Surface physics of thermotropic liquid crystals

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Phenomena occurring at the interface of liquid crystals with other (solid, liquid, and gaseous) phases are reviewed. The basic parameters of the macroscopic surface physics of thermotropic liquid crystals are studied: the adhesion energy, the surface order parameter, and the surface polarization; the basic methods for determining them experimentally are described. A great deal of attention is devoted to methods for obtaining a uniform orientation of liquid crystals. The role of the surface in phase transitions is analyzed in detail. The effect of the interface on the formation and structure of defects in liquid crystals is described. The role of van der Waals forces in the orientation of liquid crystals and in local Fredericks transitions is analyzed.

CONTENTS

1. INTRODUCTION

The interaction of an isotropic liquid with adjacent phases (solid, gas, another liquid) is an extremely interesting physical problem, since the surface layers of the liquid are distinguished by their structure and properties from the bulk.[1-3] Surface forces are even stronger in liquid crystals than in isotropic liquids, since owing to the ordered molecular structure of the mesophase the effect of the interface can be transferred into the bulk over comparatively large distances and can determine its thermodynamic properties.

Liquid crystals are intermediate states (mesophases) between an isotropic liquid and solid crystals. Their characteristic feature is the presence of long-range orientational order, i.e., ordering of the long (and sometimes also short) molecular axes. At the same time liquid crystals do not have a three-dimensional crystalline lattice, i.e., long-range positional order either occurs along one or two directions or does not occur at all.

There are a number of reviews[4-8] and monographs[9,10] devoted to different aspects of the physics of liquid crystals.

Among all the liquid-crystalline phases, the phase which is most sensitive to external disturbances (including also the action of surface forces) is the nematic phase, in which only one type of long-range order occurs—order in the orientation of the long molecular axes (Fig. 1a). Most studies of the surface properties of mesophases have been performed precisely on nematic liquid crystals (NLC). The other most common liquid-crystalline phases are the cholesteric (a nematic substance twisted in a spiral fashion on a macroscopic scale) and smectic A and C phases, shown in Fig. 1. The smectic substances A and C have one-dimensional (along the z axis) positional order, and these structures are distinguished by the fact that in the C phase the molecules have a matched tilting.

To carry out studies and for different practical applications liquid crystals are usually placed in flat capillaries,[10] whose solid walls orient the molecules of the mesophase. The solid wall thus has a double effect. On the one hand it alters the structure and properties of the adjacent layer of liquid crystal. This is an example, quite rare in physics, of the high sensitivity of a medium to relatively weak surface actions. On the other hand, the solid surface imposes boundary conditions for the entire bulk sample and thereby determines to a large extent the behavior of the liquid crystal in external fields of the most diverse nature. In particular, the conditions on the surface affect the threshold fields and the fast-response of liquid-crystalline materials, operating in the most diverse electrooptical display and information processing systems.[12-16] For these applications, optical uniformity of the liquid-crystalline layers, which depends entirely on the conditions at the surface, is also extremely important.[17] The question of the role of electric charge in determining the
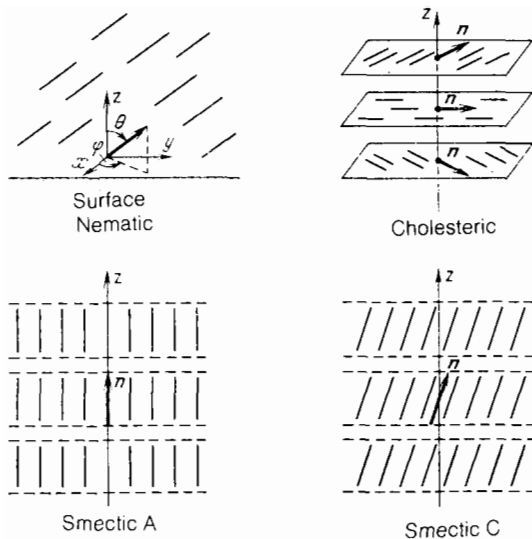
FIG. 1. The most common liquid-crystalline phases (the dark arrows indicate the vector **n**).

structure and properties of the liquid-crystal boundary layer is also very interesting.

There is also another reason for studying the surface properties of liquid crystals. It is obvious that surface effects will be all the stronger the smaller is the system. The concept of small size depends on the specific phenomena and type of system under study. Liquid crystals consist of quite large molecules and are, as a rule, very soft systems (i.e., the energies responsible for the liquid-crystalline order are usually comparatively low). Therefore a film size of the order of, for example, 5000 Å may be regarded as small for liquid crystals. For film thicknesses of this magnitude all size effects associated with surface contributions to the free energy are appreciable, while, for example, for helium or simple metals such films are practically indistinguishable from massive bulk samples. All physical phenomena in films are very important and interesting, first, because of applications, not only in microelectronics, but also in physical chemistry, etc., and, second, for studying the fundamental aspects of the physics of the two-dimensional world. Here liquid crystals are especially promising, since freely suspended films with a thickness ranging from one to several molecular layers can be prepared by fairly simple methods.[18] Such films are actually a new object in physics, since they are truly two-dimensional systems, exhibiting in a number of cases some degrees of freedom in three-dimensional space.[19]

Up to now no reviews devoted to the physics of surface phenomena in liquid crystals have been published. The reviews published[11,12,17] deal primarily with the technology for preparing oriented layers of nematics and with some questions regarding the physical chemistry of surfaces. Because of this we made an attempt to generalize, from a unified viewpoint, a large number of experimental and theoretical results, concerning the interface between a liquid crystal and other phases.

We shall start with a discussion of the general question of taking into account the contribution of the surface energy to the total free energy of a liquid crystal, and we shall study the effect of surface forces on the thermodynamics and

structure of the surface layer. We shall then discuss the role of the surface in the formation of macroscopic structure defects, after which we shall discuss the important question of the effect of long-range van der Waals forces on the orientation of the director in the volume of the sample. In concluding the review we shall list some unsolved problems, which are now on the agenda in the study of the effects of the interaction of liquid crystals with bounding surfaces.

2. SURFACE FORCES AND SURFACE ENERGY

2.1. General concepts and basic parameters

Owing to the existence of orientational ordering of molecules it is convenient to describe all liquid-crystalline phases with the help of a unit vector **n**—the director. In nematic and smectic liquid crystals the director characterizes the mean orientation of the molecular axes in a macroscopic, but small compared with the dimensions of the sample, volume. The position of the director can be fixed by two polar angles θ and φ (see Fig. 1). In cholesterics the director is determined for a macroscopic region which is small compared with the pitch of the spiral. Let the boundary of the NLC (for definiteness we assume that the nematic is in contact with a solid substrate) lie in the x, y plane and the angle between the director and the normal to the surface be

$$\theta_0 = \theta \mid_{z=0}.$$

It is then possible to distinguish three types of surface orientation of NLC: homeotropic ($\theta_0 = 0$), planar ($\theta_0 = \pi/2$), and tilted, or conical ($0 < \theta_0 < \pi/2$). The planar orientation in its turn can be homogeneous, when all molecules are oriented in the plane of the substrate in the same direction, and heterogeneous, when there exist several directions of orientation of the director in the plane. The same thing also applies to the projection of the director with tilted orientation.

The orientation of the director of a liquid crystal on the surface or, as it is customarily said, the direction of easy orientation of the director is usually fixed with the help of an appropriate treatment of the bounding solid surfaces. On the free surface of a liquid crystal, however, the direction of easy orientation arises spontaneously depending on the properties of the interface. Along the direction of easy orientation the free surface energy $F_0(\theta, \varphi)$, which, generally speaking, depends on the angles θ and φ, is minimum. The existence of anisotropy of the free surface energy F_0, associated with the
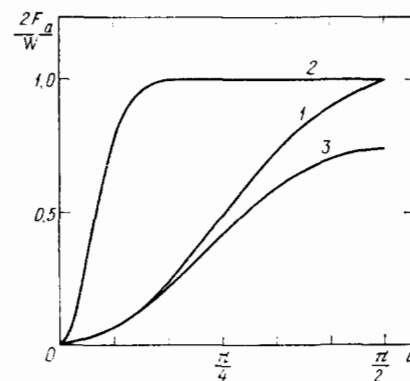

FIG. 2. Examples of the surface potential: 1) Rapini's potential,[20] 2) potential in the form of an elliptic sine ($k = 1-10^{-7}$),[22] 3) potential in the form $W_1 \sin^2 \theta + W_2 \sin^4 \theta$, $W_2 \approx -W_1/4$ ($W_1 = W/2$).[25]

tilting of the director along θ and φ from the direction of easy orientation, is a characteristic precisely of the liquid-crystalline state. In an isotropic liquid only the isotropic component F_{0_i} exists.

The question of the specific form of the anisotropic component of the function $F_0(\theta, \varphi)$ is one of the key questions in the physics of the surfaces of liquid crystals. The simplest form was proposed by Rapini[20] (curve 1 in Fig. 2):

$$F_0 = F_{0i} + F_{0a} = F_{0i} + \frac{1}{2} W \sin^2 \alpha, \tag{1}$$

where $\alpha = \theta$ or φ, while W is called the adhesion energy.

In order of magnitude the experimental values of W range from 10^{-5} erg/cm^2 up to 1 erg/cm^2. These low values of the adhesion energy for liquid crystals are very puzzling. Indeed, for a liquid crystal, as for any condensed medium, there is a natural estimate of the surface energy given by

$$F_{0i} \sim \rho c^2 a, \tag{2}$$

where ρ is the density, c is the velocity of sound, and a is the molecular size. Actually $\rho c^2 a$ is the only quantity with the dimensions erg/cm^2. Setting $\rho \sim 1$ g/cm^3, $c \sim 10^5$ cm/s, and $a \sim 10^{-8}$–10^{-7} cm, we obtain $F_{0i} \sim 10^2$ erg/cm^2. The experimentally determined isotropic part of the surface tension in liquid crystals (and, by the way, in any other organic liquids) is in fact of this order of magnitude. The adhesion energy W is the anisotropic part of the surface tension. Practically all bulk properties of liquid crystals have an anisotropic part which is of the order of 0.1 (or even larger) of the isotropic part. The anisotropic surface energy W, however, is several orders of magnitude lower than the isotropic surface tension. This fact most likely indicates that there exists a special surface layer (probably, with a large number of defects). To solve this problem further experiments are very desirable.

To study any specific effects in bounded samples of liquid crystals one must solve a problem with boundary conditions which take into account the contribution of the surface energy. The solution of this problem is constructed by the standard methods of variational calculus and does not present any special difficulties. Such an analysis is especially simple in the case when the surface energy depends only on the orientation of the director at the boundary (on the angles θ and φ).

We shall study a layer of nematic of thickness d lying between two flat surfaces $z = -d/2$ and $z = +d/2$. We shall assume for simplicity (the generalization to the three-dimensional case is trivial) that the director can vary only in the x, z plane, where the x axis is parallel to the planes bounding the liquid crystal. We shall assume that the ordering along the x axis is uniform, and therefore the director $\mathbf{n}$ (or the angle θ between the director and the z axis) depends only on z. The total free energy of the system per unit area can be written in the following form:

$$F(\theta) = \int_{-d/2}^{+d/2} f(\theta, \theta_{1z}) \, dz + F_{01} + F_{02}, \tag{3}$$

where f is the volume density of the free energy, F_{01}, and F_{02} are the surface energies on both boundaries, and $\theta_{1z} = \partial\theta/\partial z$.

The equilibrium orientation of the director is deter-

mined by minimizing the functional (3), i.e., by solving the Euler-Lagrange equation:

$$\frac{\partial f}{\partial \theta} - \frac{d}{dz} \left(\frac{\partial f}{\partial \theta_{1z}} \right) = 0 \tag{4}$$

with the boundary conditions

$$-\left(\frac{\partial f}{\partial \theta_{1z}} \right)_1 + \frac{\partial F_{01}}{\partial \theta_1} = 0,$$

$$\left(\frac{\partial f}{\partial \theta_{1z}} \right)_2 + \frac{\partial F_{02}}{\partial \theta_2} = 0; \tag{5}$$

here the indices 1 and 2 refer to the angles of orientation and the surface energies at both boundaries. We note that the first term in Eqs. (5) corresponds to the bulk contribution to the surface energy. We call attention to the fact that in (4) and (5) we did not employ the specific form (1) for the surface energy. It is important only that it depend only on the angle θ (and is independent of the derivative of the angle).

Of course, to solve this system of equations one must know the explicit angular dependence of the functions F_{01} and F_{02}. The simplest form of (1), proposed by Rapini, can be employed only for obtaining quite rough estimates. Modern data[21-27] indicate that F_0 is a function with a quite sharp minimum near the direction of easy orientation and relatively wide "plateau" for other orientations. Such a function can be approximated,[22] for example, by an elliptic sine (curve 2 in Fig. 2):

$$F_0 = F_{0i} + \frac{1}{2} W \, \mathrm{sn}^2(\alpha, \, k), \tag{6}$$

where $0 \leqslant k \leqslant 1$ is the modulus of the elliptic function (actually an additional adjustable parameter).

In some cases[23,24,26] F_0 is expanded in a series in even Legendre polynomials with the argument $\cos \alpha$ (or $\sin \alpha$) (curve 3 in Fig. 2):

$$F_0 = F_{0i} + \sum_j W_j \cos^{2j} \alpha, \tag{7}$$

where W_j are the expansion coefficients. The term W_1, for example, corresponds to the Rapini potential.

In any case, for some form of $F_0(\alpha)$ the problem of orientation in a layer of finite thickness is correctly posed on a macroscopic level and reduces to the solution of Eq. (4) with the boundary conditions (5).

The situation changes radically if the dependence of the surface energy on the derivative of the angle is also important: $F_0 = F_0(\theta, \theta_{1z})$. This dependence is described by the so-called moduli of elasticity of the second order,[27,28] introduced by Saupe and Nehring. In this case the orientation is analyzed in a manner analogous to the preceding case (see, for example, Refs. 29 and 30), but a number of difficulties of a fundamental physical character appear. For example, the boundary conditions are nonlocal, in the sense that the condition for the surface with the coordinate $z = -d/2$ contains a contribution from the surface $z = +d/2$ (of course as $d \to \infty$ or for infinite adhesion at one surface this nonlocality vanishes).

In addition, when the surface energy depends on the derivatives of the orientation a sharp distortion occurs in the configuration of the director in the near-surface layer whose thickness depends on the range of the interaction forces. Such terms can therefore be introduced correctly only on the basis of a microscopic theory.

The question of the role of the second-order coefficients

of elasticity at present has not been solved, either theoretically or experimentally, since reliable methods for measuring them do not exist, and the microscopic problem of their derivation has not been solved rigorously.

2.2. Experimental results on determination of adhesion energy

There exist tens of studies in which the magnitude of the adhesion energy W was measured by some method. The calculation of the value of W on the basis of the dependence of the threshold field for Fredericks transitions on the thickness of the liquid-crystalline layer may be regarded as the classical method.[10] Here the question is one of the threshold effect of the reorientation of the liquid crystal under the action of a magnetic or electric field applied perpendicularly to the initial direction of the director (Fig. 3a). In the case of infinitely high adhesion energy the angle θ_0 at the boundary of the liquid crystal with the wall does not change as the critical value H_c of the magnetic field is exceeded, although the deformation in the bulk of the sample has already begun (curve 1 in Fig. 3b). For a finite adhesion energy the deformation of the director in the bulk owing to elastic forces will force the director to tilt near the walls also (for $z = \pm d/2$). The curve $\theta(z)$ can then be continued beyond the wall, while the extrapolated length $b = K/W$ will serve as a measure of the adhesion energy. The quantity b can be determined both from the critical (threshold) magnetic field strength[12]

$$H_c = \frac{\pi}{d+2b} \left(\frac{K}{\chi_a} \right)^{1/2},
\tag{8}$$

where χ_a is the magnetic anisotropy of the NLC and K is the Frank modulus of elasticity, and under above-threshold conditions from the calculation of the profile $\theta(z)$ from measurements of the phase delay of monochromatic light passing through the sample.

In different experiments the geometry of the experiment (planar, homeotropic orientation by means of different factors), the type of field (electric or magnetic[31,32]), and the technique used for the optical measurements (phase delay,[3] total internal reflection, excitation of surface plasmons,[34-37] etc.) were varied. Aside from the Fredericks transition the flexoelectric effect has also been investigated.[38,39]

Without discussing in detail these numerous investigations, we mention only that, as a rule, the values of W for homeotropically oriented samples lie in the range 10^{-5}–10^{-2} erg/cm^2, though the most probable values lie in the range 10^{-3}–10^{-2} erg/cm^2. The adhesion energies of NLC oriented in a planar manner are significantly higher and fall

in the range 10^{-2}–1 erg/cm^2 and even higher. We must point out that the spread in the experimental values of W, obtained for physically identical surfaces by different methods, is quite large. This especially concerns measurements of W from the threshold of Fredericks transition in an electric field. Thus measurements on thin layers of NLC in a geometry such that the field is applied across the layer gives values of W which are much too high. It is possible that the effects of surface polarization (especially ionic; see Sec. 2.3) play a serious role in these experiments, stabilizing in some manner the starting orientation.

As an example, Fig. 4 shows the temperature dependence of W for a homeotropically oriented layer of a classical NLC MBBA, measured by comparing very carefully the threshold magnetic field for the Fredericks effect in thick and thin cells.[40] This curve is interesting in two respects. First, this is the only case of a reliable measurement of the temperature dependence $W(T)$, and here one sees clearly how the anisotropic part of the surface energy approaches zero as the temperature of the transition of the NLC into the isotropic liquid is approached. Second, the scale of the variations of W (10^{-2}–10^{-1} erg/cm^2), exceeding by one to two orders of magnitude the typical values obtained using thicker cells, is significant, and indicates the possible role of some specific surface effects.

There have appeared recently studies in which an attempt was made to determine the dependence of the energy $W(\theta)$ in a wide range of values of the tilt angles of the director from the direction of easy orientation. For this the optical properties of the NLC samples were studied under conditions of strong deformation of the director in the bulk of the sample. This was achieved either by selecting different boundary conditions on two different surfaces[23] or by imposing on the sample a strong magnetic[26] or electric[25] field, substantially exceeding the threshold for the Fredericks transition. In the latter case a second critical field can be reached when the director is oriented along the field in the entire sample, including the surface layer. An example of an experimentally determined dependence $W(\theta)$ is presented in Fig. 5. This curve can be described theoretically by a polynomial of the form $F_{0a} = W_1 \sin^2 \theta + W_2 \sin^4 \theta$ with
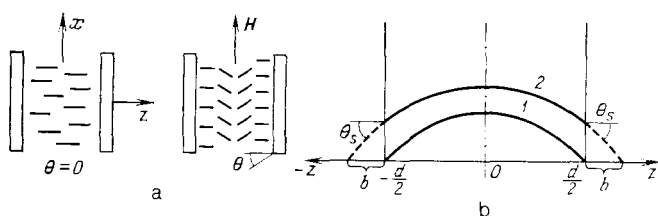

FIG. 3. Geometry of the Fredericks transition (a) and the coordinate dependence of the tilt angle of the director for $H < H_c$ (b). Curves 1 and 2 correspond to infinite ($W = \infty$, $b = 0$) and finite adhesion energies.
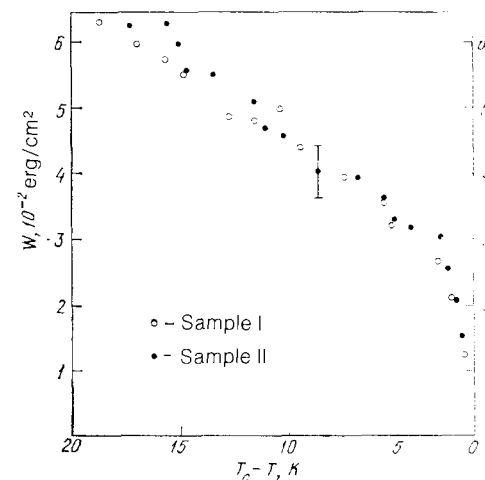

FIG. 4. The adhesion energy of a homeotropic NLC layer versus the temperature.[40] T_c is the temperature of the N-I phase transition.
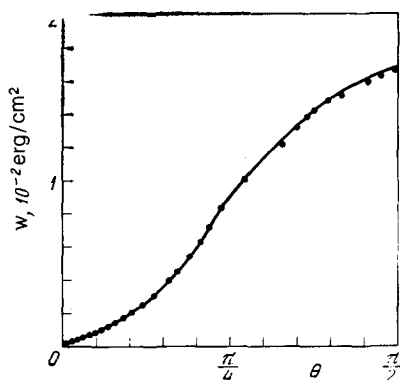
FIG. 5. Experimental dependence of the adhesion energy W on the tilt angle of the director θ near the surface.[25]

$W_2 \approx - W_1/4$. A similar dependence $W(\theta)$ (with a negative correction owing to the higher than quadratic power of $\sin \theta$) was obtained in Refs. 23 and 26. On the whole the experiment shows that the function $W(\theta)$ can be described by an expansion in even powers of $\sin \theta$. However, curves in the form of elliptic sines with different values of k also give the same possibilities for making comparisons with experiment (see Fig. 2).[22]

2.3. Surface polarization

The structure of a thin layer of liquid crystal adjacent to a solid bounding surface can differ appreciably from the structure of the matter in the bulk. In particular, near a surface there can arise a polar layer, carrying an uncompensated total moment per unit volume P with the dimensions charge (CGS)/cm². The existence of a polarized layer makes a contribution $P \cdot E$ to the free energy of a liquid crystal in a field E.

There are two fundamentally different reasons for the appearance of a polarized layer. One is ionic polarization and the other is dipolar polarization. The mechanism of ionic polarization is well known in the theory of electrolytes. A monolayer of ions with the same sign, for example, positive, can be adsorbed on a solid surface (Fig. 6a). This is the so-called Helmholtz layer. A diffusion layer of negative ions (Debye layer) lies adjacent to this dense layer from the side
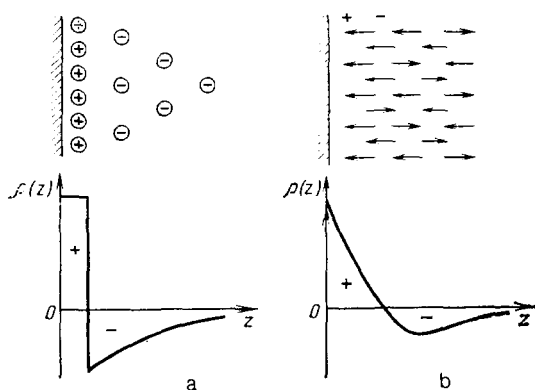
of the bulk, so that on the average the medium in the sample is neutral. A nonuniform distribution of the charge density $\rho(z)$ along the normal to the surface indicates the existence of a surface-polarized layer,

$$P(z) = \frac{1}{2} \int\limits_{-d/2}^{+d/2} z\rho(z) \, dz.$$

This mechanism is not specific to liquid crystals. It also occurs in an isotropic liquid. In a liquid crystal, however, the electric field of the surface layer can in principle cause deformation of the distribution of the director,[41] which, in its turn, is reflected in the distribution $\rho(z)$, since the liquid crystal is electrically anisotropic.

The existence of an ionic polarized layer in nematics was established experimentally from the observation of the electrokinetic effect, i.e., the appearance of a potential difference accompanying the flow of a liquid crystal along a solid surface.[42,43] The effect is formed by the drift of a diffuse layer relative to a dense layer. In the case of a homeotropically oriented NLC the magnitude and sign of the signal are extremely senstive to small ($\sim 10^{-9}$) relative amounts of impurity in the liquid crystal.

The other mechanism of surface polarization is determined by the polar character of the interaction of the molecular dipoles of the liquid crystal with the solid surface (Fig. 6b). It is believed that molecules, which have, for example, a longitudinal dipole moment μ, form under conditions of homeotropic orientation of the liquid crystal a surface monolayer with the macroscopic polarization $P = \mu n$, where n is the surface density of the dipoles. This model was first proposed in Ref. 44. The polar layer can extend into the bulk of the liquid crystal to a distance determined by the diffusion of the molecules of the liquid crystal, $l = (2D_\parallel \tau_\perp)^{1/2}$, where $D_\parallel$ is the coefficient of diffusion in the direction of the director and $\tau_\perp$ is the relaxation time of the molecules for their rotation around the short axes.[45] This depth equals several molecular lengths, while P is of the order of $\sim 10^{-3}$ charges (CGS)/cm².

The existence of a dipole-polarized layer is manifested, for example, in experiments on the electroreflection of light from the boundary of a semiconductor with a liquid crystal,[46] as well as the generation of a second harmonic in the near-surface layer of liquid crystals.[47] It should be noted, however, that it is quite difficult to separate the contributions of the ionic and dipolar components to the surface polarization.

A polar layer can also appear on the free surface of a liquid crystal. Owing to the flexoelectric effect[10] the electric polarization in the surface region should give rise to a transverse bending deformation in the distribution of the director. In the nematic phase this does not lead to any peculiarities. On the other hand, in the case of the layered structure of a smectic C phase this deformation leads to the appearance of defects—disclination lines, perpendicular to the boundary of a drop of liquid crystal. Such disclinations have been observed experimentally.[48] The surface polarization must also have an appreciable effect on the flexoelectric effect in nematics.[49]

For ferroelectric liquid crystals, which exhibit a bulk spontaneous polarization P_s, the mechanism of polar interaction of P_s with the wall is also possible. This causes the

FIG. 6. Ionic (a) and dipolar (b) mechanisms for the appearance of surface polarization.

vector $\mathbf{P}_s$ to be oriented perpendicular to the wall. Since $\mathbf{P}_s$ is oppositely oriented at the top and bottom boundaries of the layer, the director of the smectic C phase, being related with $\mathbf{P}_s$,[6] is oriented differently near these two surfaces, and a deformed structure appears in the bulk of the layer. The behavior of this structure in an external field is of practical interest.[51]

2.4. Orientation methods

We shall not describe in detail the numerous methods for preparing a uniform orientation of liquid crystals (see, for example, Ref. 17); instead, we shall examine for specific examples the basic principles on which they are based.

All methods of orientation can be roughly separated into two large groups: methods for mechanical working of the substrates and methods for depositing surfactants on the substrate. Combined methods also exist.[17]

The most common method for preparing a uniform planar orientation of the director of an NLC is mechanical grinding of glass substrates in one direction.[52-56] In so doing the surface layer of the glass becomes deformed[55] and there forms a very shallow (tens of angstroms) periodic relief, which to a first approximation can be regarded as sinusoidal,[9,52] and the direction of easy orientation of the molecules of the NLC in the plane of the substrate is identical to the direction of grinding. When the molecules of the nematic become aligned along the indicated direction, no distortions of the director field are formed (Fig.7a). If the director is oriented perpendicularly to the direction of easy orientation ($\alpha = \pi/2$), then surface distortions (Fig. 7b) penetrating into the volume of the NLC to a depth of the order of the period of the sinusoidal relief of the substrate $T \sim 10^{-4}$ cm are observed.[9]

A surface relief of different geometric form can be fixed by the photolithographic method.[57-59] When the NLC is in contact with a rectangular surface relief or a relief in the form of a trapezoid a planar orientation is obtained—the molecules become distributed along the grooves. At the same time the adhesion energy increases as the period decreases and the depth of the relief increases.[57] When nematics are in contact with substrates which have a saw-tooth relief, for angles β between the teeth less than some critical value β_c a homeotropic orientation in formed in the volume of the NLC, and for $\beta > \beta_c$ a planar orientation is formed.[58]

Among the mechanical methods of orientation we can also include the oblique deposition of thin films of different oxides (SiO, GeO, etc.) on the substrate.[60] In this case oblique steps of the deposited material, which fix a planar or conical orientation of the director, are formed on the substrate.[17]

Homeotropic orientation is most often achieved by depositing on the substrate different surfactants, which can orient the NLC, either by forming chemical bonds with the molecules of the crystal or by means of the steric effects of the intermolecular interaction.[17] The typical surfactant is lecithin, which orients the molecules of nematics with its long hydrocarbon tails.[61-64] The quality of the homeotropic orientation depends on the packing density and the length of the lecithin molecules.[62,63] For low densities, when the distance between the centers of gravity of the tails of the lecithin molecules (r) is much larger than the dimensions of the NLC molecules (a), free penetration of the molecules of the nematic between the tails can occur, and at the same time a homeotropic orientation forms; for $a \sim r$ penetration is hindered and a weakly ordered surface layer of NLC is obtained.

The orientation of NLC, in contact with substrates treated with lecithin, also depends substantially on the temperature. Thus for some critical temperature T^* a second-order orientational transition occurs from the homeotropic orientation ($T > T^*$) into the tilted orientation ($T < T^*$); in addition, T^* depends strongly on the packing density of the tails of the molecules in the lecithin layer. This orientational transition is obviously linked with phase transitions within the lecithin layer itself.[64,65]

With the help of substrates on which inorganic substances are deposited obliquely and by adding lecithin to the nematic it is possible to obtain layers of NLC with a bending deformation, in which the angle θ changes from $\theta_{01} \sim 0$ near the first substrate to $\theta_{02} = -\theta_{01}$ near the second substrate.[66,67]

Langmuir films, which are molecular multilayers removed from the surface of water onto a solid substrate, give good possibilities for obtaining uniformly oriented samples of NLC.[68-70] They are prepared using so-called amphiphilic substances, whose molecules have a polar head and a long hydrocarbon tail. Three types of Langmuir films are distinguished, depending on the arrangement of molecules in the individual monolayers: polar X and Z (with polarization $P \sim 10^2$ CGSE/cm^2 [71]) and nonpolar Y, in which the dipole moments of the monolayers are oriented opposite to one another and therefore compensate one another.[71] The polar Langmuir films, as a rule, give a stable homeotropic orientation of the NLC with a positive dielectric anisotropy ($\varepsilon_a > 0$) and, conversely, an unstable orientation for nematics with $\varepsilon_a < 0$, which is explained by the effect of the surface electric field of the Langmuir film on the NLC. Nonpolar Y films, analogously to lecithin, orient a nematic homeotropically.[72]

A special type of planar orientation of NLC is obtained on chips of solid crystals with a definite symmetry, on which
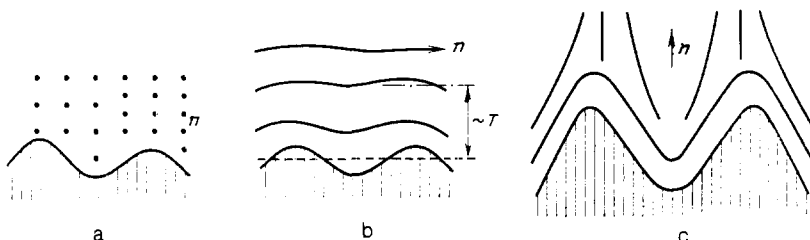

FIG. 7. Surface NLC layers near the relief of a ground glass substrate.[17] a, b) Planar orientation; c) homeotropic orientation.

there are available several directions of easy orientation, associated with the symmetry elements of the chip[73-76]; at the same time the behavior of the NLC on chips of crystals exhibiting electric polarization is of greatest interest.[77-79] Thus the orientation of a nematic on the surface of a triglycine sulfate, which contains 180° domains with oppositely oriented polarization, depends on the sign of its dielectric anisotropy ε_a and is different for positive and negative domains. For example, for NLC with $\varepsilon_a < 0$ positive domains orient the director homeotropically, while negative domains orient it in a planar fashion, and in this manner the domain pattern of the chip can be visualized. This effect could be linked with the different character of the adsorption of water monolayers on domains of different sign.[7] Of course, a fixed uniform orientation of the director can be obtained on monodomain crystalline substrates.

The orientation of smectic A liquid crystals has certain peculiarities. A ground surface, like any other relief, gives rise to wave-like deformation of the layers of smectic A, whose molecules are held in some manner perpendicularly to the substrate. This deformation is transferred from layer to layer into the bulk of the volume with a decay length[9]

$$l = \frac{1}{q^2} \lambda^*, \tag{8}$$

where q is the modulus of the wave vector of the sinusoidal relief of the substrate, $\lambda^* = (K_{11}/B)^{1/2}$ is the characteristic length for smectic A (K_{11} is the transverse bending elastic constant and B is the compression modulus of the layers). The quantity λ^* is of the order of the thickness of one smectic layer ($2\cdot 10^{-9}$ cm), $q \sim 10^{+3}$ cm^{-1}, and therefore $l \sim 10$ cm, i.e., the distortions will extend into the volume over a very large distance. This feature explains the difficulty of obtaining homeotropically oriented smectic samples, even on relatively defect-free substrates.

In general, the molecular mechanisms for orienting smectic (nonpolar) mesophases are virtually identical to the orientation mechanisms for nematics. The difference lies in the fact that because of the specific elastic properties of layered structures the orientation of the director in the bulk of the layer cannot change easily and cannot "adjust" to the orientation of the surface layers. Therefore, in order to obtain uniform samples of smectics A, B, C, and others surface treatment methods must be combined with methods for preparing a uniform molecular orientation in the bulk, and in addition the direction of orientation of the director in the bulk of the sample must match the orientation near the surface. A magnetic or electric field or a temperature gradient or gradient of the flow velocity of the liquid crystal are usually employed for volume orientation.

3. SURFACE ENERGY AND THERMODYNAMICS OF A LIQUID CRYSTAL

3.1. Theory

The presence of a free surface or interface has a strong effect on the phase diagram and thermodynamic properties of any system. Its effect can be especially strong in the case when the volume phase transition is a first-order phase transition, i.e., the order parameter and the physical quantities related to it have a jump at the transition point. Even in this case (see below), however, under certain conditions there exists for the surface quantities a critical point, near which

they vary continuously and the corresponding susceptibilities diverge. Such a surface-ordered phase (with a second-order transition) can coexist with a volume disordered phase, which introduces a new length scale, describing the change in the order parameter in the ordered surface layer, new critical indices, etc. The phase transition in bounded systems turns out to be much richer than in the case of infinite systems in all directions of the samples. Liquid crystals are not an exception in this respect, and in addition they have the additional advantage that all this richness of phase transformations can be studied relatively easily directly by optical methods.

As is well known,[9] the orientational ordering of liquid crystals is fixed by the order parameter—a symmetric tensor of rank two with zero trace. In uniaxial nematics this tensor is fixed by a unit vector—the director $\mathbf{n}$ and the modulus of the order parameter Q:

$$Q_{ij} = Q\left(n_i n_j - \frac{1}{3}\delta_{ij}\right), \tag{10}$$

where δ_{ij} is the Kronecker tensor. The anisotropic interaction of the molecules of a nematic with a solid wall bounding it (for example, van der Waals interaction) necessarily produces some surface ordering. This order is then transferred into the volume of the liquid crystal by elastic forces.

Following Ref. 80 we shall study a film of a nematic liquid crystal, which has an interface with a solid at $z = 0$ and a free surface (interface with air) at $z = 2d$. (Unlike the geometry of the preceding section, we displace the origin along the z axis.) The properties of the film are assumed to be uniform in its plane. We shall choose the potential of the substrate in accordance with the well-known Maier-Saupe theory[81] in the following form:

$$v(\theta, z) = -G\delta(z) P_2(\cos\theta); \tag{11}$$

here θ is the angle between the long axis of the molecule and the direction of predominant orientation at the surface, and P_2 is a Legendre polynomial of degree two. If this potential is averaged over many molecules (it is precisely the averaged potential that appears in the Landau–de Gennes theory), we obtain

$$V = \langle v(\theta, z)\rangle = -G\delta(z)\langle P_2\rangle = -G\delta(z) Q. \tag{12}$$

The Landau–de Gennes free energy density is given by

$$f = f_0(Q) + L\left(\frac{dQ}{dz}\right)^2 - G\delta(z) Q, \tag{13}$$

where $f_0(Q) = a(T - T^*)Q^2 + bQ^3 + cQ^4$ is the uniform part of the free energy; a, b, c, and T^* are the coefficients in Landau's expansion; and, L is the modulus of elasticity.

The total free energy per unit area is given by

$$F = \int_0^{2d}\left[f_0(Q) + L\left(\frac{dQ}{dz}\right)^2\right] dz - GQ_0, \tag{14}$$

where $Q_0 = Q(z = 0)$. The functional (14) must be minimized in two stages. First we minimize with respect to the function $Q(z)$, and then we minimize with respect to the boundary value Q_0. At the first stage we obtain the equation

$$L\left(\frac{dQ}{dz}\right)^2 = f_0(Q) + \text{const.} \tag{15}$$

The constant is determined from the boundary condition at $z = 2d$. The case of a semiinfinite sample ($d \to \infty$) is easiest

to study. The natural boundary condition on the free surface is

$$\frac{dQ}{dz}\Big|_{z\to\infty} = 0, \tag{16}$$

since on a free surface only the volume energy density (13) contributes. From here we obtain

$$\xi_0^2 \left(\frac{dQ}{dz}\right)^2 = \varphi(Q) - \varphi(Q_b), \tag{17}$$

where $\xi_0 = (L/aT^*)^{1/2}$, $\varphi(Q) = f_0(Q)/aT^*$, and Q_b is the bulk value of the order parameter. Substituting this integral into the expression (14) for F we obtain

$$\frac{F}{aT^*} = \varphi(Q_b) d + \xi_0 \left\{ 2 \int_{Q_b}^{Q_0} [\varphi(Q) - \varphi(Q_b)]^{1/2} dQ - gQ_0 \right\}, \tag{18}$$

where $d/\xi_0 \to \infty$ and $g = G/\xi_0 aT^*$ is the dimensionless potential of the substrate. The first term, proportional to d, is a volume energy, while the second term is the energy of the boundary layer F_{bl}

$$\frac{F_{bl}}{\xi_0 aT^*} = 2 \int_{Q_b}^{Q_0} [F(Q) - F(Q_b)]^{1/2} dQ - gQ_0. \tag{19}$$

The equilibrium value of Q_0 is determined from the condition $\partial F_{bl}/\partial Q_0 = 0$. This equation has many solutions, but the concrete value of Q_0 is the value which minimizes F_{bl}. Once Q_0 has been determined, the distribution of the order parameter $Q(z)$ can be calculated from (17):

$$\frac{z}{\xi_0} = \int_{Q(z)}^{Q_0} \frac{dQ}{[\varphi(Q) - \varphi(Q_b)]^{1/2}}. \tag{20}$$

This equation can be solved numerically.[80] The following results (Fig. 8) are obtained for Q_0 as a function of $T-T_c$, where T_c is the temperature of the volume phase transition, with the following values of the parameters of a typical nematic (5CB): $a = 0.065 \cdot 10^7$ erg/cm$^3 \cdot$K, $b = 0.53 \cdot 10^7$ erg/cm^3, $c = 0.98 \cdot 10^7$ erg/cm^3, $T^* = 307.14$ K, $L = 4.5 \times 10^{-7}$ erg/cm. For $g < g_0 = 0.0056$, Q_0 has a jump at $T = T_c$. For $g_0 < g < g_c = 0.012$ the jump in Q_0 (i.e., the surface phase transition) occurs at a temperature above T_c. For $g > g_c$ the surface transition vanishes and Q_0 becomes a continuous function of the temperature.

For a finite sample the situation is even more complicated. We shall employ the same boundary condition as in the semiinfinite case.

$$\frac{dQ}{dz}\Big|_{z=2d} = 0.$$

For finite d, however, in (18) we cannot separate the volume and surface contributions (we cannot determine Q_b and Q_0 separately). Therefore we must solve the system of equations

$$\varphi(Q_0) - \varphi(Q_b) = \tfrac{1}{4} g^2,$$

$$\varphi^2(Q_b) \left\{ 1 - \frac{\xi_0}{d} \int_{Q_b}^{Q_0} \frac{dQ}{[\varphi(Q) - \varphi(Q_b)]^{1/2}} \right\} = 0 \tag{21}$$

and select a pair Q_b and Q_0 which minimizes F. Once again the solution can only be found numerically. For $g_c < g < g_0$ the temperature of the transition Q_b increases as d decreases. The transition which is associated with the jump in Q_0 and Q_b can be called a volume transition (by analogy to the limit $d/\xi_0 \to \infty$). There exists a thickness $d/\xi_0 = 160$ ($g = 0.008$) below which the transition in the boundary layer vanishes completely and is reduced to a volume transition. As d decreases further the first-order transition in Q_0 and Q_b becomes continuous. For $g > g_c$ (in contrast to the semiinfinite case, where Q_0 did not undergo a sharp change, when $g > g_c$) here Q_0 always undergoes a jump with a volume first-order transition. We also note that in a finite sample there always exists some degree of orientational order at all temperatures. Therefore in this case it is more correct to call the high-temperature phase not isotropic, but rather paranematic.

The behavior studied above physically is determined by the competition between the elastic (coupling the interface with the bulk) and surface forces. When the substrate potential is weak ($g < g_0$), everything is determined by the bulk and Q_0 varies synchronously with Q_b. For $g > g_0$ (but $g < g_c$) the increase in the elastic energy cannot overcome the surface potential for $T < T_c$. This is still possible, however, at some temperature $T > T_c$. Finally, for $g > g_c$ such a temperature no longer exists.

Thus far we have studied only the situation when the surface acted on the liquid crystal like some ordering field,
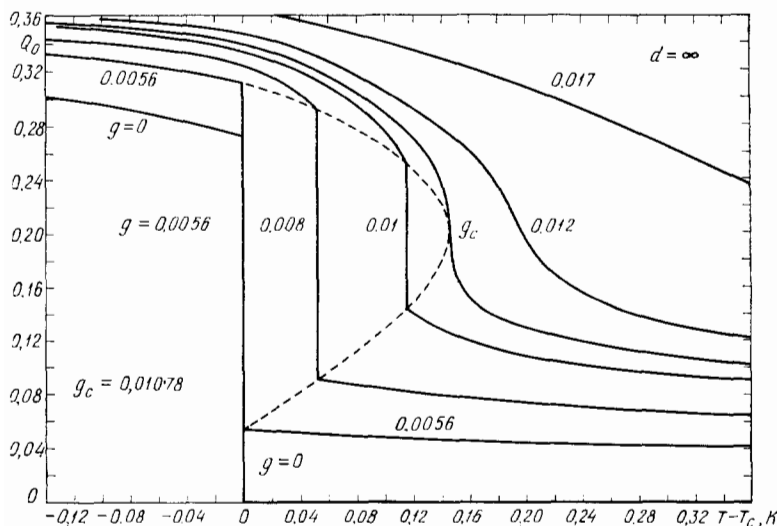

FIG. 8. Computed temperature dependences of the surface order parameter Q_0 for different values of the energies of adhesion of a semiinfinite NLC layer to the substrate.[80]

but did not give rise to any new physical property or new order parameter. This does not necessarily always occur. There exist, for example, numerous data[82-85] showing that for a homeotropic orientation the surface (including a free surface) imposes some smectic ordering on a liquid crystal. The existence of a surface layer with smectic order must be taken into account in the analysis of experimental data on the adhesion energy of liquid crystals. On the basis of Landau's theory the smectic order parameter ψ decays exponentially away from the boundary[86]

$$\psi(z) = \psi_0 \exp\left(-\frac{z}{\xi}\right), \tag{22}$$

where the "correlation" length ξ depends on the closeness to the point of the volume transition into the smectic phase (as $T \to T_{NA} \xi \to \infty$), and ψ_0 is the surface-induced smectic order parameter. This ordering leads to an additional contribution to the elastic energy, arising as the director tilts away from the normal to the smectic layers (which coincides with the normal to the surface). For small tilt angles θ this contribution can be written in the following form:

$$F_{sm} = \frac{1}{2} \int_0^d |\psi|^2 \theta^2 \, dz. \tag{23}$$

This energy competes with the magnetic energy, which in this geometry has the form

$$F_m = \frac{1}{2} \chi_a H^2 \int_0^d \theta^2 \, dz. \tag{24}$$

Thus surface-induced smectic ordering can lead to an effective increase in the adhesion energy, as determined by the Fredericks effect.

The possibility for the surface to induce some polar order parameter is discussed in Ref. 87. The polar order parameter makes a contribution to the surface energy, which in the simplest approximation has the following form:

$$F_{op} = -\gamma_p (\mathbf{nv}), \tag{25}$$

where $\mathbf{v}$ is the normal to the surface and $\mathbf{n}$ is the director. We note that F_{op} does not obey the symmetry $\mathbf{n} = -\mathbf{n}$, which occurs only for a quadrupole (nematic) order parameter. The minus sign in (25) corresponds to the obvious supposition that at equilibrium in the presence of a surface polar order parameter the molecules must be oriented perpendicularly to the boundary.

In the same notation Rapini's potential (1), corresponding to the quadrupole potential, i.e., the usual nematic ordering at the surface, can be written in the form

$$F_0 = W (\mathbf{nv})^2. \tag{26}$$

One can see that the quadrupole order strives to orient molecules parallel to the surface, which gives rise to competition with the polar order (25). In accordance with Ref. 87 for $W = \gamma_p$ a structural surface transition occurs as the average tilt angle of the molecules from the normal to the surface changes.

3.2. Experiments

Most experimental data concerning the effect of a boundary on the ordering and the temperature of phase tran-

sitions in liquid crystals can be divided into three groups.

The first group includes work in which the ordering of the isotropic liquid phase near a solid wall is studied.[88-93] The main result of this series of investigations consists of the fact that the solid wall imposes some orientational order on an isotropic phase. The order parameter Q_0 has a maximum value near the surface (characteristic values are $Q \sim 0.2$–0.3,[89-92] for solid surfaces worked by grinding) and decreases into the bulk of the isotropic liquid. The corresponding correlation lengths increase as the temperature of the transition into the nematic phase is approached and in order of magnitude equal 10 Å for $T - T_c = 1$ K.

The existence of an orientationally ordered nematic layer can be observed from measurements of the birefringence[88-92] or dichroism.[93] As an example Fig.9 shows the temperature behavior of the phase delay for light transmitted through a cell with the isotropic phase of 5CB, confined between two glasses ground in the same direction. The low values of the phase delay, to measure which a special experimental technique must be employed (compensation with a Pockels cell,[88-89] interferometry,[90-91] rotating analyzer,[92] etc.), are interesting. The values of the orientational order parameter at the surface and the correlation lengths for several liquid crystals for different methods of working the surface were determined from these experiments. On the whole the experimental results are described quite well by the theoretical curves, shown in Fig. 8.

We note that the solid wall imposes orientational ordering even in nonmesogenic liquids, for example, in acetone and benzene,[93] which, though they do not have a nematic phase, have a quite distinct molecular asymmetry.

The second group of experimental investigations includes the study of smectogenesis in a nematic phase in contact with a solid wall. It was found that in homeotropic layers of strongly polar substances (such as cyanobiphenyls with a longitudinal component of the molecular dipole moment of the order of 4 debye) a smectic film with a thickness of the order of 100 Å forms near a solid wall. This is indicated by direct measurement of the forces acting between mica substrates separated by a layer of a nematic substance.[82] The magnitude of the force between the plates oscillates as the thickness of the gap changes (Fig. 10), and in addition the
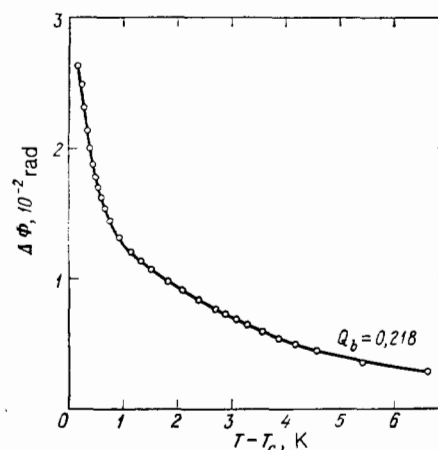
FIG. 9. Temperature dependence of the phase delay $\Delta\Phi$ for a cell with an isotropic phase.[89]
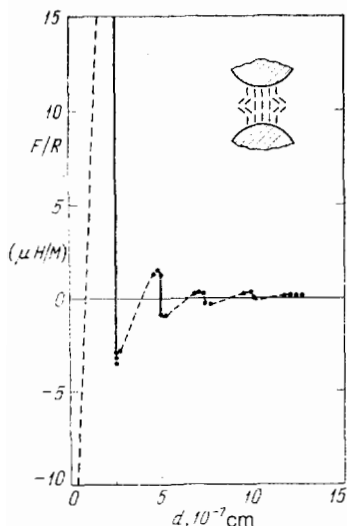
FIG. 10. Oscillations of the force acting between two mica cylinders separated by a homeotropic nematic layer (the radius of curvature of the cylinders $R = 1$ cm).[82]

FIG. 11. Temperature dependences $\dfrac{(H_c d)_{\text{thin}}}{(H_c d)_{\text{thick}}} - 1$ (*1*) and ξ / d thin (*2*).[86]

period of the oscillations corresponds to the maximum size of the molecule. This effect can be explained if it is assumed that only the smectic layer is displaced from the gap as the plates are brought closer together (inset in Fig. 10).

Smectogenesis is also observed in the measurement of the threshold field for the Fredericks transition.[86] As already mentioned, the finite adhesion energy between the molecules of the nematic and a solid wall increases the effective thickness of the NLC layer by the amount of the extrapolation length b. The appearance of a smectic near-surface layer, however, of thickness ξ, on the other hand, eliminates this layer from the analysis, since the Fredericks transition in smectics A is not observed owing to the specific nature of their elastic properties. As a result the magnetic threshold of the Fredericks transition H_c increases. The quantity ξ can be found by comparing $H_c d$ for thin and thick samples. The result is shown in Fig. 11, where the experimental values of the parameter

$$\frac{(H_c d)_{\text{thin}}}{(H_c d)_{\text{thick}}} - 1$$

are compared with ξ / d thin calculated in the mean-field approximation. One can see that the correlation length ξ increases critically as the point of the transition into the smectic A phase is approached.

The third group of studies includes studies concerned with the free surface of a liquid crystal. It has been observed that in nematics with large longitudinal molecular dipoles (cyanobiphenyls) the dipoles have a tendency to become oriented perpendicularly to the free surface, and in substances with weakly polar and nonpolar molecules (MBBA, n-azoxyanisole) parallel orientation or tilted orientation is predominantly observed. For MBBA, for example, the angle between the director and the free surface depends strongly on the temperature.[94] As the isotropic phase is approached an orientational phase transition with a change in the angle θ_0 occurs at the surface. At the transition point (it is displaced from T_c by only 0.9 K) the director acquires an orientation perpendicular to the surface. This structural transition can be explained starting from a model in which the
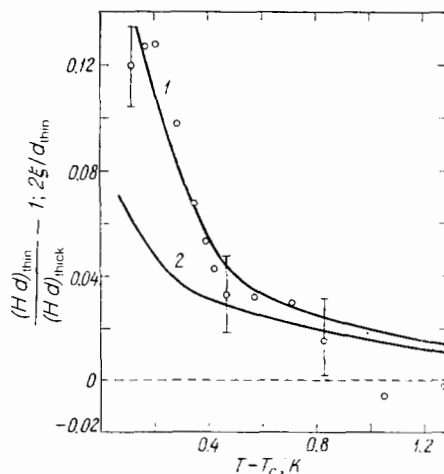
competition between the nonpolar and polar interactions of molecules at the surface is taken into account.[87]

In the case of strongly polar nematics a smectic layer whose thickness is determined by the proximity to the transition into the smectic A phase forms on the free surface. The existence of such a layer was established by direct x-ray structural studies.[84,85] The possibility that interactions of the polar type can serve as a seed for formation of this layer precisely at the surface has not been excluded. In any case, for molecules with a large longitudinal dipole moment it is energetically more favorable not simply to become oriented perpendicular to the surface, but for the entire dipole to be oriented toward the medium with the larger dielectric permittivity, i.e., into the bulk of the liquid crystal. It must be acknowledged, however, that there are not enough facts indicating an interaction between the polar and smectic order parameters.

Thus the experimental facts as a whole indicate that, as a rule, an interface stabilizes the phase with lower symmetry. A surface nematic order is imposed on an isotropic medium, and a surface smectic-A order is imposed on a nematic phase. The same tendency is also preserved for the smectic-A–smectic-C phase transition.[95] For example, in thin freely suspended films the smectic-C phase is all the more stable the thinner is the film. This can be seen clearly in Fig. 12, where the tilt angle of the molecules to the normal of the smectic layer φ (the order parameter of the smectic C) is shown as a function of the temperature for films formed by a different number N of molecular layers.

It has not been excluded that crystalline solid surfaces can impose new types of ordering on a liquid crystal (smectic B, G, H, etc.). This phenomenon is on the whole apparently related to molecular epitaxy effects.

4. EFFECT OF A BOUNDARY ON THE FORMATION AND STRUCTURE OF DEFECTS

All defects observed in liquid crystals can be divided into three groups: point, linear, and two-dimensional. Point defects are associated with the distortion of the structure of a liquid crystal near a singular point. Linear defects are characterized by the appearance of a singular line; two-dimen-
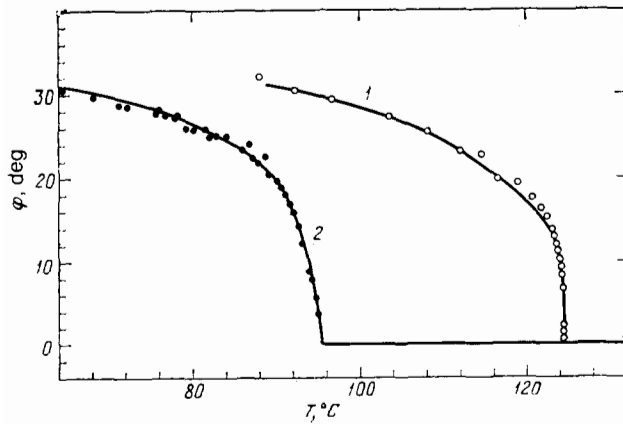
FIG. 12. Temperature dependences of the tilt angles of the molecules φ to the normal of the smectic layer for smectic C films.[95] The number of smectic layers $N = 2$ (1) and $N = \infty$ (2).

sional defects are characterized by a singular surface. Two-dimensional defects also include different polygonal formations (for example, confocal domains).[96,97]

The boundary of a liquid crystal is important for the formation and structure of defects in two respects. First, the surface fixes the boundary orientation of the director and thereby alters the degeneracy space of the order parameter and the possible topologically stable types of defects. Second, specific purely surface (and not arriving from the volume) features (defects) can exist at the surface. For example, in a nematic liquid crystal the degeneracy space of the order parameter is a sphere with identified opposite points (owing to the symmetry $\mathbf{n} = -\mathbf{n}$). This space is denoted by s^2/z^2 (the two-dimensional sphere s^2, factorized according to the group of integers z^2, consisting of two elements: 1 and a, where $a^2 = 1$). The degeneracy space, however, at the surface depends on the boundary conditions. For tangential conditions this is a circle with identified opposite points (s^1/z^2), while for normal boundary conditions it is only one point.

Both nonspecific and specific point singularities can exist at the surface. The former consist of hedgehogs, which are uniquely stable in the bulk of the nematic and emerge onto the surface and are manifested for any initial conditions. The latter are boojums, which are possible only under tangential boundary conditions.[98] We shall not discuss these problems in greater detail, since this would take us too far away from the problems addressed in this review.

Surface disclinations, whose lines are located on the interface of the liquid crystal and the solid wall, are of great interest.[99-101] The study of these disclinations enables determining the adhesion energy W. Let the substrate lie in the (x, y) coordinate plane, and let the disclination line be parallel to the y axis. In this case the equation of equilibrium is the Laplace equation, while the boundary condition has the form

$$\frac{\sin\theta_0 \cos\theta_0}{b} - \frac{\partial\theta_0}{\partial z} = 0, \quad z = 0. \tag{27}$$

where b is the extrapolation length (see Sec. 2.1).

The solution of the equation of equilibrium, taking (27) into account, is given by

$$\mathrm{tg}\,\theta_0 = \frac{z+b}{x}. \tag{28}$$

By measuring accurately the angle θ_0 near the substrate, W can be evaluated from Eq. (28).

Point singularities, which deform the interface, can appear on the free surface of an NLC or on the interface between a nematic and an anisotropic liquid under conical or tangential boundary conditions.[102,103] Point singularities near solid substrates are associated with the presence of microscopic protuberances or indentations.[103]

Two-dimensional defects—180° walls, analogous to Bloch walls in ferromagnetic substances, can be observed in nematic liquid crystals in a magnetic field.[104] The walls also arise above the critical field of the Fredericks transition.[105-107] The walls interact with solid substrates. Thus, for example, if the axis of easy orientation on the substrate is parallel to the field, while the Bloch wall is parallel to the surface, there is a repulsion with the force[108]

$$f = 8\chi_a H^2 \exp\left(-\frac{2r}{\xi_H}\right), \tag{29}$$

where χ_a is the anisotropy of the diamagnetic susceptibility of the NLC, H is the magnetic field strength, and $\xi_H = H^{-1}(K_{22}/\xi_a)^{1/2}$ is the coherence length of the magnetic field.

In thin samples of an NLC ($d < b$) walls can also be observed when there is no field.[109] The study of such walls also makes it possible to evaluate the adhesion energy.

Defects arising in the spherical volumes of liquid crystals are extremely diverse. This situation can be realized experimentally in drops of a liquid crystal suspended in an isotropic liquid. The boundary conditions are regulated by changing the composition of the liquid from tangential (MBBA in pure glycerine) to conical and normal (MBBA in a mixture of glycerine with lecithin).[110,111] The most typical defects in drops of nematics and cholesterics are hedgehogs, which can exist both in the bulk and at the surface of drops and in cholesterics are the analog of a magnetic monopole (Fig. 13a),[98,112,113] as well as purely surface defects—boojums (Fig. 13b).[98,114] As the boundary conditions change mutual transformations of boojums and hedgehogs with the formation (or vanishing) of a pair of surface disclinations is possible. Thus, for example, as the orientation at the surface of a drop of NLC changes from normal to tangential the hedgehog transforms into a boojum (see Fig. 13).[115]

5. VAN DER WAALS FORCES

5.1. Effect of van der Waals forces on equilibrium properties

The van der Waals (dispersion) interaction, which, as first shown by F. London,[116] is of an electromagnetic fluctu-
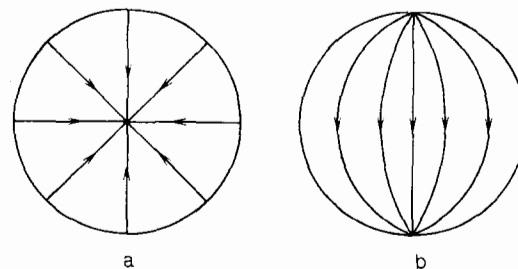

FIG. 13. Defects in drops of a nematic suspended in an isotropic liquid.[115] a) Hedgehog; b) boojum.

ation origin, is universal, and is characteristic of all micro and macroobjects. The characteristic features of the van der Waals forces include a power law decay with distance r and the existence of two limiting regimes, differing by the exponents of r, namely, the normal regime and the retardation regime.[117-120] Thus, for example, the force of interaction between two flat dielectrics separated by a vacuum or a dielectric medium in the normal state (for $r \ll \lambda_0$, where λ_0 is the characteristic wavelength of the absorption spectrum), decays as r^{-3}, while in the retardation regime ($r \gg \lambda_0$) it decays as r^{-4}.[117] In terms of the macroscopic theory the dispersion forces are determined by the dielectric permittivities ε_{ij} of the interacting bodies.[117,120-122] Depending on the ratio of the dielectric permittivities the van der Waals forces can be attractive or repulsive, but they are usually attractive.

The anisotropic dispersion interaction in liquid crystals strongly affects the properties of a mesophase, since the short-range forces between the molecules of liquid crystals are relatively weak. For example, the van der Waals interaction can give rise to the formation of cholesteric[123-126] and smectic phases.[126] The dispersion forces can also renormalize the elastic moduli of a nematic, striving to reduce K_{22} and increase K_{11} and K_{33}.[126] The dispersion interaction makes a flat disclination in an NLC unstable in the region lying outside a sphere of finite radius, drawn around a disclination nucleus.[127]

When a nematic is in contact with isotropic substrates the van der Waals interaction makes a contribution to the surface energy which is comparable to the short-range adhesion forces (of the order of several erg/cm²),[128,129] and in addition, depending on the ratio of the dielectric permittivities, some orientation of the director is stabilized near the substrate. The van der Waals forces can fix a uniform orientation of the director in liquid-crystalline layers up to 10^{-2} cm thick.[130]

The anisotropy of a liquid crystal confined between isotropic substrates gives rise to a number of new interesting effects. Thus, for example, for two substrates separated by a cholesteric layer there arises a strongly temperature-dependent quasiperiodic correction to the dispersion interaction force.[131]

For an NLC in contact with substrates cut out of uniaxial crystals, because of the anisotropy of the dispersion interaction there arises a torsional van der Waals moment, which strives to orient the molecules of the nematic along this axis.[132,133] If the plane of the crystalline substrate contains several symmetry elements, as for example, for 11 symmetry classes of crystalline substrates, cleaved along the cleavage planes ($C_1 - C_6, C_s, C_{2v} - C_{6v}$), it becomes possible to obtain a complicated, combined orientation of the director. Thus in drops of nematics on chips belonging to different surface symmetry classes, patterns of the director distribution whose symmetry corresponds to the symmetry of the chip are obtained.[73,74,76] Figure 14 shows drops of NLC on chips of NaCl(C_{4v}) and C(NH$_2$)$_3$Al(SO$_4$)$_2$·6H$_2$O(C_{3v}) crystals, consisting of four- and six-segment planar heterogeneous patterns, respectively.[1)] Low-symmetry chips (C_1, C_s) orient nematics, as a rule, homeotropically.[74,76]

A simple approach to the description of the van der Waals interaction in a system consisting of an anisotropic uniaxial substrate and an amorphous screening film of a nematic was proposed in Ref. 135. It was shown that under the condition $A/K \ll \delta \ll \lambda_0$, where A is Hamaker's constant ($A \sim 10^{-3}$ erg) and K is the modulus of elasticity of the NLC in the one-constant approximation, there exists a normal regime and the dispersion free energy of the NLC can be written as

$$F_d = \int_\delta^\infty U(z)\, dz. \tag{30}$$

Here $U(z) = A/z^3$ is the dispersion potential and z is the coordinate perpendicular to the substrate. In what follows, we shall employ a potential of the form (30) to describe local Fredericks transitions.

The van der Waals forces determine not only the orientation of a liquid-crystalline film, but also its equilibrium thickness on the surface of a solid. As is well known, if the liquid is located on the interface with a solid, then its equilibrium shape, thickness, etc., are determined by the condition of equilibrium

$$\gamma_{sv} - \gamma_{sl} = \gamma_{lv} \cos \theta, \tag{31}$$

where γ_{sv}, γ_{sl}, and γ_{lv} are the surface tensions at the solid-vapor, solid-liquid, and liquid-vapor interfaces, respectively, and θ is the contact angle.[2)] Wetting ($\cos \theta > 0$), no wetting ($\cos \theta < 0$), and complete wetting ($\cos \theta = 0$) phenomena can occur depending on the ratios of γ_{sv}, γ_{sl}, and γ_{lv}. In the latter case the edge of the liquid transforms continuously into the film forming on the solid wall. The thickness of this film is of the order of 10^{-5}–10^{-6} cm, and is determined by the range of the van der Waals forces. If $\gamma_{sv} > \gamma_{sl} + \gamma_{lv}$, then equilibrium is impossible for any form of the drop and the drop spreads along the surface of the solid. This case is usually called spreading.[136] It is convenient to introduce the spreading coefficient

$$\Gamma = \gamma_{sv} - (\gamma_{sl} + \gamma_{lv}). \tag{32}$$

Usually, if we are concerned with a volatile liquid, so that $\Gamma > 0$ for the liquid, solid, and vapor separately, then the adsorption of vapor on the surface of the solid changes all surface tensions so as to ensure equilibrium ($\Gamma = 0$ and $\cos \theta = 1$). This is the case of complete wetting, If, however, the liquid is nonvolatile and $\Gamma > 0$, then this mechanism of equilibrium is no longer possible and the liquid spreads out. Both cases (volatile liquid with $\Gamma = 0$ and nonvolatile with $\Gamma > 0$) are distinguished according to the equilibrium thickness of the film. For complete wetting the equilibrium thickness of the film is determined by the van der Waals forces and equals[136]

$$l_1^* = \left(\frac{A}{6\pi\rho g} \right)^{1/4}. \tag{33}$$

FIG. 14. Orientation of nematic drops on chips of solid crystals.[74] a) NaCl(C_{4v}) chip; b) C(NH$_2$)$_3$Al(SO$_4$)$_2$·6H$_2$O(C_{3v}) chip.

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where A is Hamaker's constant, ρ is the density of the liquid, and g is the acceleration of gravity. For a spreading nonvolatile liquid the equilibrium thickness now depends on the spreading coefficient Γ:

$$l_2^* = \frac{1}{2}\left(\frac{A}{\pi\Gamma}\right)^{1/2}. \qquad (34)$$

The formulas (33) and (34), as already pointed out above, are equally valid for films of isotropic liquids and nematics. In the latter case, however, it is assumed that the orientation of the director on the free surface of the nematic is identical to the orientation at the interface with a solid. If these orientations are not the same, for example, they form an angle φ, then as the thickness of the film decreases the Frank energy E increases. In a rough approximation (all Frank moduli are equal, and the thickness of the film l is so small that $(\nabla\varphi)^2 \sim \varphi^2/l^2$) we have

$$E = \frac{K\varphi^2}{2l^2}. \qquad (35)$$

The total free energy of the film, including the contributions of the van der Waals forces, Frank forces, surface tension forces, and gravity, has the following form:

$$F = \int \left[-\Gamma + \frac{1}{2}\gamma_{lv}\left(\frac{dz}{dx}\right)^2 + U(z) + G(z) + E(z)\right] dx, \qquad (36)$$

where $z(x)$ is the equation of the surface of the film (for simplicity we neglect the dependence on the second coordinate y), $U(z) = A/12\pi z^2$ is the van der Waals energy, $E(z) = K\varphi^2/2z^2$ is the Frank energy, $G(z) = (1/2)\rho g z^2 + \rho g z h$ is the gravitational energy, and the parameter h plays the role of a Lagrangian multiplier, which is determined, for example, from the condition that the volume of the spreading drop is fixed. Minimization of (36) yields the first integral

$$\frac{1}{2}\gamma_{lv}\left(-\frac{dz}{dx}\right)^2 = U(z) + E(z) + G(z) - \Gamma. \qquad (37)$$

The equilibrium thickness of the drop l is determined from the following two conditions. First, at the center of the drop $dz/dx = 0$, whence, from (37)

$$U(l) + E(l) + G(l) = \Gamma. \qquad (38)$$

The second condition fixes the volume of the drop. It is simplest to employ the following mechanical analogy. Equation (37) corresponds to the law of conservation of energy of the particle: the coordinate is z, the time is x, the mass is γ_{lv}, the potential energy is $U + E + G$, and the total energy is Γ. The spreading of the drop, in this case, corresponds to the period of oscillations of the particle becoming infinite. For this Γ must equal the maximum of the potential, i.e.,

$$\frac{\partial}{\partial z}[U(z) + E(z) + G(z)]_{z=l} = 0. \qquad (39)$$

The Lagrange multiplier h can be eliminated from (38) and (39), and an explicit expression can be derived for l.

In the case of an isotropic liquid or a film of a nematic with a uniform orientation, we obtain from here the expression (34) for the equilibrium thickness of the film. For a nematic with unsymmetric boundary conditions $E(l) \gg U(l) + G(l)$, and the equilibrium thickness is

$$l_3^* = \frac{K\varphi^2}{2\Gamma}. \qquad (40)$$

5.2. Local Fredericks transitions

Changes in the volume orientation of the director, occurring owing to the competition between the orienting effect of different surface forces, are called local Fredericks transitions. The van der Waals interaction forces between a liquid crystal and a solid substrate often appear as such forces. The name "local Fredericks transition" was proposed by de Gennes and Dubois-Violette[137] by analogy to Fredericks transitions in external fields. The term local appears because the counteraction of the orienting forces is realized in a relatively small near-surface region. We shall examine several examples.

a) A local Fredericks transition can occur in a nematic in contact with a thin amorphous film (thickness $\delta \sim 10^{-6}$ cm), screening the dispersion field of the crystalline substrate, under the condition that the short-range NLC-film adhesion forces and the van der Waals field of the substrate stabilize a different orientation of the director, for example, planar and homeotropic, respectively (Fig. 15). The critical energy of adhesion of the NLC to the screening film W_c, for which a first-order orientational transition from the initial homeotropic orientation to the planar orientation occurs, can be determined from the condition that the free energies $F(\theta = 0)$ and $F(\theta = \pi/2)$ are equal[137]:

$$F\left(\theta = \frac{\pi}{2}\right) = W_c - \int_\delta^\infty U(z)\,dz = F(\theta = 0) = 0. \qquad (41)$$

If the condition (41) does not hold, then depending on the thickness of the film one or two orientational second-order phase-transition points can occur as W changes. Thus for $\delta < \tilde{\delta}$, where $\tilde{\delta}$ is some critical thickness of the screening film, there occurs one second-order transition from the homeotropic orientation into the tilted orientation at $W = W'(W_c > W')$, and the transition from the tilted orientation into the planar orientation is, in principle, not achievable. For $\delta > \tilde{\delta}$ two second-order transitions occur at $W = W'$ and $W = W''$ ($W_c < W''$) from the homeotropic into the tilted and from the tilted into the planar orientation, respectively.[137] We note that the values of W' and W'' can be affected by the contribution of the second-order elastic moduli.[138] The local Fredericks transition described above was first observed in an NLC layer screened from a glass substrate by a thin carbon film with a definite thickness, with W varying as a function of the temperature.[109] In Ref. 139 a local Fredericks transition was achieved in nematics in contact with Langmuir films screening the dispersion field of the
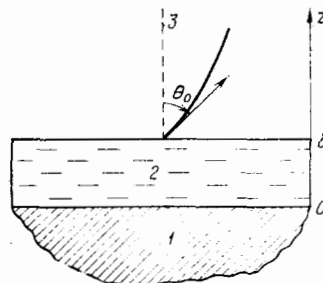

FIG. 15. Possible geometry of a local Fredericks transition.[137] 1) Crystalline substrate, 2) amorphous screening film, 3) NLC layer.

substrate; in this case the film thickness δ rather than W was varied. The critical thicknesses δ_c of the orientational transition were of the order of 10^{-6} cm, and for NLC with $\varepsilon_a > 0$ as the electric polarization of the Langmuir film increased δ_c and, conversely, for nematics with $\varepsilon_a < 0$ it decreased, which is attributable to the effect of the surface electric field of the Langmuir films on the orientation of the NLC (see Sec. 2.2).

b) An orientational transition from the planar texture of NLC into the homeotropic texture can occur as the thickness of the nematic film decreases to values much less than λ_0 (see Sec. 5.1). In this case the short-range adhesion forces (the energy W) fix the planar orientation of the director, while the van der Waals forces of the substrates fix the homeotropic orientation. The thickness of the NLC layer, for which a local Fredericks transition occurs, is determined by comparing the free energies for different orientations[130]:

$$d_c = \left(\frac{\hbar\omega_0}{\gamma_{sl}}\right)^{1/2},\qquad(42)$$

where γ_{ls} is the surface tension between the solid substrate and the NLC, ω_0 is the characteristic frequency corresponding to λ_0, and $\hbar$ is Planck's constant. It was established from the decrease in the order parameter in the planar-oriented NLC layer, confined in a quartz wedge, that a local Fredericks transition occurs at thicknesses $d_c \sim 10^{-6}$ cm.[140] The experimental value of d_c agrees with the theoretical value calculated using the formula (42).

c) The so-called spontaneous Fredericks transition—spontaneous breakdown of the uniform homeotropic orientation of the NLC above some critical thickness of the cell—apparently has an analogous physical nature. In this case the dispersion field of the substrates fixes a homeotropic orientation, while the short-range adhesion forces fix the planar orientation. Unlike the local transition described in the preceding section, the spontaneous Fredericks effect is a second-order orientational transition.[141-144]

d) An orientational transition can be observed in NLC cells with a mixed orientation of the director.[26,50,145,146] For example, if a planar orientation (rigid anchoring) is fixed on one substrate and homeotropic (finite W_1) orientation is fixed on the other, then a planar orientation will exist in the entire cell for thicknesses less than some critical value d_c. For $d > d_c = (K_{11} + K_{13})/W_1$ an orientational transition will occur.[145] In the case of finite adhesion energy (W_2) the situation is more complicated for the planar orientation. Now there are two critical thicknesses of the NLC layer: d_c^h, below which the nematic is oriented homeotropically, and d_c^p, below which the planar orientation is stable.[146] For $K_{11} \approx K_{33}$ and $W_1 > W_2$ below d_c^h the sample is oriented homeotropically, while for $W_1 < W_2$ and $d < d_c^h$ the sample has a planar orientation. If $K_{11} \ll K_{33}$ and $W_1 \neq W_2$, then the critical thickness exists only for $W_1 > W_2$. In this case for $d < d_c^h$ the homeotropic orientation is stable, while for $W_1 < W_2$ the NLC is in a distorted state for any thickness of the cell. If $K_{11} \gg K_{33}$ and $W_1 \neq W_2$, then the liquid crystal assumes a planar orientation for $W_1 < W_2$ and $d_c < d_c^p$. In the opposite case ($W_1 > W_2$) the nematic is in a distorted state for any thickness of the cell.

e) The local Fredericks transition in NLC on a glass substrate ground in one direction and screened by Langmuir films is interesting. As already pointed out, the relief formed by the grinding of the glass orients the NLC in a planar orientation, while the Langmuir films are oriented homeotropically. In this case the deformation of the substrate is apparently transferred, growing progressively weaker, along the layers of the Langmuir film, as happens for smectic A, and thus as the thickness of the film increases the homeotropic orientation becomes increasingly more favorable energetically.[139] The above-described local transition has been observed experimentally in the form of a smooth change in the tilting of the director as the thickness of the Langmuir layer increases from $2.5 \cdot 10^{-8}$ up to $2 \cdot 10^{-7}$ cm.[139] The question of the critical thickness must in this case be studied at the molecular level.

6. CONCLUSIONS

We deliberately excluded from this review the very important question of the role of the surface in diverse electro- and magnetooptical effects observed in liquid crystals. There is an extensive literature (see, for example, Refs. 10 and 15) devoted to this question, in which, in particular, the effect of the finite energy of adhesion W of the molecules of the liquid crystal to the wall on the character of the distortions of the director field under the action of different types of perturbations (electric and magnetic fields, light wave, hydrodynamic flow, etc.) is analyzed in detail.

From the applied viewpoint the effect of the surface on the Fredericks transition and, in particular, on the so-called twist effect, employed in most information display systems, is of greatest interest. It has been shown theoretically that the slope of the contrast curve increases as W decreases. In addition, different hysteresis effects on the "external stress—contrast" curve, enabling realization of bistable switches, have been predicted. The switching times must increase as W decreases because of the increase in the effective thickness of the cell (see the role of the extrapolation length in Fig. 3). Unfortunately, because of the low reproducibility of the technology for controlling surface properties, reliable experiments confirming these conclusions still have not been performed.

A number of interesting problems, which have not yet been adequately studied and which must be solved in the near future, were also excluded from the review. Thus the specific characteristics of the interaction of highly-ordered smectic phases with a solid surface, not mentioning diskotic polymer and lyotropic phases, are not yet understood. In this respect the blue phase of cholesteric liquid crystals is of special interest. The point is that according to modern ideas (see the review of Ref. 7 and the literature cited there) the blue phase is a cubic structure of disclinations. The disclinations have a finite volume density, and therefore the energy of the disclination boundaries, i.e., the surface energy, is of the same order of magnitude as the volume energy. It is precisely the surface energy that makes the blue phase stable and determines its properties.

The effects of surface polarization as well as the interaction of liquid crystals with active surfaces remain poorly studied. We are talking about, for example, solid surfaces undergoing phase transitions, the interface of a liquid crystal with a photosensitive material, etc.

The question of surface waves also deserves special discussion. The extensive collection of material parameters and

types of ordering in liquid crystals makes it possible in principle to observe different types of surface waves ranging from Langmuir waves (with a dispersion law $\omega \sim q^{3/2}$, where ω is the frequency and q is the wave vector) characteristic for ordinary isotropic liquids up to Rayleigh waves (with the disperion law $\omega \sim q$) characteristic for solids.

Freely suspended films of liquid crystals with a fixed thickness down to one molecular monolayer are also extremely interesting. Here we are actually talking about a completely new object in the physics of the condensed state. The existence itself of such freely suspended films is a characteristic property precisely of layered liquid crystals. Freely suspended monomolecular films, for example, of an isotropic liquid, are impossible, since here surface tension energy is lost, which loss in smectics is compensated by a gain associated with the existence of an order parameter.

As already pointed out in the Introduction, based on their properties freely suspended films are an intermediate object falling between ideal two- and three-dimensional systems.[19] On the one hand a monomolecular free film is truly two-dimensional, but on the other it "resides" in a real three-dimensional space, in which, in particular, flexural (three-dimensional) oscillations of the film are admissible. The spectrum of these oscillations also differs from the flexural waves in solid-state membranes (see Ref. 19 for a detailed discussion).

Finally, we emphasize that the concept of an interface is also fully applicable to more complicated heterogeneous liquid-crystalline systems (micellar solutions, sols, membranes, pores, encapsulated systems and emulsions, etc.). The study of the physics of such systems is only beginning, and surface effects will play a key role in the determination of the bulk properties of composite materials.

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[1] Distribution of the director field in an NLC drop on a crystalline substrate can be calculated by minimizing on a computer the free-energy functional taking into account boundary conditions reflecting the directions of easy orientation associated with the symmetry elements of the chip.[76,134]

[2] Equation (31) is equally valid for isotropic and anisotropic systems. In the latter case all surface tension coefficients appearing in formula (31) also depend on the orientation of the given surface relative to the principal axes.

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