Equilibrium structure of a cholesteric with homeotropic orientation on the walls

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We consider the distribution of the director of a cholesteric liquid crystal (CLC) in planar cells on whose walls the director orientation is maintained rigidly along the normal to the boundary. At a cell thickness $L_{cr} = 2K_{33}P/K_{22}$, where P is the pitch parameter of the free CLC, a transition of the Fréedericksz type takes place from a stable homogeneous homeotropic distribution (for $L < L_{cr}$) to a stable twisted distribution (for $L > L_{cr}$). Application of the Noether theorem to the variation equation has yielded a conservation law for the specific moment of the transmitted force and for the analog of the pressure. This resulted in an exact equation for the helix profile.

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1. INTRODUCTION

We consider a cell with a nematic liquid crystal (NLC) in which the walls make the orientation strictly normal to the boundary (see Fig. 1). The free energy in the absence of external field is then reached when the director has a homogeneous homeotropic orientation: $\mathbf{n}(\mathbf{r}) = \mathbf{e}_z = \text{const}$, where the z axis is perpendicular to the walls. This statement is valid regardless of the cell thickness L.

Assume now that a chiral (i.e., a right-left-asymmetric) impurity is added to the nematic and transforms the NLC into a cholesteric liquid crystal (CLC). At low density of the additive, the "wave number" q of the twist of the free CLC is small ($q = 2\pi/P$, where P is the pitch of the free homogeneous helix of the CLC). It is clear that at $qL \ll 1$ the chiral additive could distort the homeotropic orientation of the direction inside the cell only weakly. On the other hand, at $qL \gg 1$ a nearly homogeneous helical structure, with pitch $P = 2\pi/q$, should be established in practically the entire volume of the cell.

A change of the parameter qL from values $qL \ll 1$ to $qL \gg 1$ can be obtained also at a fixed chemical composition of the CLC, by simply changing the thickness (Fig. 2). Small variations of qL can be obtained also be varying the temperature or the hydrostatic pressure.

This raises the question of describing the transition from one picture (at $qL \ll 1$) to the other ($qL \gg 1$). We have shown earlier[1] that up to the parameter value

$$qL \leqslant (qL)_{cr} = \pi K_{33}/K_{22},$$

a strictly homogeneous homeotropic orientation remains stable. A helical perturbation sets in starting with $(qL)_{cr}$. This behavior of a cell of CLC with homeotropic pinning of the director on the walls was called in Ref. 1 a Fréedericksz transition without an external field.

We determine and investigate here the exact stationary structure of a CLC in such a cell. To do this we use essentially the free-energy symmetry with respect to rotations about the z axis and to translations along the z axis. This has made it possible to obtain with the aid of the Noether theorem two integrals of the variational equations, viz., the analogs of the z components of the pressure and of the specific moment of the force. The use of these integrals made it possible to solve the problem exactly in quadratures.

2. THE NOETHER THEOREM AND THE CONSERVATION LAW

We assume the free energy F [erg/cm^3] per unit volume of the CLD in the form

$$F = {}^1/_2 K_{11} (\operatorname{div} \mathbf{n})^2 + {}^1/_2 K_{22} (\mathbf{n} \operatorname{rot} \mathbf{n} + q)^2 + {}^1/_2 K_{33} [\mathbf{n} \operatorname{rot} \mathbf{n}]^2, \quad (1)$$

where $\mathbf{n}(\mathbf{r})$ is the unit vector of the director and K_{ii} are Frank's constants. We represent $\mathbf{n}(\mathbf{r})$ in the form

$$\mathbf{n}(\mathbf{r}) = (\mathbf{e}_x \cos\varphi + \mathbf{e}_y \sin\varphi) \sin\theta + \mathbf{e}_z \cos\theta \quad (2)$$

and confine ourselves to a problem homogeneous in the (x,y) plane, i.e., we assume $\mathbf{n}(\mathbf{r})$ to depend only on the coordinate z: $\theta = \theta(z)$, $\varphi = \varphi(z)$. Equation (1) takes then the form

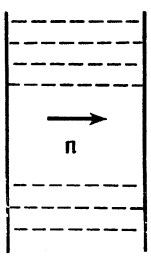

FIG. 1. Cell with nematic liquid crystal and with homeotropic orientation on the walls.

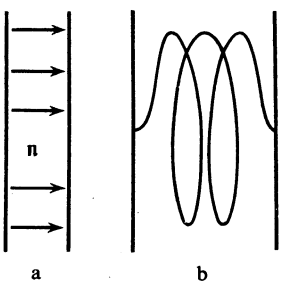

FIG. 2. Cell with cholesteric liquid crystal with homeotropic orientation on the walls: a) $qL \ll 1$, b) $qL \gg 1$.

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$$F=\frac{1}{2}\left(\frac{d\theta}{dz}\right)^2[K_{11}\sin^2\theta+K_{33}\cos^2\theta]+\frac{1}{2}\left(\frac{d\varphi}{dz}\right)^2\sin^2\theta$$
$$\times[K_{22}\sin^2\theta+K_{33}\cos^2\theta]+\frac{1}{2}K_{22}q^2-\frac{d\varphi}{dz}K_{22}q\sin^2\theta. \quad (3)$$

The Euler variational equations that follow from (3) are

$$\frac{d}{dz}\left(\frac{\partial F}{\partial(d\theta/dz)}\right)-\frac{\partial F}{\partial\theta}=0, \quad (4)$$
$$\frac{d}{dz}\left(\frac{\partial F}{\partial(d\varphi/dz)}\right)-\frac{\partial F}{\partial\varphi}\equiv\frac{d}{dz}\left(\frac{\partial F}{\partial(d\varphi/dz)}\right)=0, \quad (5)$$

and we do not expand them in greater detail because the resultant equations are too unwieldy. The homeotropy of the director orientations on the walls $z=0$ and $z=L$ corresponds to the boundary conditions

$$\theta(z=0)=0, \quad \theta(z=L)=0. \quad (6)$$

It is easily seen that both (1) and (3) are invariant to two transformations that commute each other: to translations along the z axis and to rotations about the same axis:

$$\varphi'(z)=\varphi(z-\delta z), \quad \theta'(z)=\theta(z-\delta z), \quad (7)$$
$$\varphi'(z)=\varphi(z)-\alpha, \quad \theta'(z)=\theta(z). \quad (8)$$

According to the known Noether theorem (see, e.g., Ref. 2) this leads to the existence of two integrals of the variational equations

$$\frac{dp}{dz}=0, \quad p=\frac{d\theta}{dz}\frac{\partial F}{\partial(d\theta/dz)}+\frac{d\varphi}{dz}\frac{\partial F}{\partial(d\varphi/dz)}-F, \quad (9)$$

$$\frac{dm}{dz}=0, \quad m=\frac{\partial F}{\partial(d\varphi/dz)}$$
$$=[K_{22}\sin^2\theta+K_{33}\cos^2\theta]\sin^2\theta\frac{d\varphi}{dz}-K_{22}q\sin^2\theta. \quad (10)$$

The quantity p has the dimensionality (dyn·cm^{-2}) and is the analog of the pressure (more accurately, of the zz component of the stress tensor); m has the dimensionality dyn/cm in analogy with the z component of the moment of the force transmitted through a unit area normal to the z axis. We note that it would be quite difficult to deduce the form of the integral $p(z)$ without using Noether's theorem.

The boundary condition $\theta=0$, superimposed on at least one of the boundaries, predetermines a zero value of the specific moment of the force, $m(z)=0$. In other words, a homeotropically oriented surface cannot transmit a z component of the moment.

3. EXACT SOLUTION OF THE PROBLEM OF THE HELIX PROFILE

Using the equality $m(z)=0$, we can write the expression for the conserved quantity p in a shorter form

$$\text{const}=2p=\left(\frac{d\theta}{dz}\right)^2(K_{11}\sin^2\theta+K_{33}\cos^2\theta)$$
$$-\frac{q^2K_{22}K_{33}\cos^2\theta}{K_{22}\sin^2\theta+K_{33}\cos^2\theta}. \quad (11)$$

This enables us to find in terms of quadratures the law governing the variation of $\theta(z)$:

$$K_{33}^{1/2}\int_0^{\theta(z)}\frac{(1-\Delta_1\sin^2\psi)^{1/2}(1-\Delta_2\sin^2\psi)^{1/2}\,d\psi}{[q^2K_{22}(1-\sin^2\psi)+2p(1-\Delta_2\sin^2\psi)]^{1/2}}=z. \quad (12)$$

We have introduced here the notation

$$\Delta_1=(K_{33}-K_{11})/K_{33}, \quad \Delta_2=(K_{33}-K_{22})/K_{33}, \quad (13)$$

and actually $0<\Delta_1<\Delta_2<1$ in all liquid crystals. The $\varphi(z)$ dependence is given by an expression that follows from the conservation law $m(z)=0$:

$$\varphi(z)-\varphi(z=0)=\frac{K_{22}q}{K_{33}^{1/2}}\int_0^{\theta(z)}\left(\frac{1-\Delta_1\sin^2\psi}{1-\Delta_2\sin^2\psi}\right)^{1/2}$$
$$\times\frac{d\psi}{[q^2K_{22}\cos^2\psi+2p(1-\Delta_2\sin^2\psi)]^{1/2}}, \quad (14)$$

where $\theta(z)$ is defined by (12). It is interesting to note that in the single-constant approximation we have

$$\varphi(z,\ \Delta_1=\Delta_2=0)-\varphi(z=0)=qz \quad (15)$$

regardless of the actual variation of $\theta(z)$.

Before proceeding to investigate the problem of a finite-thickness cell, we examine the limiting case of a half-space $0\leqslant z<+\infty$ we have

$$\theta(z)=\pi/2+\text{const}\cdot\exp[-qz(K_{33}/K_{11})^{1/2}].$$

Therefore the constant p is zero (no "pressure" is transmitted at infinity). At $p=0$ the variation of $\theta(z)$, defined by Eq. (12), becomes a universal function of qz and of the two dimensionless parameters Δ_1 and Δ_2. This universal function can be easily obtained with a computer for each concrete liquid crystal, using the equation

$$\int_0^{\theta(z)}\frac{(1-\Delta_1\sin^2\psi)^{1/2}(1-\Delta_2\sin^2\psi)^{1/2}}{\cos\psi}d\psi$$
$$=qz\left(\frac{K_{22}}{K_{33}}\right)^{1/2}=qz(1-\Delta_2)^{1/2}. \quad (16)$$

We indicate here only the asymptotic behavior of $\theta(p=0, qz, \Delta_1, \Delta_2)$ at $qz\ll1$ and $qz\gg1$. In the former case

$$\theta(z)=qz(K_{22}/K_{33})^{1/2}, \quad qz\ll1, \quad (17a)$$

and in the latter case (at $qz\gg1$)

$$\theta(z)=\tfrac{1}{2}\pi-A\exp[-qz(K_{33}/K_{11})^{1/2}], \quad (17b)$$
$$A=\sqrt{2}\exp\left[\frac{K_{33}}{(K_{11}K_{22})^{1/2}}\int_0^1\ln(1-x)\frac{df_1}{dx}dx\right]. \quad (18)$$

Similarly, in the semi-infinite problem (i.e., at $p=0$), $\varphi(z)$ is given by the universal function

$$\varphi(z)-\varphi(z=0)=\int_0^{\theta(z)}\left(\frac{K_{22}}{K_{33}}\right)^{1/2}\left(\frac{1-\Delta_1\sin^2\psi}{1-\Delta_2\sin^2\psi}\right)^{1/2}\frac{d\psi}{\cos\psi}, \quad (19)$$

where $\theta(z)$ is defined in (16). Again, at small and large qz we have

$$\varphi(z)-\varphi(z=0)=(K_{22}/K_{33})qz, \quad qz\ll1, \quad (20a)$$
$$\varphi(z)-\varphi(z=0)=qz-B+O\{\exp[-qz(K_{33}/K_{11})^{1/2}]\}, \quad qz\gg1, \quad (20b)$$

$$B=\int_0^1 \ln(1-x)\left[\left(\frac{K_{33}}{K_{22}}\right)^{1/2}\frac{df_1}{dx}-\left(\frac{K_{22}}{K_{33}}\right)^{1/2}\frac{df_2}{dx}\right]dx. \tag{20c}$$

To determine the dimensionless constants A and B we have introduced here the notation

$$f_1(x)=[(1-\Delta_1x^2)(1-\Delta_2x^2)/(1+x)^2]^{1/2},$$
$$f_2(x)=[(1+x)^2(1-\Delta_2x^2)/(1-\Delta_1x^2)]^{-1/2}.$$

The quantity B is the "incomplete twist" of the angle φ near the homeotropically orienting boundary, and is connected with the presence of one more than one constant ($B=0$ at $\Delta_1=\Delta_2=0$). In the single-constant approximation have for the semi-infinite problem ($p=0$)

$$\sin\theta(z,\ p=0,\ \Delta_1=\Delta_2=0)=\mathrm{th}\,(qz),\quad \varphi(z)-\varphi(z=0)=qz. \tag{21}$$

4. CELL OF FINITE THICKNESS

The constant p for a cell with homeotropic orientation on both walls ($z=0$ and $z=L$) can be determined from the equation

$$\frac{d\theta}{dz}\left(z=\frac{L}{2}\right)=0, \tag{22}$$

which expresses the symmetry property relative to the center of the cell. It follows then from (11) that

$$2p(\theta_m)=-q^2K_{22}K_{33}\cos^2\theta_m/(K_{22}\sin^2\theta_m+K_{33}\cos^2\theta_m), \tag{23}$$

where $\theta(z=L/2)=\theta_m$ denotes the maximum value of the angle θ, and θ_m is defined by the equation

$$2\frac{K_{33}}{K_{22}}(1-\Delta_2\sin^2\theta_m)^{1/2}\int_0^{\theta_m}\frac{(1-\Delta_1\sin^2\psi)^{1/2}(1-\Delta_2\sin^2\psi)^{1/2}}{(\sin^2\theta_m-\sin^2\psi)^{1/2}}\,d\psi$$
$$=qL \tag{24}$$

under the assumption that $\theta_m\neq0$. At $qL\gg1$ the solution of this equation is of the form

$$\theta_m=\frac{\pi}{2}-2A\exp\left(-\frac{qL}{2}\left(\frac{K_{33}}{K_{11}}\right)^{1/2}\right), \tag{25}$$

where the constant A coincides with the constant A from (17c). The total twist to the angle $\varphi(L)-\varphi(0)$ at $qL\gg1$ is

$$\varphi(L)-\varphi(0)=qL-2B. \tag{26}$$

In the intermediate case $qL\sim4$ to 6, Eqs. (12), (14), and (26) must be solved numerically. We note here the single-constant case, when Eq. (23b) takes the form

$$2K(\sin\theta_m)=qL. \tag{27}$$

Here $K(z)$ is a complete elliptic integral of the first kind.

5. FRÉEDERICKSZ TRANSITION WITHOUT AN EXTERNAL FIELD, AND HYSTERESIS

The homogeneous orientation of a CLC is the solution of the stationary balance conditions (4) and (5) at any cell thickness L.

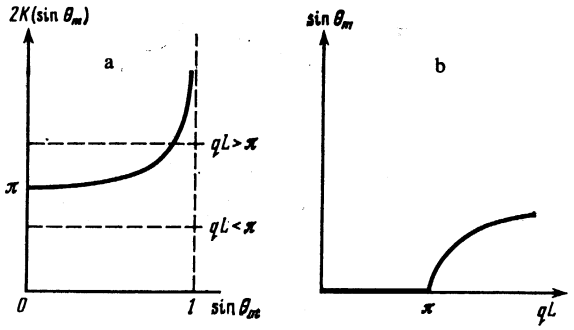

FIG. 3. a) For use in the solution of Eq. (27) that determines the equilibrium angle θ_m in the single-constant case; b) the function $\theta_m(qL)$.

As shown by us earlier 1 and as will be demonstrated below on the basis of Eq. (24), this solution $\theta(z)\equiv0$ is also found to be stable at sufficiently small qL. On the contrary, at $qL\gg1$ a solution of the helical discussed in detail in Sec. 3, is stable.

To discuss the distance transitions between such states when qL varies from 0 to ∞, it is convenient first to consider the single-constant case. Figure 3a shows for the case $K_{11}=K_{22}=K_{33}$ a plot of the function $2K(\sin\theta_m)$, the left-hand side of Eq. (27), vs. $\sin\theta_m$. The dashed horizontal lines show the right-hand sides of Eq. (27), vs. $\sin\theta_m$. The dashed horizontal lines show the right-hand sides of Eq. (27) for the different ordinates qL. It is seen that at $qL\leqslant\pi$ Eq. (27) written under the assumption $\theta_m\neq0$ has no solution. Consequently at $qL\leqslant\pi$ the solution of the balance equations (4) and (5), in the form $\theta(z)\equiv0$, is unique and stable (the stability was domonstrated in Ref. 1 by a direct analysis of the linearized time-dependent problem). At $qL>\pi$ the solution $\theta(z)\equiv0$ becomes unstable, but a new solution appears, which turns out to be stable. At small excesses of the parameter qL above the critical value π the value of $\sin^2\theta_m$ is proportional to the excess above threshold, i.e.,

$$\sin\theta_m\approx[(qL-\pi)/\pi]^{1/2}. \tag{28}$$

The behavior of the stable value of θ_m in the single-constant case as a function of qL is shown in Fig. 3(b) and is quite similar to the picture of the Fréedericksz transition in nematics to which external fields are applied.[1]

The actual differences beteen Frank's constants lead to qualitative differences in the pictures of the Fréedericksz transition in the absence of an external field. Namely, the left-hand side of (24) turns out to be at $K_{11}-3(K_{33}-K_{22})<0$ a nonmonotonic function of $\sin^2\theta$ [see the solid curve of Fig. 4(a)]. At $qL<(qL)_1$ Eq. (14) has no solution and the only equilibrium state $\theta(z)\equiv0$ is stable. At $(qL)_1<qL<(qL)_2$ there are three solutions: $\sin\theta_m=a$ (unstable) and $\sin\theta_m=0$, $\sin\theta_m=b$ (both stable). Finally, at $(qL)_2<qL$ the solution $\theta(z)\equiv0$ becomes unstable, the other solution ($\sin\theta_m=c$) is stable, and the nontrivial solution vanishes. A plot of θ_m in the stable state as qL varies in succession from 0 to ∞ and back is shown in Fig. 4(b). Thus, at $K_{11}-3(K_{33}-K_{22})<0$ the Fréedericksz transitions without an external field should have hysteresis. The position of

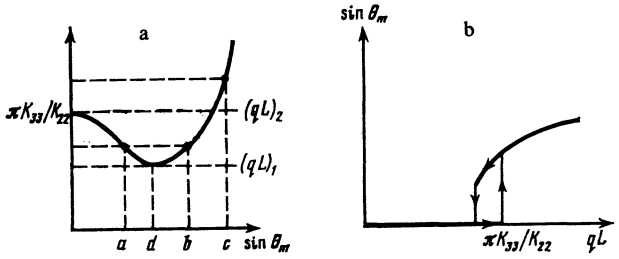

FIG. 4. a) For use in the solution of (24) with allowance for the presence of more than one constant; b) hysteresis of Fréedericksz transition with zero external field.

the point $(qL)_2$ can be obtained by considering the linearized stability test of the trivial solution $\theta(z) \equiv 0$ (Ref. 1). It can also be obtained by direct calculation of the integral (24) as $\theta_m \to 0$. The result is

$$(qL)_2 = \pi K_{33}/K_{22}. \tag{29}$$

The time-dependent behavior of the perturbations near the threshold of the Fréedericksz transition in the absence of an external field was considered in Ref. 1. For the region where two stable states exist ($\theta_m = 0$ and $\theta_m \neq 0$, see Fig. 4), it is of interest to ascertain which of them corresponds to the lower value of the free energy. The state of the sample under these conditions can be represented in the form of domains of two phases, wherein the domains with the lower energy should gradually "eat up" the foreign phase. At the same time, the onset of two-dimensional circle of a new (even more favored) phase calls for consumption of the "boundary" energy. "Superheating" and "supercooling" effects should therefore be observed.

It is unfortunately impossible to calculate the energy of the phase with $\theta_m \neq 0$. We consider therefore the problem in an approximation in which $D/C \ll 1$, where

$$D = (-1+\Delta_1+3\Delta_3)/4,$$

$$C = (1/96)(19-10\Delta_1-6\Delta_2+30\Delta_1\Delta_2-9\Delta_1^2-9\Delta_2^2).$$

In this case θ_m^2 is small in the phase-coexistence region:

$$\theta_m^2 \approx \frac{D+(D^2+4C\rho)^{1/2}}{2C}, \quad \rho = \frac{q-q_{cr}}{q_{cr}}. \tag{30}$$

The phase-coexistence region is in this case small in terms of the parameter D, namely, $-\rho_1 = D^2/4C < \rho < 0$. Analysis shows that in the solution with $\theta_m \neq 0$ is more suitable in the interval $-3\rho/4 < \rho < \infty$, and the solution with $\theta_m = 0$ in the interval $-\rho_1 < \rho < -3\rho_1/4$.

CONCLUSION

The present results were obtained under the assumption that all the structure distortions are one-dimensional [$\mathbf{n}(\mathbf{r})$ depends only on the coordinate z normal to the cell plane] and that the pinning of the director to the walls is ideally rigid. The possibility of non-one-dimensional perturbation is of great interest, but nothing can be said of it at present. As for nonrigid pinning, only the following estimates are possible. Let the rigidity of the pinning of the director to the wall be characterized by the constant σ[erg/cm^2]. Then our analysis is valid at $\sigma \gg K_{ii}\pi^2 L^{-1}$ on the contrary, at $\sigma \ll K_{ii}\pi^2 L^{-1}$ the cholesteric (as well as the nematic) does not feel at all the influence of the walls.

From the viewpoint of practical applications, greatest interest attaches apparently to the hysteresis, as well as to the possibility of registering small values of q.

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