

Disjoining pressure in free-standing smectic-A films and its effect on their reflectivity

L. V. Mirantsev

Institute of the Problems of Mechanical Engineering, Academy of Sciences of Russia, St. Petersburg, 199178, Russia

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The results of calculations of a disjoining pressure and smectic layer spacings in free-standing smectic-A films (FSSAF's) heated above the temperature of disappearance of the smectic order in bulk liquid crystal samples are presented. An effect of the disjoining pressure on the optical reflectivity of FSSAF's having a different number of the smectic layers is investigated. The results of calculations are in agreement with results of experimental optical-reflectivity investigations of FSSAF's.

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I. INTRODUCTION

Smectic liquid crystals possess a unique ability to form free-standing films with surface area as large as $\sim 1 \text{ cm}^2$ [1] and thickness varying from thousands of molecular layers down to two and even one smectic layer [2,3]. Such an ability allows one to consider these films as ideal objects for the investigation of the behavior of two-dimensional physical systems. In addition, liquid crystal (LC) free-standing films exhibit phenomena [4–20] that are not observed in bulk (LC) samples. Therefore during last 10–20 years free-standing smectic films have been the object of intensive experimental [2–28] and theoretical [29–41] investigations.

One of most effective techniques of the experimental investigation of free-standing smectic films is the study of their optical properties, namely, the optical transmission spectra [27] and the optical reflectivity [3,4,14–19]. For example, measuring the optical reflectivity of free-standing smectic-A films (FSSAF's) of certain LC materials [14,15] revealed a remarkable phenomenon of layer-thinning transitions in FSSAF's upon heating above the temperature of the bulk smectic-A-isotropic (Sm-A-I) or smectic-A-nematic (Sm-A-N) phase transition. Via these transitions the film with initial thickness of several tens of smectic layers can thin step by step to two layers, and the temperature of the existence of the final two-layer film can be about 10–20 K higher than the bulk Sm-A-I or Sm-A-N transition temperatures.

Subsequent high-resolution optical reflectivity investigations [19] of FSSAF's of the compounds exhibiting such behavior—for example, partially perfluorinated LC 2-4-(1,1-dihydro-2-(2-perfluorobutoxy) perfluoroethoxy) phenyl-5-octyl pyrimidine [H8F(4,2,1)MOPP]—revealed a substantial compression of the smectic layers in these films. An average smectic layer spacing in N -layer FSSAF was determined from its optical reflectivity R by means of a simple relation

$$R = cN^2, \quad (1)$$

where $c = [(n_o^2 - 1)k_0L]^2/4$, n_o is the ordinary refraction index, k_0 is the wave vector of the incident monochromatic radiation, and L is the average film layer thickness. The refraction index n_o was assumed to be temperature independent and equal to the ordinary refraction index for the bulk smectic-A phase. It was found that upon heating the N -layer

film ($N=10,9,8,7,\dots,3$) to its maximum temperature $T_c(N)$ of existence, the average film layer thickness L decreases monotonically to a certain minimum value L_m , and then, at the thinning transition to the $(N-1)$ -layer film, L jumps to a nearly initial value. Upon further heating, the average smectic layer thickness in the new $(N-1)$ -layer FSSAF exhibits a similar behavior. It should be noted that a change in the average layer spacing can be as large as $\sim 1A$, and the minimum value of L in the N -layer film, which is reached at the temperature $T_c(N)$, decreases with decreasing the number N of the film layers. In other words, the minimum value of L in the nine-layer FSSAF is smaller than in the ten-layer film, and L_m for eight-layer film is smaller than that in the nine-layer one, etc. Measurements of the optical-reflectivity of FSSAF's of another partially perfluorinated LC compound H10F5MOPP, which also exhibits layer-thinning transitions upon heating above the bulk Sm-A-I transition temperature, revealed a similar behavior of the smectic layers in these films [19]. However, their reflectivities decay with increasing temperature about 2 times slower than those of similar films of LC H8F(4,2,1)MOPP.

These results are in contrast with data [17] on the optical reflectivities of FSSAF's made of a hydrogenated LC compound 54COOBC composed of molecules having ordinary alkyl tails without fluorine atoms. Though free-standing films of this material also undergo layer-thinning transitions upon heating above the bulk Sm-A-I transition temperature, their reflectivities, at a given number N of the film layers, do not change with increasing temperature up to its maximum value $T_c(N)$. According to Eq. (1), the faster decay of the reflectivity of the film with growth of its temperature, the stronger the compression of the film layers. If the reflectivity of the N -layer FSSAF does not change upon heating up to the temperature $T_c(N)$ of its thinning transition, then the average layer thickness in this film is completely temperature independent. Hence, the compression of the smectic layers in H10F5MOPP free-standing films should be smaller than that in FSSAF's of the LC compound H8F(4,2,1)MOPP, and in 54COOBC free-standing films this compression is absent at all. The origin of such diverse behavior of the smectic layers in free-standing films of different mesogens is not clear up to now.

It should be noticed that Eq. (1), which was used in all experimental papers [3,4,14–19] on the optical reflectivity of FSSAF's, holds only for spatially homogeneous dielectric

film with a refractive index independent of the distance from its boundary surfaces [42]. But free-standing smectic-*A* films can be assumed to be spatially uniform only for temperatures significantly lower than the bulk Sm-*A-I* or Sm-*A-N* transition temperatures. In this case the Sm-*A* structure is well developed in whole volume of the film, and both orientational and translational molecular ordering in internal film layers should be similar to those near the boundary free surfaces. Since, in LC's, the ordinary n_o and extraordinary n_e refractive indices are determined by the magnitude of the orientational order parameter s [43], these indices should also be almost equal for all film layers. As said above, however, compression of the smectic layers in FSSAF's was observed at temperatures sufficiently higher than the bulk Sm-*A-I* transition temperatures. According to the microscopic model proposed in Refs. [34,35,38,40], which describes many features of the behavior of the FSSAF's at these temperatures, well above the bulk Sm-*A-I* or Sm-*A-N* transition points the internal film layers can be significantly less ordered than the outermost ones. This theoretical result has been experimentally confirmed by experiments on optical transmission spectra [27] of cyanobiphenyl free-standing films of different thickness. Indeed, it was found that the orientational molecular order in the outermost film layers exceeds that in the internal ones. In addition, a substantial decay of the orientational order in FSSAF's upon heating was observed. Consequently, in such films the refractive indices n_o and n_e should change with both the distance from the boundary free surface and the temperature. These dependences are completely ignored in fitting experimental data [3,4,14–19] on the optical reflectivity of FSSAF by means of the simple relation (1). Therefore, such a fitting could not give the correct temperature dependence of the average film layer thickness and, hence, the correct compression of the smectic layers in FSSAF's. For example, an experimentally observed absence of noticeable change of the optical reflectivity of 54COOBC free-standing film upon heating up to the temperature $T_c(N)$ of its thinning transition does not indicate the absence of such compression in this film.

In the present paper we show that the compression of the smectic layers in free-standing smectic-*A* films is caused by a so-called “disjoining” pressure, which appears in FSSAF's upon their heating above the bulk Sm-*A-I* or Sm-*A-N* transition temperature. For free-standing smectic-*A* films of different thickness, the magnitude of this pressure as a function of temperature is calculated in the framework of the microscopic model [34,35,38,40]. The smectic layer thickness profiles and the temperature dependences of the average thickness L of the film layers compressed by the disjoining pressure are also obtained. The calculation of the film layer thicknesses is performed with taking into account the smectic layer compressibility B profile and its temperature dependence which are also determined from the model [34,35,38,40] for FSSAF's. The effect of the disjoining pressure on the optical reflectivities of the films with different number N of smectic layers is investigated. In the calculation of the optical reflectivity of FSSAF we use a characteristic matrix M [42] for the layered dielectric slab. Each i th layer of this slab is characterized by a thickness L_i equal to the

thickness of the i th film layer, which is compressed by the disjoining pressure, and by a “local” refractive index n_i . The latter is calculated by taking into account the orientational order parameter s profile in the FSSAF also determined from the microscopic model [34,35,38,40]. The results of calculations are in agreement with results [19] of measurements of the optical reflectivities of free-standing smectic-*A* films and allow us to explain the difference between the temperature dependences of these reflectivities of FSSAF's of partially perfluorinated LC's and those of free-standing films of the hydrogenated LC compound 54COOBC.

The paper is organized as follows. In the next section we define the disjoining pressure in FSSAF and calculate the thicknesses of the film layers, which are compressed by this pressure, by taking into account the smectic layer compressibility B profiles obtained from the microscopic model [34,35,38,40]. In Sec. III, using the formalism of a characteristic matrix M for a layered dielectric slab [42], we obtain an expression for the optical reflectivity of spatially nonuniform FSSAF with compressed smectic layers. Section IV presents the results of numerical calculations of the temperature dependences of the disjoining pressure, thicknesses of the film layers, their average thickness, and optical reflectivity for different free-standing Sm-*A* films, followed by a discussion.

II. DISJOINING PRESSURE AND COMPRESSION OF THE SMECTIC LAYERS IN FSSAF'S

Let us consider N -layer FSSAF with unit surface area. We also suppose this film to be in contact with a reservoir of a similar LC. This reservoir is necessary to provide a stable state of the film [1], because it compensates the molecular loss of the film caused by evaporation. Let us assume that the FSSAF under consideration undergoes a thinning by one smectic layer at both fixed temperature T and external pressure P_{ext} . It is obvious that LC molecules, which are lost by the film due to this thinning, transfer to the reservoir. Let F_N and F_{N-1} be the Helmholtz free energies of the initial N -layer and final $(N-1)$ -layer FSSAF, respectively, and F_{r1} be the free energy of the reservoir before thinning and F_{r2} the analogous free energy after thinning. Then the change ΔF of the total free energy of the system (FSSAF + reservoir) coming from such thinning is given by

$$\Delta F = (F_{N-1} + F_{r2}) - (F_N + F_{r1}). \quad (2)$$

When the temperature T is well below the bulk Sm-*A-N* or Sm-*A-I* transition temperature, a Sm-*A* phase similar to the smectic-*A* structure of the film occurs in the reservoir, and thinning the film by one smectic layer is equivalent to a simple transference of this layer in the space without any change of its state. Obviously, in this case the change ΔF of the total free energy of the system (FSSAF + reservoir) is practically equal to zero, and a work associated with thinning the film can be ignored.

The situation is quite different when the film under consideration undergoes thinning by one smectic layer above the

bulk Sm-A- N or Sm-A- I transition temperature. In this case a nematic or isotropic phase occurs in the reservoir, and the smectic layer transferring to it must undergo a transition to one of these less ordered states. Consequently, the change ΔF of the total free energy of the system (FSSAF + reservoir) associated with thinning the film differs from zero. For example, if FSSAF is formed of LC compound, in which the Sm-A phase transits to an isotropic state, which can be, for simplicity, considered as a state with zero free energy, then $F_{r1} = F_{r2} = 0$, and ΔF is simply equal to

$$\Delta F = F_{N-1} - F_N. \quad (3)$$

The value ΔF , which can be obtained from the model [34,35,38,40] for any N -layer FSSAF at any temperature T from the range of its existence, is equal to a work which must be performed on the film with unit surface area to decrease its thickness by one layer. This work is associated with an additional pressure

$$\Delta P = -\Delta F/L, \quad (4)$$

acting on the film layers from the boundary free surfaces. It has been shown [44] that this pressure, which is called the ‘‘disjoining pressure,’’ must occur in all confined liquid layers with structure different from that of a bulk liquid phase.

It should be noticed that we define here the disjoining pressure in terms of a finite change ΔF in the free energy associated with a finite change L in the film thickness by one smectic layer, whereas this pressure should be defined in terms of the change in the free energy corresponding to an infinitesimal change in the film thickness. The point is that the model [34,35,38,40] for FSSAF is a discrete model in which a minimum change in the film thickness, giving rise to a change in its structure, is the average thickness L of a single smectic layer. Since the disjoining pressure is associated with the structure of FSSAF, this minimum, but finite, change in the film thickness is considered here as infinitesimal.

When the value ΔF in Eq. (4) is positive, the disjoining pressure prevents the thinning of FSSAF, and the film layers are subjected to a stretching force. On the contrary, if $\Delta F < 0$, then the disjoining pressure promotes a thinning of the film, and its layers are subjected to a compressive force. We will see below that just the latter situation occurs in FSSAF’s upon their heating above the temperature of disappearance of the smectic order in the bulk LC sample.

An action of the disjoining pressure on the smectic layers of FSSAF should give rise to a change of their thicknesses. According to the Hooke law, the thickness L_i of an i th film layer can be defined as

$$L_i = L_0(1 - \Delta P/B_i), \quad (5)$$

where L_0 is the thickness of the smectic layer in the absence of the disjoining pressure, and B_i is the compressibility modulus of the i th layer of FSSAF. The values of these moduli can be determined from the following speculation. It is well known that the smectic layer compressibility modulus B in the bulk smectic-A phase is proportional to τ^2 , where τ

is the translational order parameter [43]. If we assume that this relationship is valid for smectic layers of FSSAF’s, then the elastic moduli B_i can be also found from the model [34,35,38,40]. The model allows us to determine the local orientational s_i and translational τ_i order parameters for each film layer at any temperature T within the interval of its existence. In addition, for very thick films ($N \rightarrow \infty$), this model gives the order parameters s_i and τ_i for the interior film layers which completely coincide with the results of well-known McMillan theory [45] for the bulk Sm-A phase. So if we know the value of the elastic constant B for the bulk Sm-A phase at a certain temperature T_0 [$B(T_0) \equiv B_0$], below the bulk Sm-A- I or Sm-A- N transition temperature, then from the model [34,35,38,40] we can find value of the order parameter $\tau(T_0) \equiv \tau_0$ at T_0 and, using the relationship

$$B_i(T) = B_0[\tau_i(T)/\tau_0]^2, \quad (6)$$

determine the values of the elastic moduli B_i for each layer of FSSAF of a given thickness at any temperature T within the interval of its existence.

III. REFLECTIVITY OF FREE-STANDING SMECTIC-A FILMS

In the calculation of reflectivity of the N -layer free-standing smectic-A film we consider the latter as a nonuniform dielectric slab consisting of layers with thicknesses L_i equal to those of the smectic layers of FSSAF and ‘‘local’’ refractive indices n_i . According to Ref. [42], optical properties of this slab are completely described by a characteristic 2×2 matrix M which in the case of the normal incidence of monochromatic light has the following elements:

$$M_{11} = M_{22} = 1, \quad (7)$$

$$M_{12} = -ik_0 \sum_{i=1}^N L_i, \quad (8)$$

$$M_{21} = -ik_0 \sum_{i=1}^N n_i^2 L_i. \quad (9)$$

The reflectivity R of such a layered dielectric slab is equal to

$$R = |r|^2, \quad (10)$$

where

$$r = [(M_{11} + M_{12}) - (M_{21} + M_{22})] / [(M_{11} + M_{12}) + (M_{21} + M_{22})]. \quad (11)$$

If the FSSAF is sufficiently thin ($N \leq 10$) and the wavelength of incident radiation is within the visible range, then the condition

$$k_0 \sum_{i=1}^N (n_i^2 + 1)L_i \ll 1$$

is satisfied, and a simple calculation leads to the following expression for R :

$$R \approx (k_0^2/4) \left[\sum_{i=1}^N (n_i^2 - 1) L_i \right]^2. \quad (12)$$

One can verify that if, as in Refs. [3,4,14–19], the film is assumed to be spatially uniform ($n_1 = n_2 = \dots = n_i = \dots = n_N = n_o$), then Eq. (12) transforms into Eq. (1).

The local refractive indices n_i of the layers of the FSSAF can be determined by means of a speculation analogous to that used above in the determination of the elastic moduli B_i . It is known that, for the bulk LC sample, the dependences of the ordinary n_o and extraordinary n_e refractive indices on the orientational order parameter s [43,46] can be written as follows:

$$n_o^2 = 1 + A[\bar{\beta} - (1/3)\Delta\beta s], \quad (13)$$

$$n_e^2 = 1 + A(\bar{\beta} + (2/3)\Delta\beta s), \quad (14)$$

where A is a certain constant essential to given LC compound, $\bar{\beta}$ is an average polarizability of the LC molecules, and $\Delta\beta$ is their polarizability anisotropy. If we know the values of these refractive indices for the bulk Sm-A phase at the above-mentioned temperature T_0 [$n_o(T_0) \equiv n_o^{(0)}$, $n_e(T_0) \equiv n_e^{(0)}$], below the bulk Sm-A-I or Sm-A-N transition temperature, then, from the model [34,35,38,40] we can find value of the orientational order parameter $s(T_0) \equiv s_0$ at T_0 and, combining Eqs. (13) and (14), determine the values $A\bar{\beta}$ and $A\Delta\beta$. Further, if we assume that, for FSSAF's, the local refractive indices n_i can be expressed in terms of the local orientational order parameters s_i in the same manner as for the bulk LC sample, then the local refractive indices can be calculated by means of Eqs. (13) and (14) by substituting into them the values $A\bar{\beta}$, $A\Delta\beta$ and the local order parameters s_i determined from the microscopic model [34,35,38,40]. In the case of the normal incidence of the monochromatic light, the final expression for the local refractive indices n_i is

$$n_i^2 = [(n_e^{(0)})^2 + 2(n_o^{(0)})^2]/3 - [(n_e^{(0)})^2 - (n_o^{(0)})^2](s_i/s_0). \quad (15)$$

Equations (12) and (15), as well as the above obtained Eqs. (4)–(6), allow us to determine the reflectivity R of the N -layer FSSAF at any temperature T within the interval of its existence.

IV. RESULTS OF NUMERICAL CALCULATIONS AND DISCUSSION

Numerical calculations of the disjoining pressure ΔP , thicknesses L_i of the film layers, their average thickness $L = (1/N)\sum_{i=1}^N L_i$, and reflectivity R have been carried out for FSSAF's consisting of $N = 10, 9, 8, 7$, and 6 smectic layers. These films are assumed to be created of LC exhibiting a ‘‘strong’’ first-order Sm-A-I phase transition. According to the McMillan theory [45] for the bulk Sm-A phase and the

microscopic model for FSSAF's proposed in Refs. [34,35,38,40], in this case the model parameter $\alpha = 2 \exp[-(\pi r_0/L)^2]$ used in the theory must be $\alpha \geq 0.98$. Here r_0 is a characteristic radius of the model pair potential proposed by McMillan. In our calculations we used $\alpha = 1.05$. This choice of value of the model parameter α is caused by the fact that LC compounds exhibiting such a bulk phase transition were used in measurements [17,19] of the optical reflectivity of FSSAF's. According to the McMillan theory, for $\alpha = 1.05$, the bulk Sm-A-I transition temperature is equal to $T_{AI} = 0.2249(V_0/k_B)$, where V_0 is the intermolecular interaction constant and k_B is the Boltzmann constant. The magnitude of the intermolecular interaction constant V_0 has been chosen to provide a coincidence between the absolute bulk Sm-A-I phase transition temperature T_{AI} given by theory and the experimentally found one (344 K [19]) for the partially perfluorinated LC compound H8F(4,2,1)MOPP. An orienting action of the boundary free surfaces of FSSAF's on the LC molecules is assumed to be strong enough. The ratio W/V_0 , where W is the interaction constant, which, in the framework of the model [34,35,38,40], determines the strength of the ‘‘effective field’’ simulating this action, has been set to $W/V_0 = 1.8$. According to the model, for such a sufficiently strong orienting action of the boundary free surfaces of the film on the LC molecules, the N -layer film does not rupture upon heating above the maximum temperature $T_c(N)$, but undergoes a layer thinning transition. Just the same phenomena were observed in experiments [17,19] on FSSAF's of the compounds H10F5MOPP, H8F(4,2,1)MOPP, and 54COOBC. The smectic layer spacing L_0 in the absence of the disjoining pressure has been set to $L_0 = 30\text{\AA}$ (typical value for LC's), and the smectic layer compressibility modulus B_0 for the bulk Sm-A phase is assumed to be determined at the temperature T_0 just below the bulk Sm-A-I transition temperature T_{AI} . As for its absolute value, it has been set to $B_0 = 5.5 \times 10^8 \text{ dyn/cm}^2$, which is about an order of magnitude larger than the typical values ($B_0 \sim 10^7 - 10^8 \text{ dyn/cm}^2$) for ordinary LC's composed of molecules with alkyl tails. Such very large values of the smectic layer compressibility modulus are typical for partially perfluorinated LC compounds [18,24,25] which form FSSAF's exhibiting layer-thinning transitions upon heating. For simplicity, the refractive indices $n_o^{(0)}$ and $n_e^{(0)}$ are also assumed to be determined at the temperature T_0 just below the bulk Sm-A-I transition temperature T_{AI} . The ordinary refractive index has been set to $n_o^{(0)} = 1.48$. This value was used in experimental papers [3,4,14–19]. As for the extraordinary refractive index $n_e^{(0)}$, in our calculations we use three of its values, namely, $n_e^{(0)} = 1.6, 1.65$, and 1.7. The reason for such a choice will be discussed later.

First of all, using the model [34,35,38,40] for FSSAF's of various thickness, we have calculated the disjoining pressure ΔP for all temperatures within the intervals of their existence. The dependence of ΔP on a reduced temperature $T^* = k_B T/V_0$ is shown in Fig. 1. The dependence obtained corresponds to heating the initially ten-layer FSSAF above the bulk Sm-A-I transition temperature T_{AI} . The heating gives

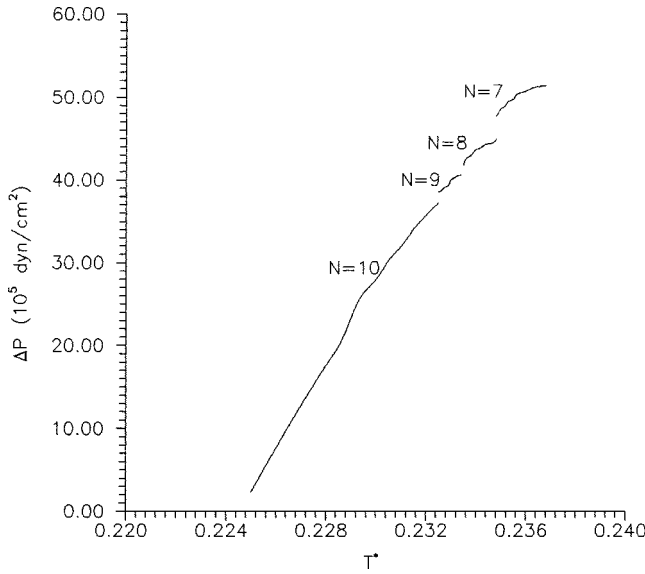


FIG. 1. Temperature dependence of the disjoining pressure ΔP upon heating initially ten-layer FSSAF above the bulk Sm-A-I transition temperature. Superscriptions ($N=10, \dots, N=7$) above distinct regions of the dependence denote corresponding numbers of the film layers.

rise to a sequence of layer-thinning transitions ($10 \rightarrow 9 \rightarrow 8 \rightarrow 7 \rightarrow \dots$) which are manifested as small jumps in the demonstrated dependence. These jumps separate it into distinct intervals describing the behavior of the disjoining pressure in ten-layer, nine-layer, eight-layer, and seven-layer FSSAF, respectively. This pressure is positive within each interval, and it grows monotonously with temperature reaching a maximum value at the maximum temperature of the existence of the film with a given number of smectic layers. Consequently, in all FSSAF's the smectic layers are subjected to the compressive force which grows upon heating. It can be easily seen that the maximum value $(\Delta P)_{max}$ of the disjoining pressure in the nine-layer film is larger than $(\Delta P)_{max}$ in the ten-layer film, $(\Delta P)_{max}$ in the eight-layer film is larger than that in the nine-layer one, etc. It is also seen that the absolute value of the disjoining pressure in the free-standing smectic-A films can be sufficiently large. So, for example, for seven-layer FSSAF, $(\Delta P)_{max}$ is about 5 times larger than atmospheric pressure.

Further, using the temperature dependence of the disjoining pressure obtained above and Eqs. (5) and (6), we have calculated the analogous dependences for the thicknesses of the film layers. The results obtained can be illustrated by means of Fig. 2, in which the film layer thickness profiles for ten-layer (curves 1 and 2) and nine-layer (curves 3 and 4) films are plotted. Curve 1 corresponds to ten-layer film at a temperature just below the bulk Sm-A-I transition point. It is seen that all film layers have the same thickness almost equal to the smectic layer spacing L_0 in the absence of the disjoining pressure. This result agrees with that shown in Fig. 1, according to which the disjoining pressure below the bulk Sm-A-I transition temperature T_{AI} is very small. Curve 2 presents the film layer thickness profile in the same film at a temperature just below the critical temperature $T_c(10)$ at

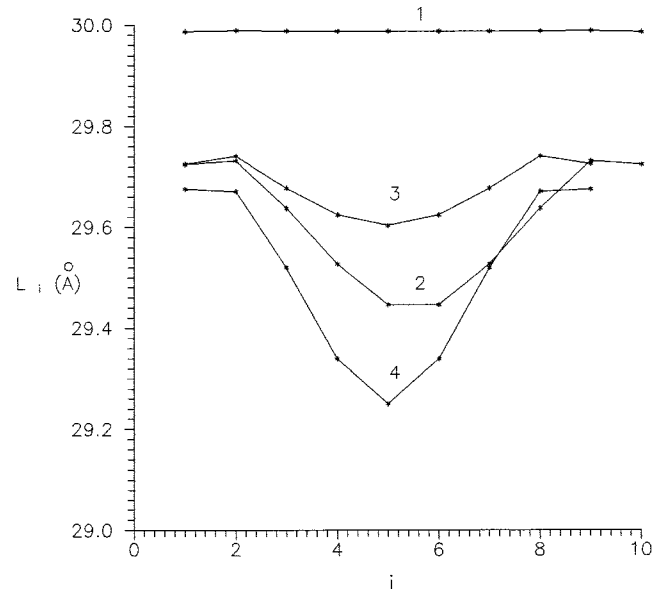


FIG. 2. Smectic layer thickness profiles in ten-layer and nine-layer FSSAF's: (1) ten-layer film at a temperature just below the bulk Sm-A-I transition temperature T_{AI} , (2) the same film at a temperature just below the critical temperature $T_c(10)$, (3) nine-layer film at a temperature just above $T_c(10)$, and (4) the same film at a temperature just below the critical temperature $T_c(9)$.

which the ten-layer film undergoes the thinning transition to the nine-layer one. This temperature is sufficiently higher than T_{AI} , and, according to Fig. 1, in such superheated FSSAF, the film layers are subjected to a significant disjoining pressure. Hence, all film layers must be compressed, and curve 2 clearly displays this fact. In addition, it is seen that the interior film layers are compressed much stronger than the outermost ones. This result is a direct consequence of the translational order parameter profile for superheated FSSAF's (for example, see Fig. 1 in Refs. [34,35]) predicted by the model [34,35,38,40]. According to this model, near the critical temperature $T_c(N)$, the translational order parameters τ_i in the interior of the N -layer film are significantly smaller than those in the outermost film layers. Since the smectic layer compressibility moduli B_i are proportional to τ_i^2 , then according to Eq. (5), the thicknesses L_i of the interior film layers must be smaller than those of the outermost ones. Curve 3 presents the film layer thickness profile in the nine-layer FSSAF just above the $10 \rightarrow 9$ transition temperature $T_c(10)$. It is seen that the thicknesses of the outermost film layers are almost the same as in the ten-layer film just before the thinning transition, whereas the thicknesses of the interior layers exhibit an observable growth. According to the model [34,35,38,40], this result is a direct consequence of a recovering of the translational order in the interior film layers upon thinning. As for curve 4, it shows the film layer thickness profile in the nine-layer FSSAF at a temperature just below its critical temperature $T_c(9)$. One can see again a significant growth of the compression of the film layers, and the thicknesses of the interior layers are significantly smaller than those in the ten-layer film just below $T_c(10)$. It should

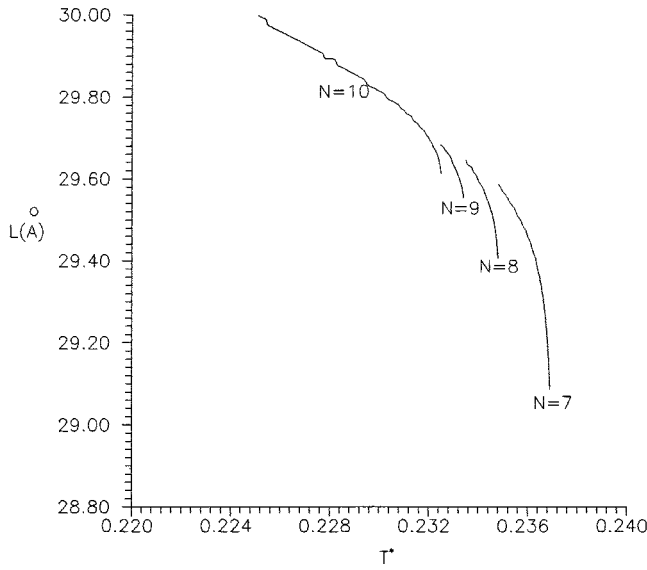


FIG. 3. Dependence of the average thickness L of smectic layers in different FSSAF's on the reduced temperature T^* . The initial FSSAF consists of ten smectic layers. Superscriptions denote the same as in Fig. 1.

be also added that similar behavior is obtained for other FSSAF's under consideration.

The results obtained allow us to calculate the temperature dependence of the average thickness L of the film layers, which was experimentally determined in Ref. [19]. This dependence is plotted in Fig. 3. As in Fig. 1, it consists of distinct intervals for ten-, nine-, eight-, and seven-layer FSSAF, respectively, separated by jumps at temperatures corresponding to the layer-thinning transitions. Within each interval, the average thickness L decays monotonously with temperature, reaching a minimum value at the maximum temperature of the existence of the film with a given number of smectic layers. However, thinning the film by one smectic layer gives rise to a discontinuous growth of L . A simple qualitative explanation of this theoretical finding, which is in good agreement with results of experiments [19] on FSSAF's of the LC compound H8F(4,2,1)MOPP, is the following. As said above, the model [34,35,38,40] predicts the monotonous growth of the disjoining pressure in the N -layer free-standing film upon heating up to the highest temperature $T_c(N)$ of its existence (see Fig. 1) Furthermore, the model predicts that heating the film gives rise also to a decrease of the local orientational $s_i(T)$ and translational $\tau_i(T)$ order parameters and, hence, to a decay of the film layer compressibility moduli B_i . Consequently, according to Eq. (5), the thicknesses L_i of the film layers should decrease with increasing temperature (see Fig. 2, curves 2 and 4). When the limit temperature $T_c(N)$ is reached, the N -layer film loses one smectic layer, and such a thinning, according to the model [34,35,38,40], gives rise to a discontinuous growth of both the disjoining pressure ΔP and local order parameters $s_i(T)$ and $\tau_i(T)$. However, a jump in the value of the disjoining pressure is small enough (see Fig. 1), whereas a discontinuous growth of the local order parameters $\tau_i(T)$, and, consequently, the moduli B_i , is very substantial. As a result,

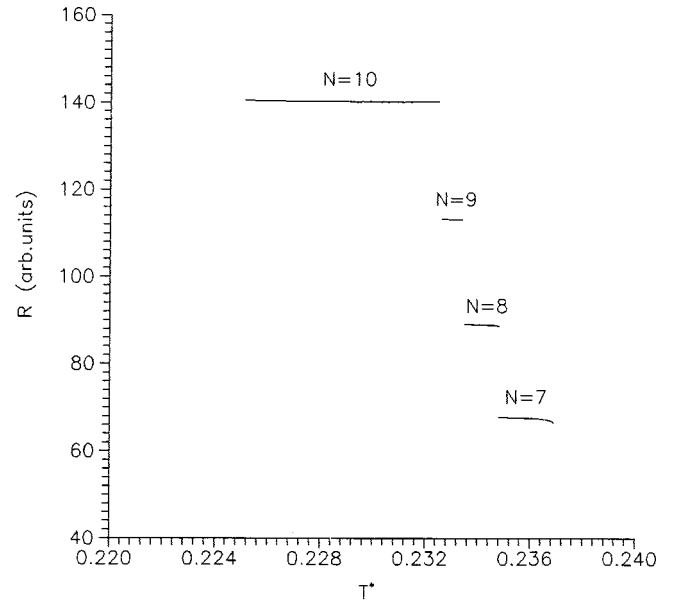


FIG. 4. Analogous dependence for the reflectivity R . $n_e^{(0)} = 1.6$. Superscriptions denote the same as in Figs. 1 and 2.

according to Eq. (5), the thicknesses L_i of the smectic layers of $(N-1)$ -layer FSSAF should undergo a discontinuous growth with respect to those of the N -layer one (see Fig. 2, curve 3). It should be also noted, that calculated minimum values of the average layer thickness L in the N -layer film, which are reached at the limit temperature $T_c(N)$, decay with decreasing number N of the film layers (see Fig. 3) because of growth of the maximum value of the disjoining pressure (see Fig. 1). This result, as well as the order of magnitude ($\sim 1\text{\AA}$) of the calculated absolute value of the decrease of the average thickness L of the film layers, is in good agreement with the experiment [19].

Using Eqs. (12) and (15), we have also calculated the temperature dependence of the reflectivity R for initially ten-layer FSSAF upon heating above the bulk Sm-A-I transition temperature T_{AI} (see Fig. 4). In this calculation we used previously calculated temperature dependences of the thicknesses L_i of the film layers. As said above, used in the calculation the value of the ordinary refractive index $n_o^{(0)}$ for the bulk Sm-A phase is set to $n_o^{(0)} = 1.48$. As for the value $n_e^{(0)}$ of the extraordinary refractive index for the bulk smectic-A phase, in the calculation of the dependence depicted in Fig. 4, it has been chosen to be $n_e^{(0)} = 1.6$. The reason for this choice is the following. As a rule, for LC's composed of molecules with the usual alkyl tails, the birefringence $\Delta n = n_e - n_o$ is of the order of 0.2 [46]. However, substituting hydrogen atoms in alkyl tails by fluorine ones significantly lowers the magnitude of Δn [19]. Since in Ref. [19] the reflectivity of FSSAF's of partially perfluorinated LC H8F(4,2,1)MOPP has been measured and we compare the results of our calculations with data present in this paper, the value Δn has been set to be about twice smaller than for the usual LCs. Similarly to the above-mentioned temperature dependences of ΔP and L , depicted in Figs. 1 and 3, respectively, the temperature dependence of the reflectivity R

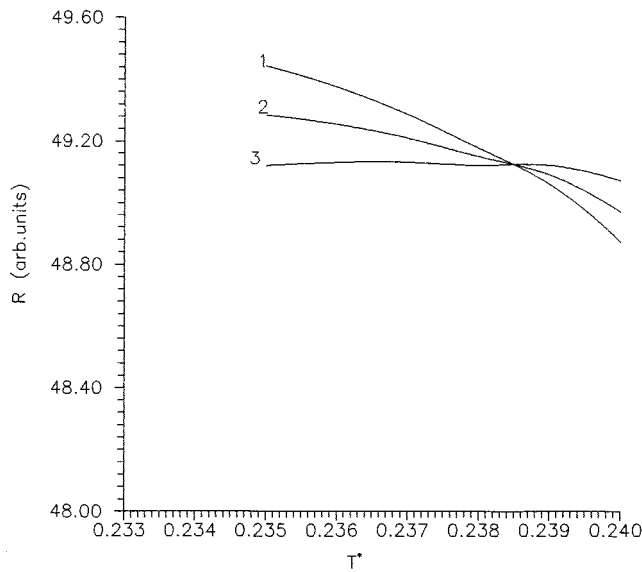


FIG. 5. Temperature dependences of the reflectivity R of six-layer FSSAF for different values of the extraordinary refractive index $n_e^{(0)}$ in the bulk Sm-A phase: (1) $n_e^{(0)}=1.6$, (2) $n_e^{(0)}=1.65$, and (3) $n_e^{(0)}=1.7$.

shown in Fig. 4 consists of distinct regions (steps) separated by discontinuities corresponding to layer-thinning transitions in FSSAF. Each step describes the temperature dependence of R for the film with a given number of smectic layers. It is seen that these steps have a small negative slope that is completely in agreement with results of experiment [19].

Finally, we have investigated dependence of behavior of the reflectivity of FSSAF with a given number of layers of the value $n_e^{(0)}$ of the extraordinary refractive index in the bulk LC sample. The temperature dependences of the reflectivity R of the six-layer film calculated for $n_e^{(0)} = 1.6, 1.65$, and 1.7 , respectively, at the same value of the smectic layer compressibility modulus $B_0 = 5.5 \times 10^8$ dyn/cm², are shown in Fig. 5. It is seen that, for the two first values of $n_e^{(0)}$, the reflectivity of the film decays monotonously with increasing temperature, and for $n_e^{(0)}=1.6$, this decay is about twice faster than for $n_e^{(0)}=1.65$. For $n_e^{(0)}=1.7$, the reflectivity of the film is practically independent of temperature. A qualitative explanation of these results is the following. From Eqs. (12) and (15) it follows that the behavior of the reflectivity R of FSSAF with a given number N of smectic layers is gov-

erned by two competing processes. The first of them is a decrease of the thicknesses L_i of the smectic layers caused by both the growth of the disjoining pressure ΔP and the decrease of the elastic moduli B_i with increasing temperature. The second process is an increase of the local refractive indices n_i caused by, according to Eq. (15), decay of the local orientational order parameters s_i in the film upon heating. From Eq. (15) it also follows that the larger difference between refractive indices $n_e^{(0)}$ and $n_o^{(0)}$, the stronger the growth of the local refractive indices n_i and vice versa. Consequently, when the birefringence Δn is small, the second of the competing processes is less important than the first one, and the reflectivity of the film decreases with increasing temperature. If we take a larger value of Δn , then the decay of R becomes slower. Finally, when the value of Δn for the bulk Sm-A phase is sufficiently large, the growth of the local refractive indices n_i can completely compensate the thinning the film layers, and the reflectivity of FSSAF will not change upon heating. This theoretical result allows us to account for the difference mentioned in the Introduction in the behavior of FSSAF's prepared of the partially perfluorinated LC's, H10F5MOPP and H8F(4,2,1)MOPP, and LC 54COOBC composed of molecules with ordinary alkyl tails. As said above, the birefringence of the perfluorinated LC compounds should be smaller than that of the hydrogenated ones. Therefore, heating FSSAF's formed of H10F5MOPP and H8F(4,2,1)MOPP gives rise to a decrease of their reflectivities. On the contrary, the birefringence Δn of the hydrogenated LC compound 54COOBC should be $\Delta n \sim 0.2$. At the same time, this LC exhibits a "strong" first-order Sm-A- I phase transition similar to those exhibited by the perfluorinated compounds, whereas most hydrogenated mesogens demonstrate either a "weak" first-order or second-order Sm-A- N phase transition. Therefore, for LC 54COOBC, the smectic layer compressibility modulus B_0 is assumed to be similar to that for the perfluorinated mesogens. Then its behavior should correspond to curve 3 in Fig. 5, and heating free-standing films of 54COOBC with a given number N of smectic layers does not change their reflectivities.

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