Orientational structure of encapsulated cholesterics

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The equation of state of a liquid crystal in a polymer spherical capsule is solved. The solution is inhomogeneous both in the azimuth ϕ and the polar angle θ. It is shown that owing to boundary conditions induced by pyrimidine impurities at the capsule boundary the spatial distribution in the angle θ has one inhomogeneity scale L, while in the angle ϕ it has two pitches of a helix. The basic pitch p_0 is conserved inside the capsule, while the new pitch p induced by boundary conditions on the sphere is realized on the outside. This accounts for two temperature ranges of selective light reflection by encapsulated cholesterics with pyrimidine additives [G. M. Zharkova and S. I. Trashkeev, Kristallografia **34**, 695 (1989) Sov. Phys. Crystallogr. **34**, 414 (1989)].

INTRODUCTION

Cholesteric liquid crystals (CLC) are widely used as color indicators of various fields, owing to a helical structure in the homogeneously oriented film. The period of the helix is commensurable with the visible-light wavelengths. This gives rise to light diffraction by the CLC helical structure. Since the pitch of the CLC helix is very sensitive to external effects, the diffraction pattern makes it possible to detect small variations of these effects (electric, magnetic, temperature, strain, etc.).

Optical properties of homogeneous cholesteric films have been studied in detail both experimentally and theoretically.[1] Liquid crystals (LC) in polymers have recently become of interest, since this combination increases the number of physical effects in LC and enlarges the range of their practical applications.[2] The shape of LC inclusions in polymers can vary, depending on the type of the polymer. In particular, in polymers such as polyvinyl acetate this shape is close to spherical.[3] The LC state in such spherical capsules is determined both by the interaction of the LC molecules, but also by their interaction with the polymer at the boundary provided that the capsule is sufficiently small. Therefore the optical properties of an encapsulated LC differ from those of an ideal LC. In particular, the reflected light spectra are affected, the reflection maxima get broadened, their intensity drops, and the temperature dependence of the wavelength is modified.[4]

If we vary the formation conditions of spherical capsules or introduce various additives into polymer CLC, qualitatively new features of light diffraction arise, namely new temperature ranges of selective light reflection.[5,6] A typical temperature dependence of the wavelength in the selective reflection maximum in an encapsuled CLC is shown in Fig. 1. The existence of a second temperature range of light reflection denoted by II is due to an extra period of the CLC structure which is realized in a CLC capsule only at a definite pyrimidine concentration (according to Ref. 6, of order 2% and higher).

As far as we know, these features of encapsulated CLC have not yet been explained. Therefore we will determine the spatial distribution of the CLC order parameter in spherical capsules. As we show below, a superstructure of the director field can exist in a spherical capsule. This superstructure is, in the simplest case, a sphere with one pitch of the helix in the director azimuth surrounded by a spherical layer with another pitch of the helix. Moreover, the external layer is characterized by director field modulation in the polar angle with its own period. Such solutions in capsules are due only to the boundary conditions for the polar angle and its radial derivative, created by pyrimidine impurities through their surface activity.

The LC state in a spherical volume has been considered in several papers. The most studied, both theoretically[7–9] and experimentally,[10–13] are nematic LC in spherical geometry. Some subtle size and surface effects have been discovered, and equilibrium configurations characterized by one or two topological defects at the center or the poles of the sphere have been found. In these papers nematic drops of size larger than 1 μm have been considered far from the nematic–isotropic liquid phase transition, so that the order parameter in the capsule volume has been assumed homogeneous. A different situation arises in submicron drops near the phase transition.[14–16]

Equilibrium configurations of cholesterics in the encapsulated state have been considered in less detail. We note here the studies in which solutions have been found for director fields associated with topological defects,[17–19] and also the paper by Zharkova and Trashkeev[20] where the equations of state for CLC in spherical capsules have been solved. In these solutions it has been assumed that the molecule orientation in the polar angle is $\pi/2$ everywhere except in a thin transition layer near the boundary, whose thickness is of the order of the pitch of the helix p_0, and is in azimuth a helix with a constant or monotonically varying pitch. Note that all the solutions considered in Ref. 20 have only one characteristic scale.

EQUATION OF STATE FOR CLC IN A SPHERICAL CAPSULE

The density of the LC free energy in a spherical volume is[21]

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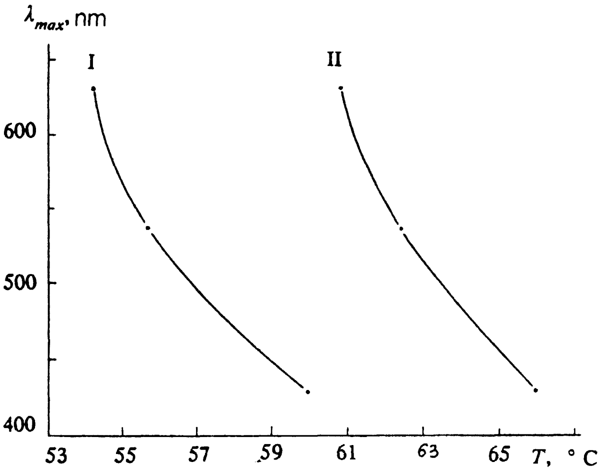

FIG. 1. The temperature dependence of the wavelength in the maximum of selective light reflection in the system PVA-CLC-2,4-di(0-oxyphenyl)-6-phenyl-pyrimidine (4% of the LC weight). CLC composition: cholesterol nonanoate and cholesterol propionate (90:10 weight %), according to Ref. 6.

$$F=\tfrac{1}{2}\,[K_1(\operatorname{div}\mathbf{n})^2+K_2(\mathbf{n}\operatorname{rot}\mathbf{n}+q_0)^2+K_3[\mathbf{n}\operatorname{rot}\mathbf{n}]^2], \qquad (1)$$

where $\mathbf{n}=\mathbf{n}(\mathbf{r})$ is the director, K_i are the moduli of elasticity, $q_0=2\pi/p_0$, and p_0 is the pitch of the helix in CLC of unbounded volume. The geometry of the system in question is shown in Fig. 2. The vector $\mathbf{n}$ can be represented in the form

$$\mathbf{n}=\mathbf{e}_r\cos\theta+\mathbf{e}_\gamma\sin\theta\cos\phi+\mathbf{e}_\alpha\sin\theta\sin\phi, \quad |\mathbf{n}|=1, \qquad (2)$$

where the angles θ and ϕ are in the general case functions of the three spherical coordinates r, γ, and α. Consider a simple version of spherical symmetry, assuming that[20]

$$\theta=\theta(r), \quad \phi=\phi(r). \qquad (3)$$

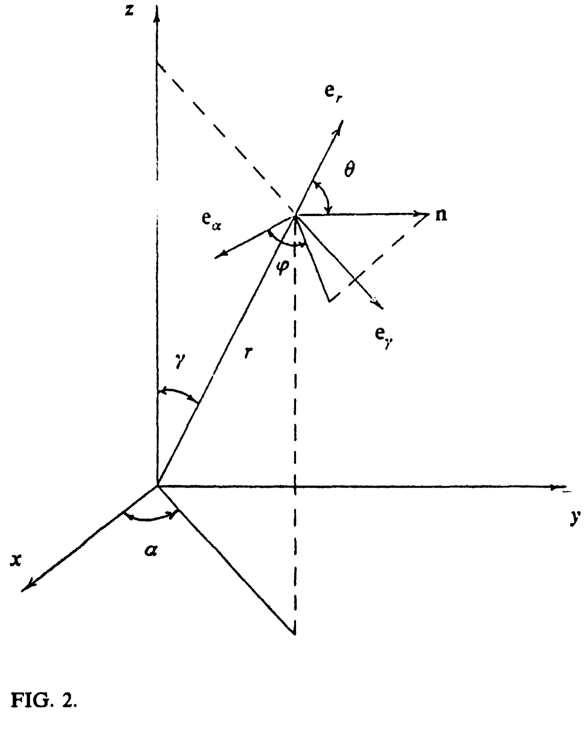

FIG. 2.

Then the expression for the free energy (1) acquires the following form:

$$F=\frac{1}{2}\left[\frac{A}{r^2}+\frac{2B}{r}\,\theta_r+f\theta_r^2+g\phi_r^2-2K_2q_0\sin^2\theta\phi_r+K_2q_0^2\right.$$
$$+\frac{\cot^2\gamma}{r^2}\,(K_1\sin^2\theta\cos^2\phi$$
$$\left.+K_2\cos^2\theta\sin^2\theta\sin^2\phi+K_3\sin^4\theta\sin^2\phi)\right],$$
$$A=4K_1\cos^2\theta+K_3\sin^2\theta, \quad B=\frac{1}{2}\,(K_3-2K_1)\sin 2\theta,$$
$$g=\sin^2\theta(K_2\sin^2\theta+K_3\cos^2\theta),$$
$$f=K_1\sin^2\theta+K_3\cos^2\theta, \qquad (4)$$

where θ_r and ϕ_r are radial derivatives. The terms proportional to $\cot\gamma$ are discarded, as the integral over γ makes them vanish. Note that the assumption (3) leads to defects at the poles of the sphere ($\gamma=0,\pi$). As a result, we get a logarithmic singularity near these poles. Therefore we restrict the solutions considered to the region $\beta<\gamma<\pi-\beta$. The value of the bounding angle can be estimated as a ratio of the smallest dimension in the theory, which is simply the LC correlation radius, to the capsule radius R. Since the correlation radius is the pitch of the helix, we find that $\beta\approx 1/q_0R$. The solutions (3) are most natural near the equatorial plane.

The variational equations for the director field have the form

$$\frac{\partial F}{\partial\theta}=\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{\partial F}{\partial\theta_r}\right), \quad \frac{\partial F}{\partial\phi}=\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{\partial F}{\partial\phi_r}\right) \qquad (5)$$

provided that we have chosen at the center of the capsule free boundary conditions

$$r^2\frac{\partial F}{\partial\theta_r}\bigg|_{r=0}=0, \quad r^2\frac{\partial F}{\partial\phi_r}\bigg|_{r=0}=0, \qquad (6)$$

corresponding to a free field distribution at the center, while on the surface of the sphere the field variation equals zero, as usual. In the general case, we cannot exclude that the field variation can also be zero as $r\to 0$, owing to introduction, for example, of a pyrimidine impurity into the center of the capsule.

The equation of state for the director field has the following form

$$f\theta_{rr}+\frac{1}{2}\frac{\partial f}{\partial\theta}\,\theta_r^2+2\,\frac{f}{r}\,\theta_r-\frac{1}{2}\frac{\partial g}{\partial\theta}\,\phi_r^2+\left[K_2q_0\phi_r+\frac{K_1}{r^2}\right.$$
$$-\frac{1}{4r^2}\frac{f(\beta)}{\cos\beta}\,(K_1\cos^2\phi+K_2\cos 2\theta\sin^2\phi$$

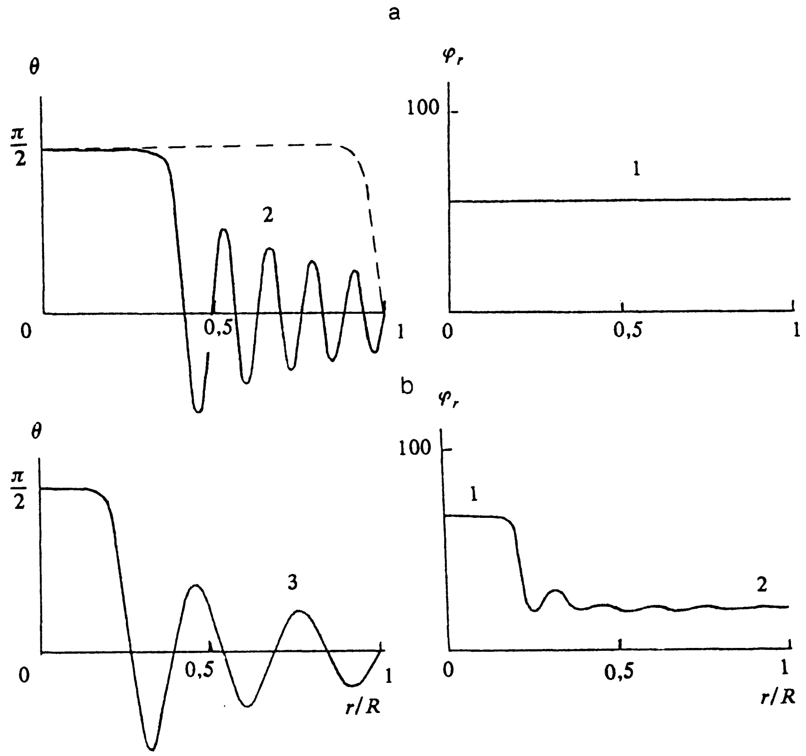

FIG. 3. Radial dependences of the polar angle θ and the pitch of the helix in the azimuth ϕ_r: (a) the case of equal elastic constants, $q_0R=54$, $K_1=K_2=K_3=5.6\cdot10^{-7}$ dyne; Curve *1* corresponds to the period $p_0/2=290$ nm, Curve *2* to the period $L=650$ nm; (b) the case of different constants, $q_0R=64$, $K_1=5.3\cdot10^{-7}$ dyne, $K_2=2.2\cdot10^{-7}$ dyne, $K_3=7.4\cdot10^{-7}$ dyne; the radius of the sphere $R=5$ μm; Curve *1* corresponds to the period $p_0/2=250$ nm, Curve *2* to $p/2=700$ nm, and Curve *3* to $L=1500$ nm.

$$+2K_3\sin^2\theta\sin^2\phi)\Big]\sin 2\theta=0,$$

$$\frac{1}{r^2}\frac{d}{dr}\,[r^2(g\phi_r-K_2q_0\sin^2\theta)]=\frac{2f(\beta)\cos\beta}{r^2}$$

$$\Big(-K_1\sin^2\theta\sin 2\phi+\frac{1}{4}K_2\sin^2 2\theta\sin 2\phi$$

$$+K_3\sin^4\theta\sin 2\phi\Big),\quad 0\leqslant r\leqslant R \qquad (7)$$

where the function

$$f(\beta)=-2\cos\beta+\ln\frac{1+\cos\beta}{1-\cos\beta} \qquad (8)$$

results from integration over γ, and R is the radius of the LC sphere. The director field distribution in a spherical volume is determined by Eq. (7) and by the boundary conditions at the LC-polymer boundary which are given by the orientation of LC molecules at the sphere boundary. We consider here a planar orientation when the angle θ between the director and spherical surface is $\pi/2$, as homeotropic (normal) when $\theta(R)=0$, and as tilted one when $0<\theta(R)<\pi/2$.

THE SOLUTION OF THE EQUATION OF STATE

The equation of state (7) for the director field is simplified if we assume that all the elastic moduli K_i are the same (single-constant approximation):

$$\theta_{rr}+\frac{2}{r}\,\theta_r-\frac{1}{2}\,\phi_r^2\sin 2\theta+\left(q_0\phi_r+\frac{1}{r^2}-\frac{f(\beta)}{4r^2\cos\beta}\right)$$

$$\times\sin 2\theta=0,$$

$$\frac{1}{r^2}\frac{d}{dr}\,[r^2\sin^2\theta(\phi_r-q)]=0. \qquad (9)$$

Hence we find at once the solution for the azimuth:

$$\phi_r=C/r^2\sin^2\theta+q_0, \qquad (10)$$

where the integration constant C is zero owing to the free boundary conditions (6). As a result, the equation for the polar angle aquires the following form:

$$\theta_{rr}+\frac{2}{r}\,\theta_r+\left[\frac{q_0^2}{2}+\frac{1}{r^2}\left(1-\frac{f(\beta)}{4\cos\beta}\right)\right]\sin 2\theta=0. \qquad (11)$$

This equation describes the evolution of a heavy pendulum with damping. For this pendulum $\theta=\pi/2$ is the point of unstable equilibrium corresponding to the free-energy minimum. If the initial condition of the pendulum dynamic evolution given by Eq. (11) is such that $\theta(R)<\pi/2$ and the initial velocity $\theta_r(R)$ is not large, the solution for $\theta(r)$ has the character of oscillations of a nonlinear pendulum whose period decreases as the boundary condition deviates from $\pi/2$ and becomes equal to p_0 for small $\theta(R)$ and large r.

If we specify only the initial position of the pendulum, $\theta(R)<\pi/2$, and select the initial velocity $\theta_r(R)$ from the condition that free energy be a minimum, we get a rapid transition into the unstable-equilibrium point with a subsequent stay at this point, which corresponds to the soliton solution of the sine-Gordon equation. This solution is shown in Fig. 3 by a dashed line and was found numerically in Ref. 20. If the initial velocity is lower than that corresponding to the soliton solution, the oscillating solution is realized. The smaller $\theta_r(R)$, the more oscillations we get. The energies of different solutions are related as follows. The ground state is the trivial solution $\theta(r)=\pi/2$

with energy of order RK ($\sim 5 \cdot 10^{-10}$ erg or, in terms of energy per capsule area unit, $RK/4\pi R^2 \approx 10^{-4}$ erg $\cdot$ cm^{-2}). The soliton solution has an energy of order 70 RK, and the oscillating solutions have energies of order 100 RK and higher depending on the number of oscillations. The energy values have been found numerically.

Thus, to solve Eq. (11) it is important to decide whether we must specify the initial value of the derivative $\theta_r(R)$ or find it by determining the free energy minimum. To find the boundary conditions which can be created by pyrimidine impurities on the LC capsule surface, note that pyrimidine molecules have a dipole moment and create a dipole electric field. In the case of an undistorted LC specimen, the macroscopic dipole moment of pyrimidine impurities is absent and the electric action of the pyrimidine on the CLC state is zero. The encapsulated CLC state leads to two effects. The first is adhesion of pyrimidine molecules to the polymer-CLC boundary, due to their high polar activity, and the second is alignment of dipole moments of pyrimidine molecules along the normal to the capsule surface, resulting both from the polar activity of the molecules and the flexoelectric effect.[21,22]

Thus, we can assume that around the CLC capsule there arises a thin spherical layer of a radially distributed dipole density P, whose thickness depends on the pyrimidine concentration. If the latter is 4% and if the pyrimidine molecules are of the same size as the CLC molecules (i.e., of length ~ 20 Å and width ~ 5 Å), we find that the total number of CLC molecules in a capsule of radius $R = 5 \cdot 10^{-4}$ cm is about $2.5 \cdot 10^{12}$ and the number of pyrimidine molecules is about 10^{10}. Assuming next that all the pyrimidine molecules are concentrated in the near-surface layer normally to the surface (which, of course, overestimates the pyrimidine polarizing effect on the encapsulated CLC state), we find a dipole layer thickness $\Delta \approx 200$ Å and a polarization $P \approx 10^3$ in CGS units. This coincides with the values found earlier for the surface polarization in a nematic LC with homeotropic orientation in a CL-semiconductor system in a thin crystalline layer.[23]

The electric field of the dipole distribution $\mathbf{P}(\mathbf{x})$ in a volume V is

$$\mathbf{E}(\mathbf{r}) = \int_V d^3x \left[\frac{3(\mathbf{P}(\mathbf{x})(\mathbf{r}-\mathbf{x}))(\mathbf{r}-\mathbf{x})}{|\mathbf{r}-\mathbf{x}|^5} - \frac{\mathbf{P}(\mathbf{x})}{|\mathbf{r}-\mathbf{x}|^3} \right]. \tag{12}$$

Taking it into account that the spherical layer thickness Δ is small, we can approximate the length of the radius-vector, $|\mathbf{x}|$, by the capsule radius R, except for the case when the vector $\mathbf{r}-\mathbf{x}$ vanishes. The integral in Eq. (12) diverges, since the macroscopic description of electric field at small distances comparable to the dipole layer thickness Δ is not valid. Owing to radial symmetry, the electric field of the dipole spherical layer is directed along the radius and, on the basis of the above considerations, can be written as

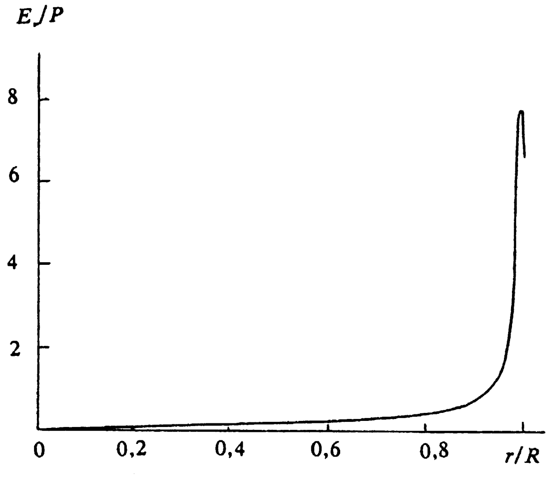

FIG. 4. The radial dependence of the electric field induced by the spherical layer of pyrimidine impurities.

$$E_r(r) = 2\pi\varepsilon P \int_{-1+\varepsilon^2/2}^{1-\varepsilon^2/2} \times \frac{[(3+\cos^2\theta)a - 2(1+a^2)\cos\theta}{(1+a^2-2a\cos\theta)^{5/2}} \, d\cos\theta, \tag{13}$$

where $a = r/R$ and $\varepsilon = \Delta/R$. The integration limits are on θ angle chosen to avoid divergence for $a=1$ and $\theta \to 0$. The continual description is no longer valid at distances of order Δ, whence the natural restriction on the angle θ: $\Delta/R \leqslant \theta \leqslant \pi - \Delta/R$. For the variable $\cos\theta$ we get respectively: $1+\varepsilon^2/2 \leqslant \cos\theta \leqslant 1-\varepsilon^2/2$. It is easily seen from (13) that at $r=R$, i.e., on the spherical layer itself, the integral diverges like $1/\varepsilon$, which is compensated by the pre-integral factor ε. As $r \to R$, we get $E_r \to 2\pi P$. But, as soon as r differs from R by a value of order Δ, the divergence in (13) vanishes and the field drops to $2\pi\varepsilon P$, i.e., the electric field of the dipole layer is significant only in a narrow spherical layer of the order of the dipole spherical layer thickness. Numerical calculations of the integral (13) confirm these estimates (Fig. 4).

The anisotropy energy related to the polarizing electric field of the pyrimidine spherical layer (12) could be estimated from the formula

$$W_s = -\frac{\Delta\epsilon}{4\pi} \int (\mathbf{E}(\mathbf{r})\mathbf{n})^2 d^3r, \tag{14}$$

where $\Delta\epsilon$ is the anisotropy of the CLC dielectric constant. Bearing in mind that the polarizing field exists only near the capsule surface in a layer of thickness Δ, we can approximate the integral (14) as follows:

$$W_s \approx \frac{\pi}{2} \Delta\epsilon P^2 4\pi R^2 \Delta \approx 10 \cdot 4\pi R^2 \text{ erg/cm}^2. \tag{15}$$

In spite of the fact that we have greatly overestimated the anisotropy energy by using a simplified polarizing-layer model, we believe that a realistic estimate, in terms of energy per spherical surface unit, is of order 1 erg · cm^{-2}.

The anisotropy energy (15) is localized near the surface, therefore it may be defined as surface anisotropy energy forming the CLC state at the capsule boundary. We have neglected the surface energy due to the polymer interaction with the LC molecules, since it is of order 10^{-5} to 1 erg · cm^{-2} (Refs. 24–27) and cannot noticeably influence the estimate (15).

Depending on the ratio of the anisotropy energy to characteristic energies of the bulk state of an encapsulated CLC (strictly speaking, to the difference of the energies of different bulk states), we can allow for the surface in three possible ways. If the ratio is significantly in favor of bulk energies, the effect of the polarizing field on the bulk CLC state can be neglected. If the bulk energy is of the order of the anisotropy energy, we need to consider the bulk state of an encapsulated CLC together with the surface energy (14). And, at last, the boundary effects can be allowed for by rigid boundary conditions determined by the anisotropy energy minimum. As noted above, the scale of excess bulk energies related to inhomogeneous solutions reaches, in the most unfavorable case, $5 \cdot 10^{-2}$ erg · cm^{-2}. This estimate is easily found in the following way:

$$\frac{K}{4\pi R^2}\frac{n}{p_0^2}\frac{4\pi L^3}{3},$$

where n is the number of oscillations and L is the radial distance over which the oscillations of the angle θ occur. Substituting $K \approx 10^{-6}$ dyne, $L \approx R/2$, $n=5$, $R \approx 5 \cdot 10^{-4}$ cm, and the oscillation period $p_0 \approx 5 \cdot 10^{-5}$ cm into the formula, we get a bulk energy equal to $3 \cdot 10^{-2}$ erg · cm^{-2}, which agrees, in order of magnitude, with the numerical calculations. Thus, the role of pyrimidine reduces to rigid boundary conditions for the polar angle: $\theta(R)=0$.

Furthermore, the above consideration shows that the polarizing field of the spherical boundary layer, though it decreases rapidly, is still significant at the depth of order $\Delta \approx 200$ Å, and, in this sense, the boundary conditions for the angle θ are nonlocal. This has been noted in Refs. 24 and 25. In order not to obscure the results, we use in the present study a crude approximation, to allow for the surface effects, in the form of boundary conditions for the angle $\theta(R)$ and its derivative $\theta_r(R)$.[24,26,27]

It is easily seen from Fig. 4 that the polarizing field tends to keep the value of θ equal to zero. This means that the initial value of the derivative θ_r will be effectively reduced in comparison with what is needed for the soliton solution, and the oscillating regime of the "heavy-pendulum" evolution will thus be realized. Numerical investigations of Eq. (11) show that only the reduction of the initial value of the derivative in comparison with the soliton solution matters, while the value itself does not affect the character of the oscillating solution and, as noted above, changes only the number of oscillations.

Thus, at large r the solution of Eq. (11) oscillates with the period p_0. When the radius decreases, the oscillations become damped with diminishing amplitude. On the other hand, as seen from Eq. (11), the pendulum length becomes smaller even faster, which leads to an increasing oscillation amplitude. Which of two tendencies is dominating can be found only from the numerical solution shown in Fig. 3a. It is seen that the second tendency prevails, leading to divergent oscillations which, at a certain intermediate value of the radius $r<R$ become stationary with $\theta=\pi/2$. Moreover, we have numerically found a critical capsule radius R_c such that if the capsule is smaller than R_c an oscillatory angle θ becomes impossible for any initial velocity whatsoever. For $p_0=0.5$ μm we have $R_c \approx 1$ μm.

We have also considered numerically a plane-parallel CLC plate with pyrimidine. It has turned out that we have either a purely oscillating regime throughout the plate thickness or a homogeneous solution $\theta(r)=\pi/2$.

It is possible to find analytically the second limiting asymptote as $r \to 0$. Since the ground state of the field $\theta(r)$, according to (4), is $\pi/2$, we seek the asymptotic solution near $r=0$ in the form $\theta(r)=\pi/2-cr^{\mu}$. Substituting this into (11), we find for small r the following equation for μ:

$$\mu(\mu-1)+2\mu-2+\frac{f(\beta)}{\cos\beta}=0,$$

whence

$$\mu=-\frac{1}{2}+\left(\frac{1}{4}+2-\frac{f(\beta)}{\cos\beta}\right)^{1/2}$$

In particular, in the equatorial plane, where $f(\beta)/\cos\beta=0$, we have $\mu=1$. Thus, as the radius grows, the polar angle slowly decreases from $\pi/2$. Joining these two asymptotes, we find the qualitative behavior of $\theta(r)$ which coincides with the results of the numerical solution of Eq. (11) for the normal boundary condition $\theta(R)=0$ shown in Fig. 3.

Summing up the single-constant approximation, we note that even in this approximation the solution for the director field in a spherical capsule has two characteristic structure periods: one, in the azimuth, in the form of a simple helix with a pitch $p_0=2\pi/q_0$ and the other, in the polar angle, with a period coinciding with the pitch of the helix in the limit of large r and small oscillation amplitude. Note that we have also carried out numerical calculations for different β up to $\beta=1°$. The form of the solutions remained practically unchanged.

Consider now the case of different elastic constants. Restricting ourselves for simplicity to the vicinity of the capsule equatorial plane, we find from (7)

$$f\theta_{rr}+\frac{1}{2}\frac{\partial f}{\partial\theta}\theta_r^2+2\frac{f}{r}\theta_r-\frac{1}{2}\frac{\partial g}{\partial\theta}\phi_r^2+\left(K_2q_0\phi_r+\frac{K_1}{r^2}\right)$$

$$\times\sin 2\theta=0,$$

$$\frac{d}{dr}\left[r^2(g\phi_r-K_2q_0\sin^2\theta)\right]=0. \qquad (16)$$

It is easily seen from the boundary conditions (6) that, as in the single-constant approximation, the solution for the azimuth has the form

$$\phi_r = \frac{K_2 q_0}{K_2 \sin^2\theta + K_3 \cos^2\theta}. \tag{17}$$

It is seen that the case of different elastic constants leads to a new effect, namely to the modulation of the helix pitch in the angle ϕ by the oscillations of the polar angle θ. The bigger the difference between the constants K_2 and K_3, the larger the effect.

Substituting (17) into (16), we find the equation for θ:

$$\theta_{rr} + \frac{(1-K_3/K_1)\sin 2\theta\theta_r^2}{2\alpha} + \frac{2}{r}\theta_r + \frac{1}{\alpha} \times \left(\frac{1}{r^2} + \frac{K_3 q_0^2}{2K_1\zeta^2}\right)\sin 2\theta = 0, \tag{18}$$

where

$$\alpha = \sin^2\theta + \frac{K_3}{K_1}\cos^2\theta, \quad \zeta = \sin^2\theta + \frac{K_3}{K_2}\cos^2\theta.$$

Considering again an asymptote with large radius and small oscillations of the angle θ, we find the period of the structure in the polar angle:

$$L = (K_3/K_2) p_0. \tag{19}$$

Thus, we find one more effect outside the limits of the single-constant approximation: the period of the structure in the angle θ and the pitch in the azimuth do not coincide even in the limit of a large radius and small oscillations; this is confirmed by numerical solutions of Eq. (18) shown in Fig. 3b. The radial dependence of ϕ_r has two distinguishing features. The first is that owing to the relation (17) between the polar angle and ϕ_r the oscillations of θ bring about weak oscillations of ϕ_r with another period. However, as seen from Fig. 3b, these oscillations are weak and, probably, difficult to resolve experimentally. The second feature, much more striking, is the jump of ϕ_r at the point r_0, where the radial dependence of the polar angle changes from oscillating to stationary. Thus, the case of different elastic constants results in that the external part of the capsule with $r > r_0$ has a new helix pitch p, while the internal part with $r < r_0$ has the basic pitch p_0, p being larger than p_0. In Fig. 5 we show the results of numerical calculations of the superstructure period $2L$ and the pitch of the second helix p versus p_0. It is easily seen that for the elastic constants in the caption of Fig. 3 the relation (19) is qualitatively satisfied.

Thus, a cholesteric in a spherical volume, for a homeotropic rigid orientation of molecules at the polymer boundary, can be in an inhomogeneous state with several basic structure periods which can be found experimentally by, e.g., selective light reflection. The analysis above shows that even in the single-constant approximation the CLC structure in a spherical capsule has two basic periods, one of which is the pitch of the helix realized also in the case of an infinite specimen, while the other is realized in the spherical capsule provided that the LC molecules near the spherical surface are tilted or normal to the surface.

In the case of different elastic constants, which is in fact the only real case, we get an entirely new CLC structure which differs from the previous one in that the azimuth state of the director field turns out to a cohesion of two helices with different periods. Note that all the structures described above have higher energy than the trivial helical CLC structure with $\phi_r = q_0$ and $\theta = \pi/2$, and can be effected only by boundary conditions imposed by pyrimidine on the capsule surface for $\theta(R)$ and $\theta_r(R)$. As discussed above, these boundary conditions are created by pyrimidine near the surface of the CLC capsule.

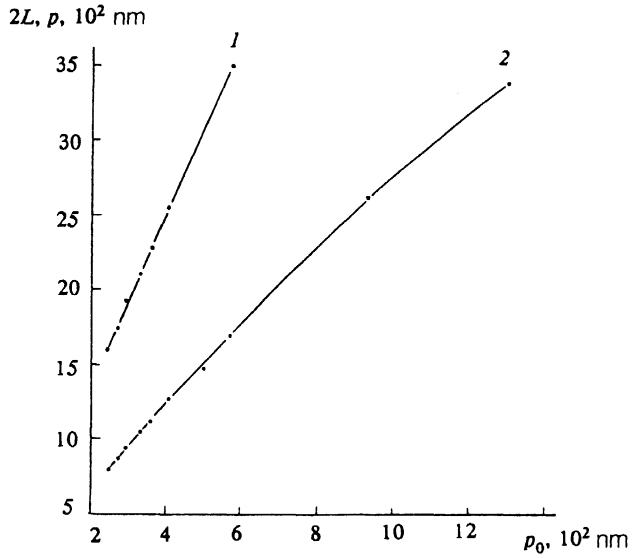

FIG. 5. The period L of the CLC superstructure in a capsule in the polar angle (curve 1) and the pitch p of the second helix (curve 2) versus the pitch p_0 of the basic helix.

For the elastic constants $K_1 = 5.3 \cdot 10^{-7}$ dyne, $K_2 = 2.2 \cdot 10^{-7}$ dyne, and $K_3 = 7.4 \cdot 10^{-7}$ dyne, which are very close to those of real encapsulated CLC,[20] the relation (19) gives a polar-angle period L equal to $3.4p_0$, a ratio of the helix pitches p/p_0 approximately equal to 3, as seen from Fig. 3. Figure 1 shows the experimental temperature dependence of the wavelength of selective light reflection in an encapsulated CLC doped by pyrimidine impurities. It is seen that at the temperature which is the end of the first temperature range of light reflection and the beginning of the second the wavelength ratio is about three, which coincides with the found ratio of the helix pitches. However we should use these ratios with caution, since the elastic moduli themselves depend both on the temperature and on the pyrimidine concentration. Moreover, we have not allowed for the effects connected with the variation of the order parameter and of the density in the capsule volume. As seen from Fig. 1, the second scale L which is due to the inhomogeneity of the polar angle has not been observed, since it lies outside the visible range.

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