Effect of van der Waals forces on orientation of a nematic liquid crystal film

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The contribution of van der Waals forces to the thermodynamic characteristics of a nematic liquid crystal film is calculated. Reorientation of the liquid crystal under the action of van der Waals forces can take place in sufficiently thin films. The thickness of the transition layer from surface orientation to volume orientation, due to the van der Waals forces, is determined for thick films.

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1. INTRODUCTION

The general theory of van der Waals forces[1] has been repeatedly applied to various inhomogeneous condensed systems in recent years[2–4] (see also the review of[5]). The contribution of long-wave fluctuations of the electromagnetic field to the thermodynamic characteristics of an infinite nematic medium was determined by Dzyaloshinskiĭ, Dmitriev, and the author.[3] The special importance of van der Waals forces for such "soft" systems as liquid crystals, for which the fundamental short-range forces are not very large, was also noted there. However, in all the specific experiments and applications, one is dealing with a thin layer of the liquid crystal (film thickness $\sim 10^2-10^3\mu$) placed between two isotropic faces. The fluctuations of the electromagnetic field in such a layered system will naturally differ from the case considered previously.[3] Such a system also differs from the classical problem,[1] since the orientation of the liquid crystal can be inhomogeneous over its thickness. Therefore, all the corresponding calculations should be repeated.

The general expressions for the free energy of the long-wave fluctuations are set down in Sec. 2. Section 3 is devoted to the investigation of thin films. As is usual in the theory of van der Waals forces, the criterion is some characteristic wavelength λ_0 in the absorption spectrum of the body. For thicknesses $l \ll \lambda_0$, the orientation of the liquid crystal is uniform and is determined by the boundary conditions (short-range forces). The energy of the fluctuation field is generally less. However, by virtue of the anisotropy of the system, the van der Waals energy has a minimum at a definite orientation of the long axes of the molecules of the liquid crystal (the director) relative to the normal to the film. If this orientation does not coincide with the surface, then a reorientation should take place upon decrease in the thickness, associated with the growth of van der Waals forces upon decrease in the thickness. Thick films are considered in Sec. 4 ($l \gg \lambda_0$). The orientation in this case is determined by an integral equation. The analytic solution is found in the case of symmetric boundary conditions, which corresponds experimentally to an identical medium on both sides of the liquid crystal film. There is a transition layer in this case in which the orientation of the molecules changes from a surface one, given by the short-range forces, to a volume one, determined by the van der Waals forces. In this same section, we consider the forces associated with the Oseen-Frank elastic moduli. If the elastic modulus K is large in comparison with the van der Waals forces, then the orientation is described by a differential equation. The van der Waals forces in this case are equivalent to a weakly inhomogeneous magnetic field. A critical thickness exists, therefore, beginning with which the orientation is the liquid crystal will be non-uniform.

2. THE FREE ENERGY OF LONGWAVE ELECTROMAGNETIC FLUCTUATIONS OF A NEMATIC LIQUID CRYSTAL FILM

We now consider a plane layer of a nematic liquid crystal of thickness l. We choose a set of coordinates in which the normal to the plane surface coincides with the x axis (see the drawing). In the region $x > l$ there is a thick isotropic covering (in this particular case, air) with a permittivity ε_1. For the region $x < 0$, there is an isotropic medium with a permittivity ε_2 (the substrate). We write the permittivity tensor of the liquid crystal $0 < x < l$ in the form

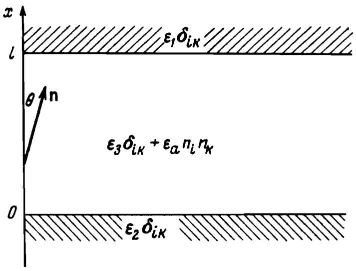
$$\varepsilon_{ik} = \varepsilon_3 \delta_{ik} + \varepsilon_a n_i n_k. \tag{1}$$

In this formula, ε_a is the dielectric anisotropy; $\mathbf{n}$ is the vector of the director.

As has already been mentioned in the Introduction, the thermodynamic properties of the system are determined by the temperature Green's function of the electric field, D_{lk}. This quantity satisfies the corresponding Maxwell's equations:

$$[\varepsilon_{il}(\mathbf{r}, i|\omega|)\omega^2 + (\mathrm{rot}^2)_{il}] D_{lk}(\mathbf{r}, \mathbf{r}', \omega) = 4\pi\omega^2 \delta(\mathbf{r}-\mathbf{r}')\delta_{ik}. \tag{2}$$

In Eq. (2), the permittivity ε_{jk} enters in the case of an



imaginary value of the frequency.

By symmetry of the problem, everything is uniform in the yz plane. We can therefore transform everywhere to the Fourier components in the coordinates y and z:

$$D_{ik}(x, x', \mathbf{q}, \omega) = \iint e^{-i\mathbf{q}\boldsymbol{\rho}} D_{ik}(\mathbf{r}, \mathbf{r}', \omega)\, d^2\rho,$$

where $\boldsymbol{\rho}$ is the radius vector in the yz plane. In contrast with Ref. 11, where one of the axes y or z could be directed along the vector $\mathbf{q}$, we must carry out our calculations for an arbitrary direction of $\mathbf{q}$. This is connected with the fact that we will need to calculate integrals of several D functions in what follows.

At $x > l$ or $x < 0$, Eqs. (2) are solved in trivial fashion (for convenience, it must be assumed that $0 < x' < l$, and then Eqs. (2) are homogeneous). In the region $0 < x < l$, in the case of an arbitrary distribution of the director, it is not possible to solve this equation. We therefore use the practical smallness of ε_a in liquid crystals ($\varepsilon_a/\varepsilon_3 \sim 0.1$–$0.01$). It will be shown in Sec. 5 how the formulas are modified if ε_a is not small, but the director departs but little from the equilibrium uniform orientation. We shall therefore in this section seek the Green's function and the energy of the fluctuation field in the region $0 < x < l$ in the form of an expansion in powers of ε_a.

The boundary conditions corresponding to continuity of the tangential components of the intensities of the electric and magnetic fields reduce to the requirement of the continuity of the quantities

$$D_{\alpha\beta}, \quad \frac{d}{dx}\left[D_{\alpha\beta} - \frac{q_\alpha q_\gamma}{w^2} D_{\gamma\beta}\right]. \tag{3}$$

Under these conditions, α, β, γ denote the components in the yz plane and $w_i^2 = \varepsilon_i \omega^2 + q^2$. The equation that is satisfied by $D_{\alpha\beta}$ can be separated from the rest of the system (2) and has the following form:

$$\left(w_3^2 - \frac{d^2}{dx^2}\right)(w_3^2 \delta_{\alpha\gamma} - q_\alpha q_\gamma) D_{\gamma\beta} = 4\pi\omega^2 w_3^2 \delta(x - x')\, \delta_{\alpha\beta}. \tag{4}$$

The remaining functions D_{ik} are expressed in terms of $D_{\alpha\beta}$ with the help of simple differentiations.

The set (2)–(4) with the boundary condition (3) reduces to algebraic equations in the zeroth order in ε_a. The free energy in this case will be a linear function of the dielectric anisotropy. After uncomplicated but cumbersome calculations, we obtain

$$\begin{aligned} D_{yy}^{(0)} = \frac{2\pi\omega^2\gamma_3}{\Delta_y} \Big[& 2 \operatorname{ch} w_3 (x - x') - \frac{\gamma_3 w_1 + \gamma_1 w_3}{\gamma_3 w_1 - \gamma_1 w_3} \exp(2w_3 l - w_3(x + x')) \\ & - \frac{\gamma_3 w_2 + \gamma_2 w_3}{\gamma_3 w_2 - \gamma_2 w_3} \exp(w_3(x + x')) \Big] + \frac{2\pi\omega^2\gamma_3}{w_3} \exp(-w_3 |x - x'|). \end{aligned} \tag{5}$$

In this formula

$$\begin{aligned} \gamma_i &= \frac{w_i^2 - q_z^2}{w_i^2 - q^2}, \\ \Delta_y &= \frac{(\gamma_3 w_2 + \gamma_2 w_3)(\gamma_3 w_1 + \gamma_1 w_3)}{(\gamma_3 w_2 - \gamma_2 w_3)(\gamma_3 w_1 - \gamma_1 w_3)} \exp(2 w_3 l) - 1. \end{aligned} \tag{6}$$

The function $D_{zz}^{(0)}$ is obtained from (5), (6) by the replacement of γ_i by $\nu_i = (w_i^2 - q_y^2)/(w_i^2 - q^2)$ and by a similar replacement, Δ_z reduces to Δ_y,

$$D_{zy}^{(0)} = \frac{q_z q_y}{w_3^2 - q_z^2} D_{yy}^{(0)}, \quad D_{yz}^{(0)} = \frac{q_y q_z}{w_3^2 - q_y^2} D_{zz}^{(0)}, \tag{7}$$

$$D_{xy}^{(0)} = \frac{i q_y}{w_3^2 - q_z^2} \frac{d}{dx} D_{yy}^{(0)}, \quad D_{xz}^{(0)} = \frac{i q_z}{w_3^2 - q_y^2} \frac{d}{dx} D_{zz}^{(0)}, \tag{8}$$

$$D_{xx}^{(0)} = -\frac{1}{w_3^2} \left[\frac{q_y^2}{w_3^2 - q_z^2} \frac{d^2}{dx^2} D_{yy}^{(0)} + \frac{q_z^2}{w_3^2 - q_y^2} \frac{d^2}{dx^2} D_{zz}^{(0)} \right]. \tag{9}$$

The free energy in this approximation, according to the general theory, is[1]

$$\delta F = \frac{1}{8\pi^2} \int_0^\infty d\omega \int d\mathbf{r}\, D_{ik}(\mathbf{r}, \mathbf{r}, \omega)\, \varepsilon_a N_{ik}(\mathbf{r}), \tag{10}$$

where $N_{ik} = n_i n_k$.

Considering that the distribution of the director depends only on the x coordinate, and using Eqs. (5)–(10), we can obtain the contribution of the van der Waals forces to the free energy of the liquid crystal film. However, the resultant expression diverges. This is connected with the fact that the fluctuations with small wavelengths, which have no relation to the inhomogeneity of the body, make an infinite contribution to δF. (Their contribution is the same both in homogeneous and inhomogeneous bodies having the same value of ε at the point in question.) These divergences can be eliminated either in explicit fashion by a cutoff of the D functions in the momenta, or by a corresponding calculation of quantities pertaining to the homogeneous system. Thus we subtract in (5)–(10) the values which are obtained at $w_3 = w_1 = w_2$:

$$\begin{aligned} \delta F = \frac{S}{8\pi^2} \int \varepsilon_a\, d\omega \int d^2 q \int_0^l dx \Big[& -\frac{2\pi\omega^2}{w_3^2 - q^2} \Big(\frac{q_y^2}{\Delta_y} \Big\{ 2 - \frac{\gamma_3 w_1 + \gamma_1 w_3}{\gamma_3 w_1 - \gamma_1 w_3} \\ & \times \exp(2w_3 l - 2w_3 x) - \frac{\gamma_3 w_2 + \gamma_2 w_3}{\gamma_3 w_2 - \gamma_2 w_3} \exp(2w_3 x) \Big\} \\ & + \frac{q_z^2}{\Delta_z} \Big\{ 2 - \frac{\nu_3 w_1 + \nu_1 w_3}{\nu_3 w_1 - \nu_1 w_3} \exp(2w_3 l - 2w_3 x) \\ & - \frac{\nu_3 w_2 + \nu_2 w_3}{\nu_3 w_2 - \nu_2 w_3} \exp(2w_3 x) \Big\} \Big) \cos^2\theta \\ & + \frac{2\pi\omega^2\nu_3}{\Delta_z} \Big(2 - \frac{\nu_3 w_1 + \nu_1 w_3}{\nu_3 w_1 - \nu_1 w_3} \exp(2w_3 l - 2w_3 x) \\ & - \frac{\nu_3 w_2 + \nu_2 w_3}{\nu_3 w_2 - \nu_2 w_3} \exp(2w_3 x) \Big) \sin^2\theta \Big]. \end{aligned} \tag{11}$$

In Eq. (11), S is the area of the surface of the liquid crystal, $\theta(x)$ is the angle between the normal to the surface and the director.

The expression (11) in principle solves the problem of the van der Waals contributions to the thermodynamic quantities of the liquid crystal film in first order in the dielectric anisotropy. For convenience, we denote the corresponding quantity per unit area as

$$f_{\text{vdW}}^{(1)} = \delta F / S. \tag{12}$$

In order to find the free energy in second order in the dielectric anisotropy, we must determine the D function in first order in ε_a:

$$\delta F^{(2)} = \frac{1}{8\pi^2} \int_0^\infty d\omega \int d\mathbf{r}\, D_{ik}^{(1)}(\mathbf{r}, \mathbf{r}, \omega)\, \delta\varepsilon_{ik}(\mathbf{r}, i|\omega|). \tag{13}$$

Making use of the fact that $D_{ik}^{(0)}$ is the Green's function for the corresponding $D_{ik}^{(1)}$ of the homogeneous equation, we get

$$\frac{\delta F^{(2)}}{S}=f_{\mathrm{vdW}}^{(2)}=-\frac{1}{32\pi^3}\int\limits_0 \varepsilon_a{}^2\,d\omega\int dx\,dx''$$

$$\times\int d^2q[D_{li}^{(0)}(x,x'',\mathbf{q})D_{mk}(x'',x,\mathbf{q})N_{im}(x'')N_{lk}(x)]. \tag{14}$$

The quantities $D_{ik}^{(0)}$ satisfy the boundary conditions (3) in (14) with the required accuracy.

3. THIN LAYER OF LIQUID CRYSTAL ($l\ll\lambda_0$)

As is easily seen from the expressions (11) and (14), the principal contribution is made by the components of first order in ε_a (Eq. (14) has an additional smallness $\sim(l/\lambda_0)^2$ in the thin film limit). In (11), it is convenient to transform from q to a new variable p:

$$q=\omega[\varepsilon_3(p^2-1)]^{1/2}.$$

We also introduce the quantities $s_i=[\varepsilon_i/\varepsilon_3+p^2-1]^{1/2}$, in a fashion similar to Ref. 1.

Because of the presence of exponential factors in Δ_y and Δ_z, the essential contribution to $f_{\mathrm{vdW}}^{(1)}$ is made by $p\gg 1$ (at $l\ll\lambda_0$). In this case $s_1\approx s_2\approx p$; $\Delta_y\approx\Delta_z=\Delta$, where

$$\Delta=\frac{(\varepsilon_1+\varepsilon_3)(\varepsilon_2+\varepsilon_3)}{(\varepsilon_1-\varepsilon_3)(\varepsilon_2-\varepsilon_3)}\exp(2p\varepsilon_3^{1/2}\omega l)-1. \tag{15}$$

Finally, by introducing the dimensionless variable

$$u=2lp\omega\sqrt{\varepsilon_3}, \tag{16}$$

we get from (11),

$$f_{\mathrm{vdW}}^{(1)}=\frac{1}{64l^3}\int\limits_0^l dx\int\limits_0^\infty d\omega\int\limits_0^\infty u^3\,du\,\frac{\varepsilon_a}{\varepsilon_3}\frac{1}{\Delta}\left[-2-\exp\left(u-u\frac{x}{l}\right)\frac{\varepsilon_3+\varepsilon_1}{\varepsilon_1-\varepsilon_3}\right.$$

$$\left.-\exp\left(u\frac{x}{l}\right)\frac{\varepsilon_3+\varepsilon_2}{\varepsilon_2-\varepsilon_3}\right]\cos^2\theta+\frac{1}{8l}\int\limits_0^l dx\int\limits_0^\infty \varepsilon_a\omega^2\,d\omega\int\limits_0^\infty\frac{1}{\Delta}u\,du$$

$$\times\left(-2-\exp\left(u-u\frac{x}{l}\right)\frac{\varepsilon_3+\varepsilon_1}{\varepsilon_1-\varepsilon_3}-\exp\left(u\frac{x}{l}\right)\frac{\varepsilon_3+\varepsilon_2}{\varepsilon_2-\varepsilon_3}\right)\sin^2\theta. \tag{17}$$

The orientation of the director in a thin layer of a liquid crystal will be constant throughout. Therefore, the quantities $\sin^2\theta$ and $\sin^2\theta$ can be removed from under the integral signs and the integral calculated over the coordinates. In this case, the inhomogeneous components diverge at the boundary. This is connected with the fact that the van der Waals forces formally make an infinite contribution to the surface energy. Actually, this circumstance means simply that the surface energy is determined by the short-range forces that were not considered in (11). To remove this divergence, we must require the vanishing of $f_{\mathrm{vdW}}^{(1)}$ at $w_1=w_3$ and $w_2=w_3$ separately. We calculate the surface energy in the same way. With account of this fact,

$$f_{\mathrm{vdW}}^{(1)}=-\frac{1}{32l^2}\int\limits_0^\infty\frac{\varepsilon_a}{\varepsilon_3}d\omega\int\limits_0^\infty u^2\,du\left[\frac{(\varepsilon_3+\varepsilon_1)(\varepsilon_3+\varepsilon_2)}{(\varepsilon_3-\varepsilon_1)(\varepsilon_3-\varepsilon_2)}e^u-1\right]^{-1}$$

$$\times\left[u+(e^u-1)\frac{\varepsilon_1\varepsilon_2-\varepsilon_3{}^2}{(\varepsilon_1-\varepsilon_3)(\varepsilon_2-\varepsilon_3)}\right]\cos^2\theta. \tag{18}$$

In writing out (18), it has also been taken into account that the second component in (17), which is proportional to $\sin^2\theta$, is much less than the first in the limit $l\ll\lambda_0$[1] (in relation to $(l/\lambda_0)^2$). As was already noted above, the surface contributions from the short-range forces should be added to (19). Phenomenologically, the corresponding surface energy can be written down with account of the symmetry requirement $\mathbf{n}\to-\mathbf{n}$, introducing the surface tension component τ:

$$f_{\mathrm{sur}}=\tau(\mathbf{n}\boldsymbol{\nu})^2, \tag{19}$$

where $\boldsymbol{\nu}$ is the normal to the surface.

The coefficient τ can be either positive or negative, depending on the medium located on the boundary. The total energy from (18) and (19) is given by

$$F=\tau\cos^2\theta-\frac{\hbar\omega_0}{l^2}\cos^2\theta, \tag{20}$$

$$\omega_0=\frac{1}{32}\int\limits_0^\infty\frac{\varepsilon_a}{\varepsilon_3}d\omega\int\limits_0^\infty u^2\,du\left[\frac{(\varepsilon_3+\varepsilon_1)(\varepsilon_3+\varepsilon_2)}{(\varepsilon_3-\varepsilon_1)(\varepsilon_3-\varepsilon_2)}e^u-1\right]^{-1}$$

$$\times\left[u+(1+e^{-u})\frac{\varepsilon_1\varepsilon_2-\varepsilon_3{}^2}{(\varepsilon_1+\varepsilon_3)(\varepsilon_2+\varepsilon_3)}\right]. \tag{21}$$

It is seen from (20) that a critical thickness

$$l_{c1}=(\hbar\omega_0/\tau)^{1/2} \tag{22}$$

exists (at $\tau>0$). At $l>l_{c1}$, the orientation is determined by the surface conditions (short-range forces). At $\tau>0$, this requires the director to be parallel to the boundary $\theta=\pi/2$. However, at $l<l_{c1}$, the van der Waals forces become significant and the orientation becomes perpendicular to the boundary $\theta=0$. In order that the effect just noted take place, it is necessary that the critical thickness not be too small. In the opposite case, the condition of applicability of the macroscopic treatment will be violated at such distances. The corresponding estimates will be given in Sec. 5.

We also note that the entire treatment in this section relates to thin films with uniform orientation. Therefore, the boundary conditions on the director should be identical at both surfaces of the liquid crystal. Here the condition (22) is valid for any of the boundaries of separation, but we should take the corresponding maximum coefficient of surface tension or their sum for τ.

4. THICK LAYER OF A LIQUID CRYSTAL ($l\gg\lambda_0$)

For thick films, we need to consider, along with (11), the component of second order in ε_a, $\sim(l/\lambda_0)^2$. Furthermore, depending on the ratio of the dielectric anisotropy to the film thickness, this term may even be the principal one. As was noted above, the orientation in the thick film is generally nonuniform. Therefore, along with the van der Waals forces, the short-range Oseen-Frank forces can also play a decisive role:

$$f_0=\frac{K}{2}\int(\nabla\theta)^2\,dx, \tag{23}$$

where K is the elastic modulus (for brevity, we assume $K_{11}=K_{22}=K_{33}$).

As has been shown previously,[3] the long-range van der Waals forces make a contribution to the free energy in the region of "large" distances (see[3] and below) of the same form as (23). We should therefore assume that K is the elasticity modulus renormalized by the long-range forces. If the short-range forces significantly exceed the van der Waals forces, then we have over the entire range of variation of the thickness formula (23), to which there are contributions of first order in the dielectric anisotropy (Eq. (11)). We therefore first concern ourselves with the transformation of this expression.

We make a change of variables (16) in the first-order free energy, but we now use the dimensionless quantity u in place of the frequency ω. Then we have in the argument of the permittivity a quantity that is close to zero in the limit $l \gg \lambda_0$. These static quantities can be taken outside the integral sign, and the remaining integral with respect to u can be calculated in terms of elementary functions. Omitting the calculations which, with accuracy to within the inhomogeneous components, are similar to those carried out in Ref. 1, we obtain the following expression for the free energy:

$$f_{\mathrm{vdW}}^{(1)} = -\frac{1}{128\pi}\frac{\varepsilon_a(0)}{\varepsilon_3(0)}\frac{1}{l^3}\int_0^1 dx' \left[\left(A_1 - \frac{B_1}{(1+x')^4} - \frac{C_1}{(2-x')^4}\right)\cos^2\theta - \left(D_1 - \frac{E_1}{(1+x')^4} - \frac{G_1}{(2-x')^4}\right)\sin^2\theta\right]. \qquad (24)$$

In this equation, $\varepsilon_a(0)$ and $\varepsilon_3(0)$ are static values of the permittivity, and we nondimensionalize the coordinate $x (x' = x/l)$,

$$A_1 = \frac{3}{2}\frac{1}{\varepsilon_3^{1/2}(0)}\int_1^\infty \frac{dp}{p^4}\frac{(s_1(0)-p)(s_2(0)-p)}{(s_1(0)+p)(s_2(0)+p)},$$

$$B_1 = \frac{3}{2}\frac{1}{\varepsilon_3^{1/2}(0)}\int_1^\infty \frac{dp}{p^4}\frac{(s_2(0)-p)(s_1(0)-p)^2}{(s_2(0)+p)(s_1(0)+p)^2},$$

$$C_1 = \frac{3}{2}\frac{1}{\varepsilon_3^{1/2}(0)}\int_1^\infty \frac{dp}{p^4}\frac{(s_1(0)-p)(s_2(0)-p)^2}{(s_1(0)+p)(s_2(0)+p)^2} \qquad (25)$$

$$D_1 = 3\frac{1}{\varepsilon_3^{1/2}(0)}\int_1^\infty dp\,\frac{p^2-1}{p^4}\frac{(\varepsilon_3(0)s_2(0)-\varepsilon_2(0)p)(\varepsilon_3(0)s_1(0)-\varepsilon_1(0)p)}{(\varepsilon_3(0)s_2(C)+\varepsilon_2(0)p)(\varepsilon_3(0)s_1(0)+\varepsilon_1(0)p)}$$

$$E_1 = \frac{3}{2}\frac{1}{\varepsilon_3^{1/2}(0)}\int_1^\infty dp\,\frac{p^2-1}{p^4}\frac{(\varepsilon_3(0)s_2(0)-\varepsilon_2(0)p)(\varepsilon_3(0)s_1(0)-\varepsilon_1(0)p)^2}{(\varepsilon_3(0)s_2(0)+\varepsilon_2(0)p)(\varepsilon_3(0)s_1(0)+\varepsilon_1(0)p)^2}$$

$$G_1 = \frac{3}{2}\frac{1}{\varepsilon_3^{1/2}(0)}\int_1^\infty dp\,\frac{p^2-1}{p^4}\frac{(\varepsilon_3(0)s_1(0)-\varepsilon_1(0)p)(\varepsilon_3(0)s_2(0)-\varepsilon_2(0)p)^2}{(\varepsilon_3(0)s_1(0)+\varepsilon_1(0)p)(\varepsilon_3(0)s_2(0)+\varepsilon_2(0)p)^2}$$

In writing down Eqs. (24), (25), we have subtracted the infinite surface energy, just as was done in Sec. 3.

Thus the contribution of the van der Waals forces to the free energy of the film is given by the following formula for $l \gg \lambda_0$ (as deduced from (23) and (24)):

$$F = -\frac{\hbar c}{l^3}\int_0^1 dx'\Lambda(x')\cos^2\theta(x') + \frac{K}{2}\int(\nabla\theta)^2 dx. \qquad (26)$$

The determination of the quantities $\Lambda(x')$ is evident from (24), (25). Furthermore, as in Sec. 3, the surface energy (19) should be added. The calculation of $\Lambda(x')$ depends weakly on the coordinates (a variation of the order of several percent over the thickness). For estimates, then, it can be assumed that $\Lambda(x') \approx \Lambda$.

The free energy (26) in this case is analogous to the free energy of the liquid crystal in a magnetic field:

$$f_m = -\frac{1}{2}\int \chi_a H^2 \cos^2\theta\, dx. \qquad (27)$$

Thus, the van der Waals forces in this case effectively renormalize the magnetic field. For example, it then follows that the critical field at which the change of orientation takes place (the Fredericks field[6]) is

$$H_c = \frac{1}{\chi_a^{1/2}}\left[\frac{\pi^2 K}{4l^2} + \frac{\hbar c\Lambda}{l^3}\right]^{1/2}. \qquad (28)$$

In the absence of a magnetic field, there exists a critical value of the thickness l_{c3} (i.e., the value of the van der Waals forces), up to which the orientation remains uniform:

$$l_{c3} = (\hbar c\Lambda/K)^{1/2}.$$

The orientation is determined here by the Euler-Lagrange equation corresponding to (26). In the case considered, it reduces to a differential equation for the elliptic functions. This problem has been frequently discussed in the theory of liquid crystals (see, for example, Ref. 6), and we shall not consider it in any detail.

Much more significant changes take place in the case in which the van der Waals forces are not small in comparison with the Oseen-Frank forces. In this case, Eq. (23) preserves its form in the range of large distances; however, it is now no longer possible to assume all the elastic moduli to be equal. All the results that follow from (26) remain in force but it is necessary, depending on the geometry of the problem, to establish some combination of the elastic moduli. Thus, for the standard experimental setup for the criticial Fredericks field (initial orientation parallel to the boundary and field perpendicular), the modulus K_{22} is introduced into (28).

So far as the region of small distances is concerned (under satisfaction of the condition $l \gg \lambda_0$), the contribution of the van der Waals forces in this region of second order in the anisotropy is not local. The corresponding expression can be obtained directly from Eq. (14). With account of the fact that the surface energy was discussed in Sec. 3, we can carry out integration in (14) by parts. Thus, after rather cumbersome calculations, similar to those performed earlier,[3] we get

$$f_{\mathrm{vdW}}^{(2)} = \frac{1}{512}\int_0^\infty \frac{\varepsilon_a^2}{\varepsilon_3^2}d\omega\int_0^l dx\int_0^l dx_1 \ln\left|\frac{x-x_1}{\omega\sqrt{\varepsilon_3}}\right|(\cos^2\theta)''(\cos^2\theta_1)'' \qquad (29)$$

(the primes denote differentiation with respect to the coordinate).

We note here that in the previous work[3] the expression for the free energy in second order in the dielectric anisotropy is written in inconvenient form, since the infinite contributions to the surface energy were not formally calculated. It can now be specified what we mean here by the terms large and small distances. We introduce a characteristic length, over which the orientation of the liquid crystal changes (δ is the thickness of the transition layer). Then Eq. (29) (see the derivation in Ref. 3) is valid for $\delta \ll \lambda$ (but, naturally, $l \gg \lambda_0$). Thus the non-local van der Waals energy at $M > K$, where

$$M = \frac{1}{512} \int_0^\infty \frac{\varepsilon_a^2}{\varepsilon_3^2} d\omega,$$

exists under the condition

$$\delta \ll \lambda_0 \ll l. \tag{30}$$

But, in the case

$$\lambda_0 \ll \delta \tag{31}$$

we always have the local (differential equation) expression (26) for the free energy.

The results in (31) were already discussed above (see (23)–(28)). Under condition (30), the free energy of the system has the following form:

$$F = -\frac{\hbar c}{l^3} \int_0^1 dx' \Lambda(x') \cos^2\theta + Ml^2 \int_0^1 dx' \int_0^1 dx_1' \ln|x' - x_1'| (\cos^2\theta)''(\cos^2\theta_1)''. \tag{32}$$

If we set $\cos^2\theta = v$, then the Euler-Lagrange equation for (32) will be

$$-\frac{\hbar c}{l^3} \Lambda(x') + 4Ml^2 \frac{d^2}{dx'^2} \int_0^1 dx_1' \ln|x' - x_1'| v(x_1') = 0. \tag{33}$$

We thus have an integral equation of the form

$$\int_0^1 dx_1' \ln|x' - x_1'| v(x_1') = \frac{\hbar c}{Ml^5} \varphi(x'), \tag{34}$$

where $\varphi(x')$ is a given function obtained by integration of $\Lambda(x')$. The solution of this equation can be obtained explicitly in the case of symmetric boundary conditions. It is physically required in this case that the dielectric properties of the medium on both sides of the liquid crystal be the same. In this case, we carry out a Fourier transformation in (34). The Fourier component of the solution is then found immediately:

$$v(k) = \frac{\hbar c}{Ml^5} \frac{\varphi(k)}{\mathscr{L}(k)} \tag{35}$$

The function $\mathscr{L}(k)$ is obtained from integration of the kernel of Eq. (34) and can be written down in the form of the series

$$\mathscr{L}(k) = \ln|k| + k/1! + k^2/2\cdot 2! + \ldots \tag{36}$$

From (35) and (36), we can find that the transition from surface orientation to volume orientation takes place in a transition layer of thickness

$$\delta \sim l(Ml/\hbar c\Lambda)^{1/3}. \tag{37}$$

As $x \to 0$, the establishment of this orientation takes place according to the law (with the boundary condition $\theta = 0$),

$$\theta \sim \frac{x^2}{\ln(l/x)} \tag{38}$$

The succession of thicknesses at which the relations obtained above are valid (in the case of van der Waals forces M that are not small) is obtained from (30), (31) and (37). At $l > l_{c3}$, the orientation is uniform. At $\lambda_0 < l < l_{c2}$, the orientation is determined by the nonlocal forces (29). (Here l_{c2} is the thickness at which δ from (37) is of the order of λ_0). And, finally, at $l > l_{c2}$, everything is determined by the differential equation (26).

5. CONCLUSION

Unfortunately, numerical estimates of the formulas that have been obtained are very sensitive to the specific dependences of the components of the permittivity tensor on the frequency. We can therefore use only very general specifications on the behavior of the permittivity ($\varepsilon_i \to 1$ at large frequencies, and ε_a falls off with increase in frequency more rapidly than $1/\omega^2$).

If we use the experimental data on the absorption spectrum of para-azoxyanisole (PAA) for an estimate of the parameter λ_0 (see Ref. 7, for example), then we must assume $\lambda_0 \sim (5-6) \times 10^{-4}$ cm.

The coefficient of surface tension in $\tau \sim 30$ dyn/cm. Therefore, the critical thickness is determined by the value of the van der Waals frequency ω_0. If we assume $\hbar\omega_0 \sim 10$ eV, as is usually the case in systems with sufficiently heavy molecules, then

$$l_{c1} \sim (2-5)\cdot 10^{-5} \text{ cm}.$$

Thus, the effect studied in Sec. 3 lies in a region of thicknesses that is experimentally attainable. In this case, all the macroscopic requirements on the basis of which the expressions for the van der Waals contributions to the free energy were obtained are still valid. In the case of thick films, similar estimates give the following for the thickness of the transition layer ($l \sim 10^{-3}$ cm):

$$\delta \sim 10^{-5} \text{ cm}, \quad l_{c2} \sim 10^{-3} \text{ cm}, \quad l_{c3} \sim 10^{-2} \text{ cm}.$$

If the transition layer is determined by the Oseen-Frank forces ($K \sim 10^{-6}$ dyn/cm), then the orientation is distorted along the entire length of the liquid crystal.

Thus, for sufficient magnitude of the van der Waals forces, the thickness $l > \lambda_0$ of the liquid crystal film remains nonuniform, in spite of the absence of external actions (except for the boundary conditions associated with the short-range forces). This is another physical effect which follows from the results of the research. We note here that the coefficient in the magnetic coherence length changes under the action of the van der Waals forces in the liquid crystal film in the region of high fields (see Ref. 3). From (27) and (32), we have

$$\xi \sim \frac{1}{Ha} \left(\frac{M}{\chi_a}\right)^{1/2}, \tag{39}$$

where a is a distance of the order of the molecular length, up to which the macroscopic consideration of the van der Waals forces is valid. This dependence differs from the case of an infinite layer of liquid crystal where $\xi \sim H^{-2/3}$.

In conclusion, we point out that all the calculations carried out above can be generalized to the case in which the dielectric anisotropy is not small. Here, it is ture, we have considered only small departures from the equilibrium orientation. For such a calculation, the zero D functions correspond to Green's functions in a homogeneous medium. The entire change reduces to the fact that the coefficients M, ω_0 and Λ are replaced by similar expressions in which the following substitution is made everywhere in the denominators:

$$\varepsilon_3 \to \varepsilon_3(\varepsilon_a/\varepsilon_3+1)^{1/2}. \tag{40}$$

The corresponding formulas are very involved and do not lead to any new effects. Corrections can be important only in light scattering. However, since the liquid crystals with an anisotropy of ε_a that is not small are unknown, we shall not concern ourselves with this problem here.

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[1)] Here λ_0 is the smallest characteristic length in the spectrum of the liquid crystal.

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Nonlinearity of acoustic damping in nonequilibrium superconductors

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The effect of the nonequilibrium state of an electron gas on sound absorption in a superconductor is considered. The nonequilibrium electron distribution function is assumed to be stationary and isotropic, and the phonons to be in equilibrium. In addition to the explicit dependence of the damping coefficient on the distribution function, a dependence on the correction to the order parameter exists that is associated with the nonequilibrium state. The sound intensities which create the nonequilibrium state and at which nonlinearity should be observed are estimated.

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A nonlinear dependence of the sound absorption coefficient on its intensity at temperatures below the superconducting transition has been observed in a number of experimental researches.[1] A certain decrease in the absorption above T_c has been observed in this case, which can be interpreted as an increase in the critical temperature. In addition, a deformation of the absorption curve was observed below T_c. A superconducting film in the field of a sound wave was studied in Ref. 2, and it was found that the temperature dependence of the superconducting parameters of the film in the presence of sound is supported by the theory that was developed earlier.[3] It is characteristic that the effect described in Ref. 2 was observed only for certain optimal film thicknesses, which were evidently most favorable in the sense of heat removal and the value of the sound intensity in the film.

In this connection, it should be noted that, in experiments on microwave irradiation of films, the vector of the electric field intensity is small in the film because of the smallness of the impedance at these frequencies. For this reason, microwave experiments are relatively less effective in the observation of the heating of electrons than, say, the acoustic experiments mentioned above, and experiments with laser radiation of superconducting samples.[4]

Phenomena are considered in the present work that are associated with the heating of the electron gas by the field of the sound wave. We shall call heating the isotropic change in the distribution function of the electrons which is generally not described by an effective temperature. We shall assume the phonons to be in equilibrium for the reason that near T_c a large part of the electrons remains in equilibrium and plays the role of a thermostat, together with the phonons.

The nonequilibrium situation in the case of sound