Surface oscillations in liquid crystals

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The surface wave spectrum in liquid crystals is investigated. Sections with linear dispersion are observed to appear in the presence of a weak external magnetic field as a result of the anisotropy of the surface-tension coefficient.

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1. The problem of surface waves in liquid crystals has attracted much attention in recent years (see, e.g., [1,2]). The reason for this interest is that the scattering of light from structures produced by surface waves makes it possible to determine exactly the material parameters of liquid crystals. In addition there is also a more general interest. It is frequently stated in the literature that a liquid crystal is merely an optically anisotropic medium. An investigation of the surface oscillations, however, shows that in a certain sense liquid crystals are also elastically anisotropic media. The coefficient of surface tension in such systems is anisotropic (it depends on the angle between the molecule orientation vector on the surface and the normal). The anisotropy of the surface-tension coefficient can be connected, for example, with van der Waals forces.[3] In view of the symmetry requirement $\mathbf{n}\to-\mathbf{n}$ ($\mathbf{n}$ is the director vector), however, a dependence of this type must of necessity be quadratic in the deviations of $\mathbf{n}$ from the equilibrium direction. In the absence of external actions, therefore, the changes introduced by the anisotropic surface tension make no contribution to the linearized hydrodynamic equations that describe the propagation of small-amplitude waves. The role of the external action reduces thus to deviation of the director from the orientation connected with the minimum of the surface energy. An external action of this type may be, for example, a magnetic field applied at an angle to the equilibrium orientation. A similar role is played simply by different boundary conditions on the surfaces of the liquid crystal. To be specific, we consider only the first case. We encounter therefore a definite linear elasticity connected with the deviation of the molecule orientation (of the director). If the surface tension were anisotropic the orientation of the molecules in the course of the oscillations would always remain at a certain angle to the surface that is bent by the oscillations (just as in the absence of the oscillations). On the other hand the anisotropy (or the magnetic field) causes the orientation to lag somewhat and results therefore in a new type of dispersion. This distinguishes our study from[1,2], where the surface tension was assumed to be isotropic. The difference between the nematic phase and an isotropic liquid has thus been reduced only to the onset of anisotropic damping. This circumstance can be explained without any calculations. In the nematic phase the relaxation time connected with the motion of the liquid

$$\tau_f\sim\rho/\eta q^2,$$

and with the motion of the director

$$\tau_d\sim\eta/Kq^2,$$

differ by many orders of magnitude (ρ is the density, η the characteristic viscosity, K Frank's elastic modulus, and q the wave vector of the wave). At values $q\sim10^3$ cm^{-1} typical of experiments on light scattering, and also at $\rho\sim1$ g/cm^3, $\eta\sim0.1$ cm, and $K\sim10^{-6}$ erg/cm we have $\tau_d/\tau_f\sim10^4$. Therefore the fluctuations of the flow are fully independent of the elastic fluctuations of the orientation. Thus, the surface-wave spectrum, just as in an isotropic liquid, is given by

$$\omega=\left(\frac{\alpha q^3}{\rho}\right)^{1/2}+i\frac{\eta q^2}{2\rho}. \tag{1}$$

Here α is the surface-tension coefficient, and the effective viscosity η depends on the geometrical characteristics and is a definite combination of the Leslie viscosity coefficients. In addition, in formula (1) we have neglected for the sake of simplicity the influence of the force of gravity, something perfectly justified for the experimental situation mentioned above.

2. In this entire analysis, however, no account was taken of a very important circumstance. The point is that liquid crystals are an unusual example of a liquid system with an anisotropic surface-tension coefficient. Therefore α is actually a function of the angle θ between the director and the normal to the surface. As already indicated, a relation of this type can result, for example, from allowance for the van der Waals forces.[3] In the most general case, with allowance for the symmetry $\mathbf{n}\to-\mathbf{n}$ ($\mathbf{n}$ is the director), we can write

$$\alpha=\alpha_0+\alpha_a\cos^2\theta, \tag{2}$$

α_a is the anisotropic part of the surface-tension coefficient. In formula (2), the sign of α_0 is fixed ($\alpha_0>0$), and α_a can have any sign (depending on the equilibrium orientation on the surface). For the sake of argument we assume that the equilibrium orientation is parallel, i.e., $\alpha_a<0$.

It follows from (2) that the boundary conditions on the surface of a system with such surface tension differ from the conditions on the surface of a viscous isotropic liquid. As is well known,[4] when the surface tension varies along the surface it is necessary, to maintain mechanical equilibrium, to compensate for not only the normal (Laplace) pressure but also for the tangential force. The latter condition makes it mandatory to take into account the dissipative part of the stress tensor (i.e., the viscosity), for only in this case can the change of α along the surface be offset by tangential components of the stress tensor.

We consider for simplicity only two-dimensional solutions. If the x axis is directed along the surface and the z axis is normal to the surface, this means that there is no dependence on the coordinate y. The aforementioned boundary conditions then call for

$$\sigma_{zz}=\alpha\left(\frac{\partial^2 u}{\partial x^2}\right)_{z=0}, \tag{3}$$

$$\sigma_{zx}=\left(\frac{\partial\alpha}{\partial x}\right)_{z=0}. \tag{4}$$

Here σ_{ik} is the stress tensor in a nematic liquid crystal, u is the vertical displacement of the surface, and

$$v_z=\partial u/\partial t. \tag{5}$$

In addition, we consider in the usual manner small displacements (small wave amplitudes u), so that the boundary conditions (3) and (4) pertain in the linear approximation to a surface that is not bent. In an isotropic liquid the right-hand side of (4) would be equal to zero.

Before we proceed to write down and solve the hydrodynamic equations for which (3) and (4) are the boundary conditions, let us discuss condition (4) in greater detail. It follows from (2) and (4) that $\alpha_a<0$, when the equilibrium value is $\theta=0$, the right-hand side in (4) is proportional to the square of the fluctuations of θ. Therefore, in the linear approximation, the condition (4) causes no changes in the usual results for surface oscillations. For the corresponding force linear in the deviations of $\mathbf{n}$ to appear, it is necessary that the orientation differ from the condition (2) for the minimum energy. As already indicated, this can be done with the aid of a magnetic field. Thus, we consider a liquid crystal having a thickness that is large in comparison with the length of the surface waves (see below). The surface energy is given by formula (2), and a magnetic field H is applied along the x axis. The geometry of the problem is shown in Fig. 1. The orientation of the molecules depends on the coordinate z and on the surface we have $z=L$ and $\theta=\theta_0\neq 0$. In weak fields $\theta_0 \sim H$. The corresponding formulas for θ_0 are given in the Appendix. Taking the foregoing into account, the boundary condition (4) in a magnetic field becomes

$$\sigma_{zx}=-\alpha_a\left(\frac{\partial\theta}{\partial x}\right)_{z=0}\sin 2\theta_0. \tag{6}$$

We write down now the hydrodynamic equations for liquid crystals. For simplicity we assume the liquid to be incompressible:

$$\operatorname{div}\mathbf{v}=0, \tag{7}$$

$$\rho\frac{\partial v_i}{\partial t}=\frac{\partial\sigma_{ji}}{\partial x_j} \tag{8}$$

(v is the velocity of the liquid).

It is necessary to add to (7) and (8) the equation of motion of the director. Before we write down this equation, let us discuss the expression for the stress tensor. In liquid crystals

$$\sigma_{ij}=-p\delta_{ij}-\Pi_{kj}n_{k,\,i}+\sigma_{ij}'. \tag{9}$$

Here p is the pressure and Π_{kj} is the part of the stress tensor connected with the Oseen–Frank elasticity,

$$\Pi_{ij}=-\partial F/\partial n_{i,\,j}, \tag{10}$$

F is the free Oseen–Frank energy, and the comma denotes differentiation with respect to the corresponding coordinate; σ'_{ij} is the dissipative part of the stress tensor. In liquid crystals σ'_{ij} is determined generally speaking by five Leslie coefficients. In nematic liquid crystals, however, some of them are small and some can be neglected when small deviations from equilibrium in the surface oscillations are considered. Thus, for the problem of interest to us we have

$$\sigma_{ij}'=2\mu A_{ij}+2(J-\mu)(A_{iz}\delta_{jz}+A_{zj}\delta_{iz})+GA_{zz}\delta_{iz}\delta_{jz},\qquad A_{ij}={}^1/_2(v_{i,\,j}+v_{j,\,i}). \tag{11}$$

As to the elastic part (10), it is quadratic in the orientation and can be omitted.

The equations of motion (7) and (8) of the liquid now take the form

$$\begin{gathered}\frac{\partial v_z}{\partial t}-\frac{\partial p}{\partial z}+J\left(\frac{\partial^2 v_x}{\partial z\,\partial x}+\frac{\partial^2 v_z}{\partial x^2}\right)+\gamma\frac{\partial^2 v_z}{\partial z^2}=0,\\ \frac{\partial v_x}{\partial t}-\frac{\partial p}{\partial x}+2\mu\frac{\partial^2 v_x}{\partial x^2}+J\left(\frac{\partial^2 v_x}{\partial z^2}+\frac{\partial^2 v_z}{\partial x\,\partial z}\right)=0,\\ \frac{\partial v_x}{\partial x}+\frac{\partial v_z}{\partial z}=0.\end{gathered} \tag{12}$$

We have put in (12) for convenience $\rho\equiv 1$ and $\gamma=4J-2\mu+G$. We seek the solution of (12) in the form

$$v_z=\sum_j A_j\exp(iqx+m_jz-i\omega t),\qquad v_x=\sum_j iA_j\frac{m_j}{q}\exp(iqx+m_jz-i\omega t),$$
$$p=\sum_j C_j\exp(iqx+m_jz-i\omega t). \tag{13}$$

Substituting (13) in (12) we obtain the connection of m_j with q and ω, and also an expression for C_j in terms of A_j:

$$C_j=\left[\frac{-i\omega-J(q^2+m_j^2)+\gamma m_j^2}{m_j}\right]A_j, \tag{14}$$

$$m_j^2=\left[\frac{-i\omega+(2\mu+2J-\gamma)q^2}{2J}\right]\pm\left[\left(\frac{-i\omega+(2\mu+2J-\gamma)q^2}{2J}\right)^2+\frac{i\omega q^2+Jq^4}{J}\right)^{1/2} \tag{15}$$

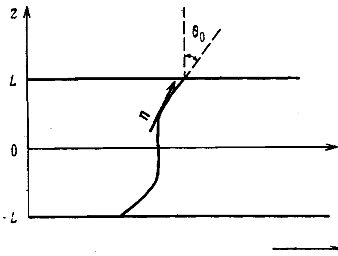

FIG. 1.

There are two different roots, which are given in the long-wave limit by the expressions

$$m_1=q, \quad m_2=\left[q^2-\frac{i\omega}{2\mu+2J-\gamma}\right]^{1/2}. \tag{16}$$

Thus, the solution is determined by two constants: A_1 and A_2.

To determine these constants (and also the connection between ω and q) it is necessary to substitute the solutions in the boundary conditions. However, the boundary conditions contain also the director orientation, which is itself determined in terms of the velocity distribution. This connection is given by the equation of motion for the director:

$$I\frac{\partial \dot{n}_i}{\partial t}+\frac{\partial}{\partial x_j}\Pi_{ij}+g_i+g_i'=0. \tag{17}$$

Here I is the moment of inertia of the molecules; $g_i = \partial F/\partial n_i$; g_i' is the dissipative force:

$$g_i'=\gamma n_i+\gamma_1 N_i+\gamma_2 n_j A_{ji}; \tag{18}$$

$$\dot{n}_i\equiv\frac{\partial n_i}{\partial t}+\mathbf{v}\nabla n_i;$$

γ is an arbitrary scalar determined from the condition $n_i\dot{n}=0$; γ_1 and γ_2 are the viscosity coefficients ($\gamma_1\approx-\gamma_2$ in nematic liquid crystals);

$$N_i=\dot{n}_i-{}^1/_2[\operatorname{rot}\mathbf{v}\times\mathbf{n}]_i\ .$$

Neglecting the moment of inertia of the molecules themselves ($I=0$) and multiplying (17) by n_i, we obtain

$$\gamma=-n_i\frac{\partial}{\partial x_j}\Pi_{ij}-n_i g_i-n_i\gamma_1(N_i-n_j A_{ij}). \tag{19}$$

Substituting (19) in (17) and designating the molecular field in terms of

$$h_i=\frac{\partial F}{\partial n_i}-\frac{\partial}{\partial x_j}\frac{\partial F}{\partial n_{i,j}}, \tag{20}$$

we obtain the equation of motion of the director:

$$\frac{\partial n_i}{\partial t}+\mathbf{v}\nabla n_i-\frac{1}{2}[[\nabla\times\mathbf{v}]\times\mathbf{n}]_i-n_j A_{ji}+n_i n_j A_{jk} n_k-\frac{h_k n_k}{\gamma_1}n_i+\frac{h_i}{\gamma_1}=0. \tag{21}$$

Introducing small deviations from the equilibrium orientation φ

$$n_x=\cos\theta-\varphi\sin\theta, \quad n_z=\sin\theta+\varphi\cos\theta \tag{22}$$

and recognizing that at the significant values of the parameters the last two terms of (21) can be neglected, we obtain

$$\frac{\partial\varphi}{\partial t}+\frac{\partial\theta_0}{\partial z}v_z+\frac{\partial v_x}{\partial z}+\operatorname{ctg}\theta_0\sin^2\theta_0\frac{\partial v_x}{\partial x}$$
$$+\cos^2\theta_0\left(\frac{\partial v_x}{\partial z}+\frac{\partial v_z}{\partial x}\right)+\sin\theta_0\cos\theta_0\frac{\partial v_z}{\partial t}=0. \tag{23}$$

Substituting the solutions (13) in (23) we obtain an expression for φ. Substituting this expression in the boundary condition (6) we obtain the dispersion of the waves. The corresponding manipulations are straight forward but very cumbersome. We shall not present all of them. We write down only the answer for the dispersion law at small values of the magnetic field ($\theta_0 \ll 1$, and the answers are accurate to θ_0^2). In addition, we have introduced the effective viscosity $\eta=2\mu+2J-\gamma$.

At $q<\alpha_a^2\theta_0^2\rho/\alpha_0\eta^2$ we have

$$\omega=\frac{|\alpha_a|\theta_0}{\eta}q+i\frac{\eta}{\rho}q^2. \tag{24}$$

Thus, in this region there are weakly-damped waves with linear dispersion.

At $q>\alpha_a\theta_0\rho/\eta^2$ the dispersion differs little from the usual capillary waves, but there is additional damping

$$\operatorname{Im}\omega\sim\text{const}\cdot|\alpha_a|^{1/2}\rho^{-1/2}q^{3/2}. \tag{25}$$

At $\alpha_a^2\theta_0^2\rho/\alpha_0\eta^2<q<\alpha_a\theta_0\rho/\eta^2$ we obtain the usual law (1).

3. The formulas obtained in Sec. 2 for the linear dispersion in the nematic phase call for a certain explanation. The fact that the dissipation η enters directly in the real part of the dispersion law is connected with the presence of two components (the velocity and the director orientation φ). Each of these quantities relaxes when the equilibrium is disturbed, but at certain parameter values the sign of the determinant is reversed and we have a propagating mode. A similar phenomenon takes place, for example, in chemical oscillations.[1] Estimates of the obtained quantities are quite difficult, since the value of the anisotropic part of the surface tension is unknown. We note here also that the formulas obtained in the Appendix make it possible in principle to determine the value of α_a from the change of the Freedericsz field. If it assumed that $\alpha_a\sim10$ erg/cm^2 and $\eta\sim0.1$, then to satisfy the inequalities (24) in fields ~100 G we need $q\ll10^3$ cm^{-1}. Such extremely long waves cannot be realized in light-scattering experiments. Incidentally, difficulties of the same kind are encountered also in the case of the usual capillary waves in liquid crystals. We note also that similar phenomena should take place also in the cholesteric and smectic phases. The main difference is that in these phases the stress tensor $\Pi_{ik}n_{k,j}$ already contains terms linear in the deviations, and it must therefore be taken into account in the hydrodynamic equations. In our entire analysis, the field strength H (and the sample thickness) determined only the width of the region in which linear dispersion exists. In rather strong fields $\chi_a H^2\gg\alpha_0 q$, however, a linear spectrum appears and is connected simply with the magnetic restoring force:

$$\omega=(\chi_a H^2/\rho)^{1/2}q.$$

These are ordinary Rayleigh waves. However, by virtue of the smallness of $\chi_a\sim10^{-7}$ cgs esu, they can hardly be observed in experiment.

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APPENDIX

We consider for the sake of argument the influence of the magnetic field on the orientation of a liquid crystal. This calls for minimizing the total free energy of the system. For simplicity we assume identical boundary conditions at $z=\pm L$. The surface energy is anisotropic:

$$F_{\text{sur}}=\alpha_a\cos^2\theta. \tag{A.1}$$

In addition, there is a volume energy (Oseen–Frank and magnetic):

$$F=\frac{K}{2}\int_{-L}^{L}dz(\nabla\theta)^2-\frac{1}{2}\chi_a H^2\int_{-L}^{L}\cos^2\theta\,dz. \tag{A.2}$$

The surface energy does not enter in the Euler–Lagrange equation:

$$\frac{d^2\theta}{dz^2}+\frac{1}{2\xi^2}\sin 2\theta=0, \tag{A.3}$$

$\xi=H^{-1}(K/\chi_a)^{1/2}$ is the magnetic coherence length. The fact that the conditions on both walls are identical means that

$$\theta(L)=\theta(-L)=\theta_0,\quad \frac{d}{dz}\theta(L)=-\frac{d}{dz}\theta(-L). \tag{A.4}$$

Actually, however, the values of α_a at $z=\pm L$ are different, so that the conditions (A.4) are not satisfied. However, the changes in the final formulas (A.11) and (A.12) are negligible. It is merely necessary to substitute for each boundary its value of α_a. In addition, there are also boundary conditions on the stress tensor:

$$\left(\frac{\partial F}{\partial n_{r,k}}n_{r,i}\right)\nu_k=a_i, \tag{A.5}$$

$$\left(\frac{\partial F}{\partial n_{i,k}}\right)\nu_k=b_i, \tag{A.6}$$

$\boldsymbol{\nu}$ is the normal to the surface, and a_i and b_i are the corresponding external forces. Equation (A.5) gives an orientation-dependent increment to the pressure. As already indicated in the text, this increment is quaratic in the fluctuations of θ and can therefore be left out in the linear approximation. On the other hand, the condition (A.6) leads to vanishing of the total torque. The corresponding force b_i is due to the dependence of the surface energy on the orientation. The expanded form of (A.6) is

$$\frac{\partial\alpha}{\partial(n_k\nu_k)}-\frac{\partial F}{\partial n_{i,j}}\nu_j=0, \tag{A.7}$$

whence

$$2\xi^2\left(\frac{d\theta}{dz}\right)_{\pm L}\pm\alpha_a\sin 2\theta_0=0. \tag{A.8}$$

From (A.3) we have for $z>0$

$$L-z=\xi\left[\mathrm{F}\left(\frac{\varphi}{\theta_m}\right)-\mathrm{F}\left(\frac{\varphi_0}{\theta_m}\right)\right], \tag{A.9}$$

$$\mathrm{F}\left(\frac{\varphi}{\theta_m}\right)=\int_0^{\varphi}\frac{du}{(1-k^2\sin^2 u)^{1/2}},$$

F is an elliptic integral of the first kind, θ_m is the maximum value of θ_0,

$$k^2\equiv\sin^2\theta_m,\qquad \sin\varphi\equiv\frac{\sin\theta}{\sin\theta_m},\qquad \sin\varphi_0\equiv\frac{\sin\theta_0}{\sin\theta_m}. \tag{A.10}$$

From (A.9) at $z=0$ we have

$$\frac{L}{\xi}=\mathrm{F}\left(\frac{\pi/2}{\theta_m}\right)-\mathrm{F}\left(\frac{\varphi_0}{\theta_m}\right). \tag{A.11}$$

The condition (A.11) gives the dependence of θ_m on the field H at fixed θ_0. Taking (A.8) and (A.11) into account, we have two relations from which we determine θ_0:

$$\frac{\xi}{\alpha_a}\chi_a H^2=(1-k\sin^2\theta_0)^{1/2}\,\mathrm{tg}\,\theta_0. \tag{A.12}$$

For weak fields it follows from (A.11) and (A.12) that $\theta_0\sim H$. As already noted in the main text, the same role as the magnetic field is assumed simply by a boundary condition at $z=-L$ which does not coincide with the condition of the minimum of the surface energy at $\nu=L$.

[1)] The author thanks G. V. Ryazanov for pointing out this circumstance.

[1] M. Papoular, J. Phys. (Paris) 30, 406 (1969).
[2] A. Rapini, Can. J. Phys. 53, 968 (1975).
[3] I. E. Dzyaloshinskiĭ, S. G. Dmitriev, and E. I. Kats, Zh. Eksp. Teor. Fiz. 68, 2335 (1975) [Sov. Phys. JETP 41, 1167 (1975)].
[4] L. D. Landau and E. M. Lifshitz, Mekhanika sploshnykh sred, Gostekhizdat, 1957 [Fluid Mechanics, Pergamon, 1959].

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