained contains diverging elements (see, for example, Ref. 3). The part of the divergences that is connected with the surface energy can be removed by integration by parts. It is possible, however, to obtain immediately an expansion in the derivatives of  $\nu(\mathbf{r})$ . For this purpose, we must introduce a set of curvilinear coordinates, one of the axes of which is tangent to the field  $\mathbf{n}^0(\mathbf{r})$ . Under certain conditions on  $\mathbf{n}^0(\mathbf{r})$  (see below), this system can be chosen to be orthogonal, and then we immediately have the expansion in the derivatives of  $\nu(\mathbf{r})$ . In Sec. 2, both methods for the calculation of the Van der Waals part of the free energy are described in detail. A nematic liquid crystal with weakly inhomogeneous distribution  $n(\mathbf{r})$  is considered as an example. In contrast with the results of Ref. 2, the frequency dependence is no longer factored out here. Therefore, for example, the polarization characteristics of the integrated intensity of the scattered light depend significantly on the frequency dispersion.

In the third section, the Van der Waals energy is obtained for a cholesteric liquid crystal. Here we do not take into account the small effects connected with the molecular optical activity (spatial dispersion of the dielectric permittivity). In the calculation we use the first method, since the system of coordinates with one of the axes along  $n^{0}(\mathbf{r})$  is not orthogonal in this case. Equation (2) for the Green's function is a Mathieu equation in this case. The explicit formulas are obtained for a sufficiently large period of the structure. It is found that the Van der Waals contributions to the free energy can be more significant close to the transition to the nematic phase (in a magnetic field). In light scattering, this effect appears as the analog of critical opalescence.

The fourth section is devoted to the calculation of the Van der Waals energy near a plane disclination in a nematic liquid crystal. It is shown that the Van der Waals forces make the plane disclination unstable at a certain ratio of the parameters. The central region corresponds here to a homogeneous nematic phase with orientation along the axis of the disclination. The transition region cannot be calculated in the general case.

In the fifth section, the light scattering at temperatures close to the point of phase transition to the isotropic phase  $(T_c)$  is considered. (In contrast to Ref. 2, where the region  $T \ll T_c$  is considered.) The character of the scattering and the width of this region depend significantly on the value of  $\varepsilon_a$  and on certain other phenomenological parameters. It is recognized that if  $T \sim T_c$ , then the order parameter is generally not uniaxial. <sup>[61]</sup> Some estimates are derived in this section. The possibility is discussed of experimental verification of the obtained effects, and also certain experimental data that relate to the type of problem considered are analyzed.

2. As has already been mentioned, the energy of the longwave electromagnetic fluctuations is determined by the radiation Green's function:

$$\delta F = \frac{1}{8\pi^2} \int_{0}^{\infty} d\omega \int d\mathbf{r} D_{ik}(\mathbf{r}, \mathbf{r}; \omega) \,\delta \varepsilon_{ik}(\mathbf{r}, i\omega), \qquad (5)$$

where  $\delta \varepsilon_{ik}$  takes into account the effect of the liquidcrystal fluctuations on the dielectric permittivity.

If Eq. (2) for the Green's function can be solved in general form  $D_{ik}^{0}(\mathbf{r},\mathbf{r}',\omega)$  for the equilibrium orientation  $\mathbf{n}^{0}(\mathbf{r})$ , then, in first order in  $\delta \varepsilon_{ik}(\mathbf{r},i\omega)$ ,

$$D_{ik}{}^{i}(\mathbf{r},\mathbf{r}',\omega) = -\frac{1}{4\pi} \omega^{2} \int D_{il}{}^{0}(\mathbf{r},\mathbf{r}'',\omega) D_{mk}^{0}(\mathbf{r}'',\mathbf{r}',\omega) \delta\varepsilon_{lm} d\mathbf{r}''.$$
(6)

With account of (3),

$$\delta \varepsilon_{ik}(\mathbf{r}) = \varepsilon_a(n_i^{0}(\mathbf{r}) v_k(\mathbf{r}) + n_k^{0}(\mathbf{r}) v_i(\mathbf{r})).$$
<sup>(7)</sup>

Finally, we have from (5) and (7):

$$\delta F = -\frac{1}{16\pi^3} \int_{\mathbf{0}}^{\infty} \varepsilon_a^{\ 2} \omega^4 \, d\omega \int d^3 \mathbf{r} d^3 \mathbf{r}' D_{ik}^{\ 0}(\mathbf{r}, \mathbf{r}') \\ \times D_{ml}^{\ 0}(\mathbf{r}', \mathbf{r}) n_i^{\ 0}(\mathbf{r}) n_k^{\ 0}(\mathbf{r}') v_l(\mathbf{r}) v_m(\mathbf{r}')$$
(8)

(in writing down Eq. (8), we have taken into account the symmetry relations for the Green's function and also the condition  $n \rightarrow -n$ ).

The expression obtained solves in principle the question of calculation of the Van der Waals energy in liquid crystals with a value of  $\varepsilon_a$  that is not small. The difficulty lies only in the determination of  $D_{ik}^0$ . Moreover, all the diverging terms that have no relation to the energy of the considered longwave fluctuations should be removed from (8). In particular, the formally infinite surface energy should be removed. For this purpose, the expression (8) should be integrated by parts a sufficient number of times. After this, the free energy of the fluctuations will be expressed in terms of the derivatives of the deviations  $\nu(\mathbf{r})$ . In some cases, such an expansion in the derivatives can be conveniently written down immediately.

For simplicity, we shall consider the two-dimensional case (generalization to three dimensions is trivial). It is convenient to introduce a curvilinear system of coordinates with axis along the field **n**  $(\cos\varphi, \sin\varphi)$ :

$$x^{(1)} = y^{(1)} \cos \varphi + y^{(2)} \sin \varphi, \quad x^{(2)} = -y^{(1)} \sin \varphi + y^{(2)} \cos \varphi.$$
 (9)

Here  $x^{(1)}$  and  $x^{(2)}$  are the new curvilinear coordinates,  $y^{(1)}$  and  $y^{(2)}$  are the old cartesian coordinates. The metric tensor

$$g_{mn} = \frac{\partial y^{(i)}}{\partial x^{(m)}} \frac{\partial y^{(i)}}{\partial x^{(n)}}$$

is determined by the derivatives of the field  $\varphi$ .

As is known, in order that the curvilinear system  $x^{(1)}$ ,  $x^{(2)}$  be orthogonal, it is required that  $g_{12} = 0$ . In first order in the derivative, this condition of orthogonality gives

$$x^{(1)}\frac{\partial \varphi}{\partial x^{(1)}} - x^{(2)}\frac{\partial \varphi}{\partial x^{(2)}} = 0.$$
 (10)

Equation (10) is always satisfied if, for example,  $\varphi$  = const or  $\varphi$  is an arbitrary function of the product of the coordinates  $x^{(1)}$  and  $x^{(2)}$ . In this case we cannot distinguish between co- and contravariant components of the tensors, and the equation for the Green's function (2) can easily be solved by expansion in the derivatives of  $\varphi$ . In the expanded form, these equations in the co-ordinates  $x^{(1)}$ ,  $x^{(2)}$  have the form

$$\begin{aligned} \varepsilon_{11}\omega^{2}D_{11}-g^{-\gamma_{1}}\left[\frac{\partial}{\partial x^{(1)}}\left(g^{\gamma_{1}}g^{\tau_{1}}\frac{\partial D_{11}}{\partial x^{(1)}}\right)+\frac{\partial}{\partial x^{(2)}}\left(g^{\gamma_{1}}g^{\tau_{2}}\frac{\partial D_{11}}{\partial x^{(2)}}\right)\right]\\ +\frac{\partial}{\partial x^{(1)}}g^{-\gamma_{1}}\left[\frac{\partial}{\partial x^{(1)}}\left(g^{\gamma_{1}}D_{11}\right)+\frac{\partial}{\partial x^{(2)}}\left(g^{\gamma_{1}}D_{21}\right)\right]=4\pi\omega^{2}\delta_{11}\delta\left(\mathbf{r}-\mathbf{r}'\right),\\ \varepsilon_{22}\omega^{2}D_{21}-g^{-\gamma_{1}}\left[\frac{\partial}{\partial x^{(1)}}\left(g^{\gamma_{1}}g^{\tau_{1}}\frac{\partial D_{21}}{\partial x^{(1)}}\right)+\frac{\partial}{\partial x^{(2)}}\left(g^{\gamma_{1}}g^{\tau_{2}}\frac{\partial D_{21}}{\partial x^{(2)}}\right)\right] \quad (11)\\ +\frac{\partial}{\partial x^{(2)}}g^{-\gamma_{1}}\left[\frac{\partial}{\partial x^{(1)}}\left(g^{\gamma_{1}}D_{11}\right)+\frac{\partial}{\partial x^{(2)}}\left(g^{\gamma_{1}}D_{21}\right)\right]=4\pi\omega^{2}\delta_{21}\delta\left(\mathbf{r}-\mathbf{r}'\right),\\ g=g^{t1}g^{t2}, \quad \varepsilon_{11}=\varepsilon_{0}+\varepsilon_{0}, \quad \varepsilon_{22}=\varepsilon_{0}.\end{aligned}$$

The formulas take the simplest form in the case of a nematic single crystal with small curvature of the field n(r). Here we can expand the metric tensor in the derivatives  $\partial \varphi / \partial x^{(i)}$  and limit outselves to the first approximation. We then have

 $(\delta_{r,s}$  is the Kronecker symbol;  $\delta g^{rs}$  is the deviation departure of the metric tensor from unity),

$$\delta g^{rs} = \begin{pmatrix} -2x^{(2)}\partial \varphi/\partial x^{(1)} & 0\\ 0 & 2x^{(1)}\partial \varphi/\partial x^{(2)} \end{pmatrix}$$

Since the field n(r) is not rectilinear, corrections also arise in the tensor of the dielectric permittivity:

$$\delta \varepsilon_{ik} = \begin{pmatrix} -(2\varepsilon_0 + \varepsilon_a) x^{(2)} \frac{\partial \varphi}{\partial x^{(1)}} & -\varepsilon_a x^{(2)} \frac{\partial \varphi}{\partial x^{(2)}} \\ \\ -\varepsilon_a x^{(2)} \frac{\partial \varphi}{\partial x^{(2)}} & 2\varepsilon_0 x^{(1)} \frac{\partial \varphi}{\partial x^{(2)}} - \varepsilon_a x^{(2)} \frac{\partial \varphi}{\partial x^{(2)}} \end{pmatrix}.$$

Substituting these expansions in (11), we obtain for the free energy an expression that is similar to (8):

$$\delta F = -\frac{1}{8\pi^2} \int_{0}^{\infty} \omega^4 d\omega \int dr^2 dr^{2'} D_{ik}^{\ 0}(\mathbf{r},\mathbf{r}') D_{ml}^{\ 0}(\mathbf{r}',\mathbf{r}) \delta \varepsilon_{il}(\mathbf{r})$$

$$\times \delta \varepsilon_{km}(\mathbf{r}') + \frac{1}{16\pi^2} \int_{0}^{\infty} \omega^2 d\omega \int dr^2 dr^{2'} D_{ik}^{\ 0}(\mathbf{r},\mathbf{r}') \frac{\partial}{\partial x^{(i)}} \frac{\partial}{\partial x^{(i)}}$$

$$\times D_{ml}^{\ 0}(\mathbf{r},\mathbf{r}') \delta g^{ij}(\mathbf{r}') \delta \varepsilon_{km}(\mathbf{r}).$$
(8a)

At small distances, when the retardation is inconsequential, the fundamental role is played by the second component. We can write down the free energy in the three-dimensional case in an entirely analogous way. The orthogonality of the system of coordinates is important for the determination of the null Green's functions  $D_{ik}^0(\mathbf{r}, \mathbf{r}')$ . It can be taken further into account that the derivatives of the various components of the metric tensor entering into (11) and (8a) have a simple physical meaning. To be precise,

$$g^{-\gamma_{s}}\frac{\partial}{\partial x^{(1)}}\left(g^{22}\right)^{\gamma_{s}}=\varkappa_{2}, \quad g^{-\gamma_{s}}\frac{\partial}{\partial x^{(2)}}\left(g^{11}\right)^{\gamma_{s}}=-\varkappa_{1}, \quad (12)$$

where  $\varkappa_1$  and  $\varkappa_2$  are the curvatures of the lines  $x^{(1)}$  = const and  $x^{(2)}$  = const. In our approximation, this is simply

$$\varkappa_2 = \frac{\partial \varphi}{\partial x^{(2)}}, \quad \varkappa_1 = \frac{\partial \varphi}{\partial x^{(1)}}.$$

Therefore, the expansion of Eqs. (11) in terms of the derivatives corresponds to expansion in small curvatures. We shall not carry through the rather cumbersome computations, but immediately give the answer for the more important region of small distances  $|\mathbf{r} - \mathbf{r'}|$  $<\lambda_0$  ( $\lambda_0$  is the characteristic wavelength in the spectrum of the body; for a detailed discussion of the quantity  $\lambda_0$ , see Refs. 1-3):

$$\delta F = -\frac{1}{128\pi^{i}} \int_{0}^{\infty} \frac{\varepsilon_{a}^{2}}{(\varepsilon_{0} + \varepsilon_{a})^{2}} d\omega \int \frac{dr^{2} dr^{2'}}{(1 + \varepsilon_{a}/\varepsilon_{0})^{-\frac{1}{2}} (x^{(1)} - x^{(1)'})^{2} + (x^{(2)} - x^{(2)'})^{2}} \times [\cos(\varphi - \varphi') \{ (\varkappa_{1}(\mathbf{r}) + \varkappa_{2}(\mathbf{r})) \varkappa_{2}(\mathbf{r}') \} + \sin(\varphi - \varphi') \varkappa_{1}(\mathbf{r}) \varkappa_{2}(\mathbf{r}') ].$$
(13)

We note here that the integration over the frequency is factored out only at  $\varepsilon_a \ll \varepsilon_0$ . A similar expression can be obtained in the three-dimensional case. However, not only do curvatures appear in this case, but also torsions of the coordinate lines. Therefore, it is more convenient to write the Van der Waals free energy directly in terms of the derivatives of  $\nu(\mathbf{r})$ . Moreover, in the three-dimensional case, the condition of orthogonality of the system of coordinates does not reduce, of course, to the equation (10). It can be shown that in place of (10) we need to satisfy the relation

$$n \operatorname{rot} n=0.$$
 (14)

3. We apply the general results obtained in the previous section to cholesteric liquid crystals. It can easily be proved that it is not convenient to expand immediately in the derivative of the displacement in this case. The corresponding natural curvilinear system of coordinates will not be orthogonal:

$$x^{(1)} = y^{(1)} \cos \alpha y^{(3)} + y^{(2)} \sin \alpha y^{(3)}, x^{(2)} = -y^{(1)} \sin \alpha y^{(3)} + y^{(2)} \cos \alpha y^{(3)}, \quad x^{(3)} = y^{(3)}$$
(15)

( $\alpha$  is the reciprocal inverse period of the cholesteric spiral). It follows from (15) that, for example,  $g_{13} = -\alpha x^{(2)} \neq 0$ , i.e., even though the unit vectors of the system (15) are mutually perpendicular at each point, the system is not orthogonal (condition (14) is not satisfied). Therefore, the corresponding contributions to the transformation tensor of the dielectric permittivity are

$$\mathbf{\varepsilon}_{ik} = \begin{pmatrix} \mathbf{\varepsilon}_0 + \mathbf{\varepsilon}_a & 0 & -\alpha \left( \mathbf{\varepsilon}_0 + \mathbf{\varepsilon}_a \right) x^{(2)} \\ 0 & \mathbf{\varepsilon}_0 & \alpha \mathbf{\varepsilon}_0 x^{(1)} \\ -\alpha \left( \mathbf{\varepsilon}_0 + \mathbf{\varepsilon}_a \right) x^{(2)} & \alpha \mathbf{\varepsilon}_0 x^{(1)} & \alpha^2 \left[ \mathbf{\varepsilon}_0 x^{(1)2} + \left( \mathbf{\varepsilon}_a + \mathbf{\varepsilon}_0 \right) x^{(2)2} \right] + \mathbf{\varepsilon}_0 \end{pmatrix}.$$

It is, of course, not possible to solve the Maxwell equations (2) exactly with such a dielectric tensor. Therefore, the second method is inappropriate in the given case. We note here that the dependence of  $\varepsilon_{ik}$  on the coordinates in the natural system (15) should also be taken into account in the solution of the optical problem in cholesteric liquid crystals.

If the first method is used (see Sec. 2), the equations for the null Green's functions are Mathieu equations. The corresponding formulas will be given only for sufficiently long-period structures, when  $\alpha |\mathbf{r} - \mathbf{r'}| < 1$ . This condition in cholesteric liquid crystals agrees with  $|\mathbf{r} - \mathbf{r'}| < \lambda_0$ . In this case, it suffices to determine only the transverse Green's function  $D_{\alpha,\beta}$  ( $\alpha, \beta$  are the components in the plane perpendicular to the axis of the spiral) and the remainder are expressed in terms of  $D_{\alpha\beta}$  with the help of simple differentiations. If we transform to the Fourier components of **q** in transverse coordinates, then, in the region of interest to us,  $q \gg \alpha \sim \epsilon_0^{1/2} \omega$ , we have

$$D_{\alpha\beta} = 2\pi\omega^2 q^{-1} \exp\left(-q|z-z'|\right) \left[\delta_{\alpha\beta} - q^{-1} \left(q_\alpha n_\beta^0 + q_\beta n_\alpha^0\right)\right] \\ \times \left[1 - 2\frac{\alpha}{q} \frac{\varepsilon_a}{\varepsilon_0} \operatorname{sh} 2\alpha |z-z'|\right]; \qquad (16)$$
$$n_x^0 = \cos\alpha z, \quad n_y^0 = \sin\alpha z.$$

Calculation of the free energy with the functions (16) is very cumbersome, but is similar to what was done earlier. <sup>[2,3]</sup> As we have already seen at  $\varepsilon_a \sim \varepsilon_0$ , integration over the frequency does not lead to a separated factor, and therefore more convenient expressions are, in the coordinate representation,

$$\delta F = \frac{1}{810\pi} \int_{0}^{\infty} \frac{\varepsilon_{a}^{2}}{(\varepsilon_{0} + \varepsilon_{a})^{2}} d\omega \int d\mathbf{r} d\mathbf{r}' \frac{\cos \alpha (z - z')}{[(1 + \varepsilon_{a}/\varepsilon_{0})^{-\gamma} (z - z')^{2} + (\mathbf{\rho} - \mathbf{\rho}')^{2}]} \\ \times \left\{ \frac{\partial^{2} \varphi}{\partial x_{1}^{2}} \frac{\partial^{2} \varphi'}{\partial x'^{2}} + 2\alpha \frac{\partial \theta}{\partial x_{1}} \frac{\partial \theta'}{\partial x_{1}'} \right\} - \frac{1}{224\pi} \alpha \int_{0}^{\infty} \frac{\varepsilon_{a}^{3}}{\varepsilon_{0} (\varepsilon_{a} + \varepsilon_{0})^{2}} d\omega \\ \times \int d\mathbf{r} d\mathbf{r}' \frac{\sin \alpha (z - z')}{[(1 + \varepsilon_{a}/\varepsilon_{0})^{-\gamma_{h}} (z - z')^{2} + (\mathbf{\rho} - \mathbf{\rho}')^{2}]^{\gamma_{h}}} \left\{ \frac{\partial^{2} \varphi}{\partial x_{1}^{2}} \frac{\partial^{2} \varphi'}{\partial x_{b}'^{2}} + 2\alpha \frac{\partial \theta}{\partial x_{1}} \frac{\partial \theta'}{\partial x_{1}'} \right\}.$$
(17)

In Eq. (17), the deviations of the director from the equilibrium orientation are written in terms of the angles  $\varphi$  and  $\theta$ :

$$n_x = \cos(\alpha z + \varphi), \quad n_y = \sin(\alpha z + \varphi), \quad n_z = \theta.$$
 (18)

We cannot write out the integrated intensity of the scattered light from the expression (17), since the frequency dependence is not factored out. However, in order of magnitude, recognizing that numerically  $\varepsilon_a \lesssim \varepsilon_0$ , and the frequency dispersion is not very large, we have

$$J_{qq} \sim T/(K_{22}q^2 + Mq^3 + N\alpha q^2),$$

$$J_{qq} \sim T/(K_{11}q^2 + K_{33}\alpha^2 + Mq^3 + M\alpha q_{\perp}^2 + N\alpha q^2).$$
(19)

Here  $K_{ii}$  are the Frank elastic moduli and the corresponding terms, which are proportional to the square of the transmitted pulse, take into account the short-range forces; the definition of the coefficients M and N is obvious from the formula (17), T is the temperature.

We note that the growth of the intensity with decrease in  $\alpha$  follows from (19). Since the short-range components are proportional to the higher powers of  $\alpha$ , it is possible in this manner to separate the Van der Waals contribution to the light scattering in cholesteric liquid crystals. One more difference arises, due to the fact that the Van der Waals forces shift the maximum of the scattering intensity toward the shortwave end. When only short-range forces are taken into account, the maximum in the scattering would take place at  $q = 2\alpha$  in one mode and at  $q = \alpha$  in the other.

4. We now consider the problem of the stability of a plane Frank disclination. As is known, <sup>[7]</sup> in the case of equal elastic moduli  $K_{11} = K_{22} = K_{33}$  the plane disclination is stable (if only short-range forces are considered). To be specific, we shall consider a disclination with Frank index m = 2.<sup>[7]</sup> Then the corresponding lines of

the field **n** are a system of circles. We study the effect of the long-range Van der Waals forces on the disclination. In this case, we can immediately apply the second method of calculation, since the system of curvilinear coordinates along the field **n** will be orthogonal. Besides, we can also use the first method, since the equations for the null Green's functions are solved exactly (they are expressed in terms of the Bessel function of imaginary argument). Of course, we should note that we do not take into account the interaction of the disclinations with the boundary and similar effects. This is admissible in the consideration of a sufficiently large region  $R \gg \lambda_0$ , in which we have a circular field **n**. The calculations, which are similar to those set forth above, give in this case

$$\delta F = \frac{1}{810\pi} \int_{0}^{\infty} \frac{\varepsilon_{a}^{2}}{(\varepsilon_{0} + \varepsilon_{a})^{2}} d\omega \int d\mathbf{r} d\mathbf{r}' \frac{\cos(\Phi - \Phi')}{\left[(1 + \varepsilon_{a}/\varepsilon_{0})^{-\frac{1}{2}}(z - z')^{2} + (\rho - \rho')^{2}\right]} \\ \times \left[\frac{\partial^{2} \varphi}{\partial x_{r}^{2}} \frac{\partial^{2} \varphi'}{\partial x_{b}^{\prime 2}} + \frac{x_{a} x_{a}'}{r^{2} r'^{2}} \frac{\partial \theta}{\partial z'} \frac{\partial \theta'}{\partial z'}\right].$$
(20)

Here  $\Phi = \arctan(x/y)$ , and  $\varphi$  and  $\theta$  are the deviations from the equilibrium orientation of the director.

It follows from (20) that the minimum of the Van der Waals energy compatible with the boundary conditions occurs in the case of uniform orientation in the central part along the axis of the cylinder. Therefore, in the case of Van der Waals forces that are not small, the plane Frank disclinations are always unstable (irrespective of the dependence on the ratio of the elastic moduli; for comparison, see Ref. 7). It follows from Eq. (20) that upon approach to the core of the disclination, the Van der Waals energy increases, roughly speaking, according to the law

$$\delta F \sim M/r^2. \tag{21}$$

So far as the energy associated with the short-range forces is concerned, it is only logarithmic:

$$F_0 \sim K \ln \left( \frac{R}{r} \right). \tag{22}$$

Therefore, there exists a critical distance  $r_c$ :

$$r_{e} \sim \left[\frac{M}{K \ln \left(R/r_{e}\right)}\right]^{\frac{1}{2}} , \qquad (23)$$

such that at  $r < r_c$ , the principal role is placed by the Van der Waals forces. The orientation at  $r < r_c$  will be uniform for this very reason. Of course, there is a transition region  $r \sim r_c$ , in which the orientation should be determined by the minimum of the total functional [(20) and of Oseen-Frank]. The corresponding Euler-Lagrange integral equation can be solved only numerically.

Naturally, all the above is valid only if M is not too small, so that  $r_c$  is also not too small, and therefore the macroscopic description of the Van der Waals forces  $(r_c \gg a, \text{ where } a \text{ is the intermolecular distance})$  is applicable.

5. Direct estimates of the obtained effects are rather difficult, since it is necessary to know the entire fre-

quency dependences of the functions  $\varepsilon_0$  and  $\varepsilon_a$ . In any case of this type, the estimates can be carried out only with the help of a high-speed computer; however, the trends can be determined also qualitatively. Thus, it follows from the formulas obtained above that the Van der Waals contribution to the intensity of the scattered light in cholesteric liquid crystals is more significant in the region of critical opalescence, i.e., as  $\alpha - 0$ . Such is the case, for example, in the transition to the nematic phase in a magnetic field. Similar moderating effects should appear also near the phase transition to the smectic phase. The experimental data on light scattering, <sup>[8]</sup> as is well known, confirm this tendency; the stronger non-analytic deviations from the Orstein-Zernike law (~ $q^{-2}$ ) take place near such transition.

Still less can be said about the effect of the Van der Waals forces on the structure of the disclinations. Rough estimates of  $r_c$  ( $M \sim 10$  eV,  $K \sim 10^{-7}$  erg/cm<sup>2</sup>,  $R \sim 10^{-2}$  cm) give  $r_c \sim 1 \mu$ , which agrees with the experimental value of the disclination core. Moreover, at such  $r_c$ , the macroscopic consideration of the Van der Waals forces is still applicable. Qualitatively, the systematic violation of the law of the rate of annihilation speaks in favor of the Van der Waals forces. If there were only short-range forces, then the annihilation time of the disclinations in a large sample (so that one can neglect the interaction with the surface) would be  $\sim r^2$ (this follows, for example, from the electrostatic analogy). However, the experimental data indicate a more rapid interaction.<sup>[9]</sup>

We note the following circumstance in conclusion. Everywhere above (as well as earlier<sup>[2,3]</sup>) we have considered only the uniaxial order parameter, i.e.,  $\varepsilon_{ik}$  $=\varepsilon_0\delta_{ik}+\varepsilon_an_in_k$ . This is valid at the temperature of the phase transition to the isotropic phase. In the isotropic phase, and also close to the transition point to the nematic phase (see below), the system is not uniaxial. The only preferred direction is that of the wave vector **q.** Moreover, from general symmetry considerations. the order parameter should be a symmetric tensor of second rank with a trace equal to zero. There exist five irreducible tensors of this type, <sup>[6]</sup> composed of the unit vector  $\mathbf{q}/q = \boldsymbol{\tau}$  and two unit vectors **m** and **m'** in the plane perpendicular to  $\tau$ . In place of m and m', it is convenient to introduce the circular components l = m + im'and  $l^* = m - im'$ . Then the irreducible tensors have the following form:

$$\sigma_{\alpha\beta}^{i} = \iota_{\alpha} l_{\beta}, \sigma_{\alpha\beta}^{2} = l_{\alpha}^{i} l_{\beta}^{i}, \sigma_{\alpha\beta}^{3} = 2^{-i_{\beta}} i (l_{\alpha} \tau_{\beta} + l_{\beta} \tau_{\alpha}), \sigma_{\alpha\beta}^{i} = 2^{-i_{\beta}} i (l_{\alpha}^{*} \tau_{\beta} + l_{\beta}^{*} \tau_{\alpha}), \sigma_{\alpha\beta}^{3} = 6^{-i_{\beta}} (3\tau_{\alpha} \tau_{\beta} - \delta_{\alpha\beta}).$$
(24)

In place of the uniaxial expansion of the dielectric permittivity tensor, we have now (in the immediate vicinity of the phase transition point)

$$\varepsilon_{ik} = \varepsilon_0 \delta_{ik} + \sum_{n=1}^{5} \varepsilon_n \sigma_{ik}^n.$$
(25)

Of course, if  $T > T_c$ , then the mean value of the dielectric permittivity tensor is

 $\langle \epsilon_{i\hbar} \rangle = \epsilon_0 \delta_{i\hbar}.$ 

The second component in (25) makes a contribution only to quadratic effects, for example, in the intensity of the scattered light. However, the Van der Waals components that are linear in  $\varepsilon_a$  do not make a contribution to the volume energy of interest to us (for more detail, see Ref. 2). Therefore, the Van der Waals energy is the same in this region on both sides of the transition temperature.

With account of everything said above, we shall have for the Van der Waals energy, in place of Eq. (8),

$$\delta F = -\frac{1}{32\pi^3} \sum_{n=1}^{5} \int_{0}^{\infty} \varepsilon_n^2 \omega^4 d\omega \int d\mathbf{r} \, d\mathbf{r}' D_{ik}^{0}(\mathbf{r}-\mathbf{r}') D_{ml}^{0}(\mathbf{r}'-\mathbf{r}) \sigma_{im}^{n}(\mathbf{r}) \sigma_{kl}^{n}(\mathbf{r}').$$
(26)

Equation (8) is obtained from (26) if only the uniaxial term corresponding to  $\sigma_{ik}$  remains.<sup>[5]</sup> The coefficient of the dielectric permittivity tensor  $\epsilon_{5}$  has the simple physical meaning of the anisotropic part of the dielectric permittivity. The remaining coefficients  $\varepsilon_n$  (at n  $\neq$  5) do not have a graphic physical interpretation. The width of the region in which departures from uniaxiality are possible is determined roughly by the ratio of the coefficients of the sixth and fourth degrees of the order parameter in the expansion of the free energy in the Landau theory. This ratio is small, experimentally, in liquid crystals, i.e., the region is extremely narrow. Moreover, because of the presence of cubic components in the order parameter, the transition to the isotropic phase is a first order phase transition. In most known liquid crystals, the ratio of the coefficients is such that a first order transition occurs directly to the uniaxial phase. We shall therefore not investigate the expansion (26) here in further detail, but simply write out the formulas for the scattering intensity.

In order not to create additional complications, we shall assume that  $\varepsilon_n \ll \varepsilon_0$ . We can then write down (26) immediately in Fourier components (see Ref. 2):

$$\delta F = \sum_{n=1}^{5} \frac{M_n}{(2\pi)^3} \int d^3q \left[ 2q^3 \sigma_{ik}{}^n(\mathbf{q}) \sigma_{ik}{}^n(-\mathbf{q}) - 4qq_i q_k \sigma_{il}{}^n(\mathbf{q}) \sigma_{kl}{}^n(-\mathbf{q}) + 3 \frac{q_i q_k q_l q_m}{q} \sigma_{il}{}^n(\mathbf{q}) \sigma_{km}{}^n(-\mathbf{q}) \right],$$
(27)

$$M_n = \frac{1}{2048\pi} \int_{0}^{\infty} \frac{\varepsilon_n^2(i|\omega|)}{\varepsilon_0^2(i|\omega|)} d\omega.$$
 (28)

Short-range forces also make a contribution to the scattering intensity here. The corresponding correlation functions  $\langle \sigma_{ik}^n(\mathbf{q}) \sigma_{lm}^n(-\mathbf{q}) \rangle$  were calculated by de Jeu *et al.*<sup>[5]</sup> For concreteness, we shall consider the isotropic phase  $(T > T_c)$  (as was noted above, the Van der Waals contributions are symmetric in  $T_c$ , but the short-range forces are not). The results depend significantly on the polarization and other geometric characteristics of the scattering.

For example, if **k** and **k'** are the waves vectors of the incident and scattered light, then, at uniform polarizations of the incident and scattered light along  $\mathbf{k} \times \mathbf{k'}$  we have the following expression for the coefficient of extinction ( $\mathbf{q} = \mathbf{k} - \mathbf{k'}$  is chosen along the z axis):

$$\frac{dh(\omega)}{d\Omega} = \frac{\omega^{4}}{16\pi^{2}} \left[ \frac{2^{l_{1}}T\varepsilon_{1}^{2}}{(T-T_{c}) + K_{22}q^{2} + M_{1}q^{3}} + \frac{2^{l_{1}}T\varepsilon_{2}^{2}}{(T-T_{c}) + K_{22}q^{2} + M_{2}q^{3}} + \frac{6^{l_{1}}T\varepsilon_{2}^{2}}{(T-T_{c}) + K_{32}q^{2} + M_{3}q^{3}} \right].$$
(29)

However, the more significant differences from the region  $T \ll T_c$  arise in the polarization characteristics of the scattering, which are the same for the short-range and the Van der Waals forces. They both depend on three independent combinations of the five coefficients  $\varepsilon_n$  (as also in Eq. (29), for example). These three coefficients correspond to the scalar and symmetric scattering processes. In the usual notation, <sup>[10]</sup> we have the following relations:

$$a^{-1}{}_{_{30}}\varepsilon_{5}^{2+1}{}_{_{15}}(\varepsilon_{1}^{2}+\varepsilon_{2}^{2})^{-1}{}_{_{18}}(\varepsilon_{3}^{2}+\varepsilon_{1}^{2}),$$
  
$$c^{-1}{}_{_{6}}\varepsilon_{5}^{2-1}{}_{_{16}}(\varepsilon_{3}^{2}+\varepsilon_{1}^{2}), b^{-1}{}_{_{10}}\varepsilon_{5}^{2+1}{}_{_{15}}(\varepsilon_{1}^{2}+\varepsilon_{2}^{2}).$$
 (30)

In the case of the uniaxial order parameter, we have from (30):

$$a=b/3=-c/5.$$
 (31)

The relations (31) are characteristic for purely symmetry scattering. In scattering of such a type (for polarized light), the angular intensity distribution is

$$I_{t} \sim \frac{9}{10} + \frac{3}{20} \sin^{2} \theta.$$
 (32)

Biaxiality does not appear in additional scattering at large angles:

$$I_2 \sim \frac{3}{2} \sin^2 \theta. \tag{33}$$

In conclusion, the authors express their deep gratitude to I. E. Dzyaloshinskii for numerous discussions of the work and useful criticism.

- <sup>1</sup>I. E. Dzyaloshinsiĭ, E. M. Lifshitz, and L. P. Pitaevskiĭ, Usp. Fiz. Nauk **73**, 381 (1961) [Sov. Phys. Usp. **4**, 153 (1961)]; Adv. in Phys. **10**, 165 (1961).
- <sup>2</sup>I. E. Dzyaloshinskii, S. G. Dmitriev, and E. I. Kats, Zh. Eksp. Teor. Fiz. **68**, 2335 (1975) [Sov. Phys. JETP **41**, 1167 (1975)].
- <sup>3</sup>E. I. Kats, Zh. Eksp. Teor. Fiz. **70**, 1394 (1976) [Sov. Phys. JETP **43**, (1976)].
- <sup>4</sup>P. G. de Gennes and E. Dubois-Violette, J. Phys. Lett. **36**, 155 (1975).
- <sup>5</sup>W. H. de Jeu, Th. W. Lathouwers, and P. Berdewijk, Phys. Rev. Lett. **32**, 40 (1974).
- <sup>6</sup>S. A. Brazovski<sup>i</sup> and S. G. Dmitriev, Zh. Eksp. Teor. Fiz. **69**, 979 (1975) [Sov. Phys. JETP **42**, 497 (1975)]; R. L. Stratonovich, Zh. Eksp. Teor. Fiz. **70**, 1290 (1976) [Sov. Phys. JETP **43**, 672 (1976)].
- <sup>7</sup>S. I. Anisimov and I. E. Dzyaloshinskii, Zh. Eksp. Teor. Fiz. **63**, 1460 (1972) [Sov. Phys. JETP **36**, 774 (1973)].
- <sup>8</sup>W. L. McMillan, Phys. Rev. 7A, 1673 (1973); 8A, 328 (1973).
- <sup>9</sup>J. A. Geurst, A. M. J. Spruijt, and C. J. Gerritsma, J. de Phys. **36**, 653 (1975).
- <sup>10</sup>L. D. Landau and E. M. Lifshitz, Elektrodinamika sploshnykh sred (Electro dynamics of continuous media) Gostekhizdat, 1957 [Pergamon, 1959].

Translated by R. T. Beyer