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Free surface-induced bilayer smectic A phase in polar liquid crystals

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Here the influence of the free surface on both a thick (semi-infinite) layer and a thin freely suspended film of a polar liquid crystal is investigated. It is shown that within the temperature range of the monolayer smectic A phase (S_{A_1}) the interaction between polar molecules and the free surface of the liquid crystal gives rise to a bilayer smectic A, a structure with long range antiferroelectric order (S_{A_2}) in the surface region of the semi-infinite layer. The dependence of the bilayer smectic order parameter on the strength of the interaction between the constituent molecules and the free surface as well as temperature and the distance to the free surface are determined. Sufficiently far from the S_{A_1}–S_{A_2} transition the latter dependence has an exponential character and the depth of the S_{A_2} phase penetration into bulk liquid crystal is equal to the longitudinal correlation length for the bilayer smectic A structure fluctuations in the S_{A_1} phase. However, near the S_{A_1}–S_{A_2} transition the bilayer smectic order parameter decays non-exponentially and more rapidly with increasing distance to the free surface. In addition, it is found that the bilayer S_{A_2} phase can form several smectic layers at the free surface of a semi-infinite polar liquid crystal layer with the S_{A_1} phase. Finally, it is shown that in a freely suspended film the free surface-induced S_{A_2} phase can completely occupy the volume of the sample. Hence in a freely suspended polar liquid crystal film the S_{A_1}–S_{A_2} transition occurs with decreasing film thickness.

1. Introduction

It is known that both a free surface and an interface between different media have a considerable influence on phase diagrams and the thermodynamical properties of various systems, including liquids and liquid crystals [1]. For example the liquid–solid substrate interface not only imposes some orientational order on the isotropic phase of liquids having a nematic phase [2–6] but also induces orientational ordering in non-mesogenic liquids [7]. Furthermore in [8–12] it has been shown that the smectic A phase can be formed at both the free surface of a nematic and a nematic–solid substrate interface, and such a surface-induced smectic A phase can be revealed by means of the Freedericksz transition [13].

The influence of the surface on strongly polar liquid crystals consisting of molecules having end groups (–CN or –NO_2) with a large permanent electric dipole moment (~ 4 D) is particularly interesting. The point is that various types of smectic A phase, namely monolayer smectic A (S_{A_1}) with a layer thickness d nearly the equal to molecular length l (see figure 1 (*a*)), partial bilayer smectic A (S_{A_d}) with $l<d<2l$, and bilayer S_{A_2} and $S_{\tilde{A}}$ phases in which a monolayer smectic A structure coexists with bilayer structures ($d \approx 2l$) with long range antiferroelectric order (see figures 1 (*b*) and (*c*), respectively) occur [14, 15]. The direct transitions between these smectic A phases (S_{A_1}–S_{A_2}, S_{A_1}–$S_{\tilde{A}}$–S_{A_2}, S_{A_d}–S_{A_2} etc.) have been observed [14–16]. Therefore, we can

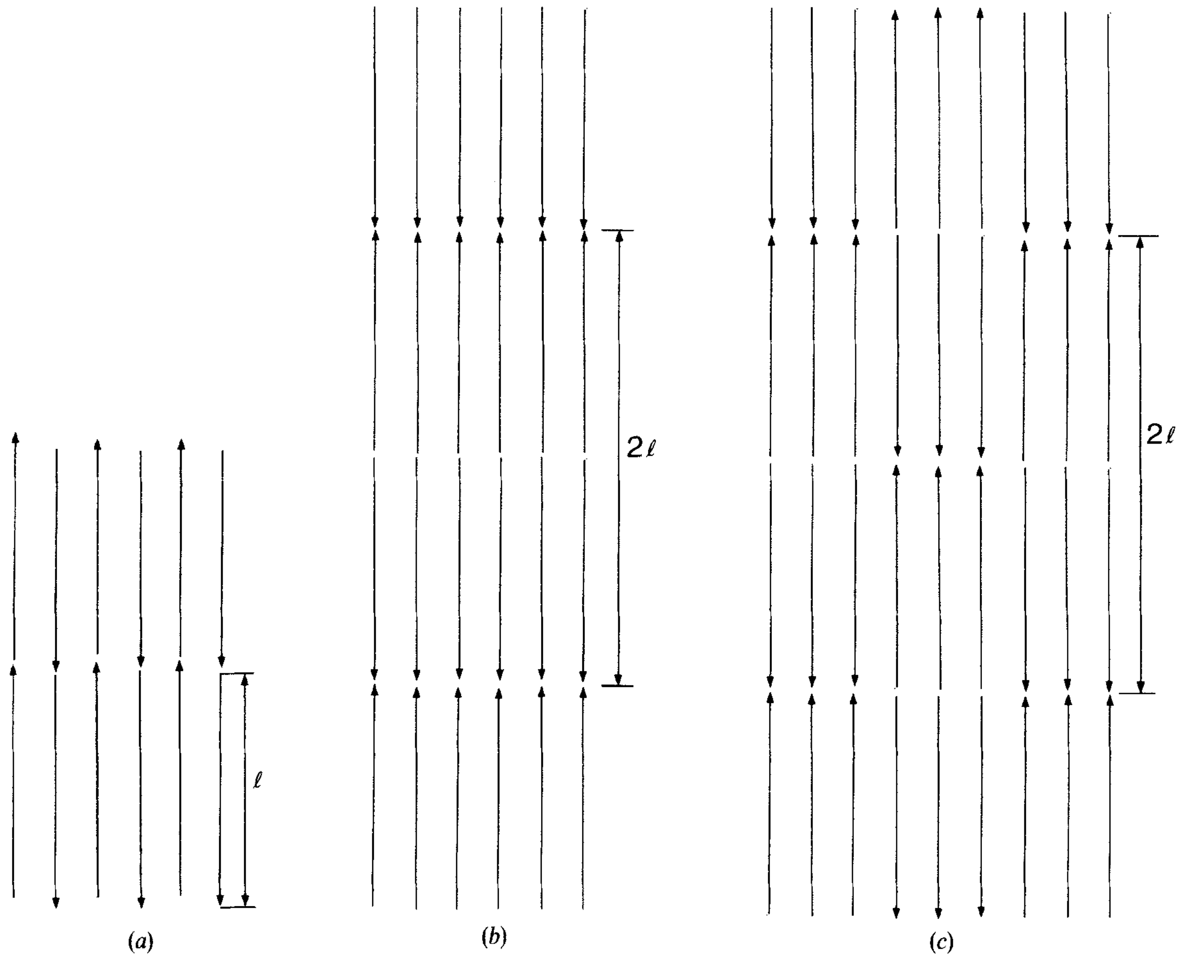

Figure 1. Smectic A structures existing in polar liquid crystals. (a) Monolayers S_{A1} phase ($d=l$). (b) Bilayer smectic A structure in a S_{A2} phase ($d=2l$). (c) Bilayer smectic A structure in a $S_{\tilde{A}}$ phase ($d=2l$).

expect particularly interesting changes in the phase diagrams of such systems to be caused by the interaction between the mesogenic molecules and the surface, for example, surface-induced transitions between different smectic A phases and the coexistence of several smectic A phases.

X-ray studies show that several layers of the bilayer S_{A_2} phase are formed at a free surface of a polar liquid crystal which exhibits only a monolayer S_{A_1} phase [17, 18]. This effect has not been observed in classic smectic A phases consisting of non-polar molecules. The following qualitative explanation of such a phenomenon has been given in [17, 18]. The free surface of the liquid crystal induces not only a homeotropic orientation of the polar molecules in the first surface layer, but also aligns the molecular polar heads into the bulk phase and the aliphatic tails towards the free surface. The next layer has the opposite orientation, and so on. As a result, there appears at the free surface the bilayer S_{A_2} phase with long range antiferroelectric order.

Here a theoretical description of this phenomenon is offered. This description is based on both de Jeu and Longa's microscopic models for the S_{A_1} and S_{A_2} phases in polar liquid crystals [19] and Parsons's idea of polar ordering of mesogenic molecules by a free surface [20]. It is shown that the interaction between polar molecules and the free surface of a thick (semi-infinite) layer results in the appearance of a surface-induced S_{A_2} phase at any temperature within range of the S_{A_1} phase in the bulk sample. The dependence of the bilayer smectic order parameter on the strength of the molecule–free surface interaction as well as temperature and the distance to the free surface are determined. Sufficiently far from the S_{A_1}–S_{A_2} transition in the bulk sample the latter dependence has an exponential character and the depth of the S_{A_2} penetration into the bulk is equal to the longitudinal correlation length for the bilayer smectic A fluctuations in the S_{A_1} phase. However, in the vicinity of the S_{A_1}–S_{A_2} transition the bilayer smectic order parameter decreases non-exponentially and more rapidly with decreasing distance to the free surface. The depth of S_{A_2} penetration into the bulk of the semi-infinite layer is found to be equal to several molecular lengths. It is also shown that in a thin freely suspended polar liquid crystal film the free surface-induced S_{A_2} phase can occupy a sample completely, i.e. the S_{A_1}–S_{A_2} transition occurs with decreasing film thickness.

2. Free energy density in a polar liquid crystal layer with regard to the interaction between the molecules and the free surface

Let us consider a polar liquid crystal layer having a free surface. The temperature is assumed to be within the S_{A_1} range for an infinite and homogeneous sample of the same material. For simplicity let us assume that the orientational order is perfect (the long axes of all the molecules are oriented parallel to the director **n**). This assumption is reasonable because the observed N–S_{A_1} transition temperatures in polar materials are considerably lower than those of the I–N transitions [14, 16]. The director **n** is assumed to be aligned along the z axis which is normal to the free surface of the layer and $z=0$ at this surface.

According to de Jeu and Longa's theory [19] in a mean field approximation the thermodynamic properties of an infinite and homogeneous sample of polar liquid crystals with perfect orientational order are completely described by the single particle distribution function.

$$P(z,s)=1+2\sigma_1\cos(2\pi z/l)+2s\sigma_2\cos(2\pi z/2l), \tag{1}$$

where σ_1 and σ_2 are the coordinate independent monolayer and bilayer smectic order parameters, respectively. They are defined by the self-consistent equations

$$\left.\begin{aligned}\sigma_1&=\langle\cos(2\pi z/l)\rangle_s,\\ \sigma_2&=\langle s\cos(2\pi z/2l)\rangle_s,\end{aligned}\right\} \tag{2}$$

and

$$\langle A(z,s)\rangle_s=\int_0^{2l}A(z,s)P(z,s)\,dz\bigg/\int_0^{2l}P(z,s)\,dz, \tag{3}$$

where s is the variable defining the molecular orientation ($s=+1$ for molecules with the dipole moment aligned parallel to the director and $s=-1$ for molecules aligned in the opposite direction). It is easily seen that the first term in equation (1) describes the nematic phase and both second and third terms describe the monolayer smectic A structure depicted in figure 1 (*a*) and the bilayer smectic A structure with long range antiferroelectric order depicted in figure 1 (*b*). When $\sigma_1=\sigma_2=0$ then the nematic phase is found; when $\sigma_1\neq0$ and $\sigma_2=0$ then the S_{A_1} phase is observed and finally, when $\sigma_1\neq0$ and $\sigma_2\neq0$ then the S_{A_2} phase occurs. In a mean field approximation the single particle distribution function can be represented as

$$P(z,s)=A^{-1}\exp[-V(z,s)/kT], \tag{4}$$

where $V(z,s)$ is the single particle molecular field pseudopotential and A is the normalization constant. When the pair potentials for the intermolecular interactions are assumed to be even functions of the distance between molecular centres, then the pseudopotential in equation (4) can be represented in its simplest form [21, 22]

$$V(z,s)=-[V_1\sigma_1\cos(2\pi z/l)+sV_2\sigma_2\cos(2\pi z/2l)], \tag{5}$$

where both V_1 and V_2 are the effective interaction constants. The free energy density f_0 in a mean field approximation is given by

$$f_0=-(N/2)\frac{1}{2}\sum_{s=\pm1}\langle V(z,s)\rangle_s-NkT\langle\ln P(z,s)\rangle_s, \tag{6}$$

where N is the number density. In order to obtain the phase diagram it is necessary to solve the self-consistent equations (2) and select from all possible solutions ($\sigma_1=\sigma_2=0$; $\sigma_1\neq0$, $\sigma_2=0$; $\sigma_1\neq0$, $\sigma_2\neq0$) the solution minimizing the free energy density in equation (6).

However, for the convenience of our further consideration, taking into account both the interaction between the molecules and the free surface, and the liquid crystal layer inhomogeneity caused by such interaction we can use the following Landau expansion of the free energy density given by equation (6) in a series of σ_1 and σ_2 parameters

$$\left.\begin{aligned}f_0&=NKTf'_0,\\ f'_0&=A_1\Psi^2+A_2\Phi^2-B\Psi\Phi^2+C_1\Psi^4+C_2\Phi^4+\ldots,\end{aligned}\right\} \tag{7}$$

where

$$\Psi=\sigma_1/T^*,\quad \varphi=\sigma_2/T^*,\quad A_1=\tfrac{1}{2}(T^*-\tfrac{1}{2}),\quad A_2=\frac{\alpha}{2}\left(T^*-\frac{\alpha}{2}\right),\quad B=\alpha^2/8,$$

$$C_1=1/64,\quad C_2=\alpha^4/64,\quad \alpha=V_2/V_1\quad\text{and}\quad T^*=kT/V_1$$

is the reduced temperature. Then in order to obtain the phase diagram of the liquid crystal it is sufficient to minimize the free energy density given by equation (i.e. to solve the equations $\partial f_0/\partial \Psi = 0$ and $\partial f_0/\partial \varphi = 0$) and to select the solution corresponding to the minimum value of f_0. It can be shown that when $\alpha < 0{\cdot}7$ then the phase sequence N–S_{A_1}–S_{A_2} occurs and the S_{A_1}–S_{A_2} transition is second order at $\alpha < 0{\cdot}35$. For the convenience of our further investigation we shall consider systems deep in the S_{A_1} phase when according to experiment [14–16] the possible S_{A_1}–S_{A_2} transition is second order in most polar compounds. Therefore, we shall set $\alpha < 0{\cdot}35$.

Further we have to take into account the interaction between the polar molecules and the free surface. In [17, 18] it is assumed that the free surface induces polar ordering of such molecules in the first surface layer (the polar molecular heads are aligned into the bulk and aliphatic tails towards the free surface). The possibility of this type of ordering was first discussed by Parsons [20]. He supposes that the energy of interaction between the polar molecules and free surface is of the form $-(\mathbf{n}\cdot\mathbf{v})$, where $\mathbf{v}$ is the unit vector normal to the free surface. When the z axis is parallel to $\mathbf{v}$ and there is perfect orientational order then such an interaction energy can be written as

$$G(z, s) = -G_0(z)s \tag{8}$$

where $G_0(Z)$ is an unknown function which decreases very rapidly with increasing distance to the free surface (the characteristic decay length for this function is of the order of a molecular length). It is easily seen from equation (8) that in the first surface layer the molecular orientation with the polar heads aligned into the bulk ($s = +1$) is energetically more favourable than that in the opposite direction ($s = -1$). Then, the contribution of the interaction between the polar molecules and the free surface to the free energy density is given by

$$f_1 = -\tfrac{1}{2}N \sum_{s=\pm 1} G(z, s)P(z, s). \tag{9}$$

Finally, we should take into account the inhomogeneity of the system (i.e. the dependence of both σ_1 and σ_2 on the z coordinate) caused by the interaction between the molecules and the free surface. When the liquid crystal layer is assumed to be homogeneous in the plane of the free surface then the (xy) dependence of both σ_1 and σ_2 can be neglected. Indeed, as a result of such interaction the values of the smectic order parameters at the free surface must differ from those in the bulk. The layer inhomogeneity along the z axis can be taken into account by adding to expression (7) for the free energy density of a homogeneous sample terms proportional to $(d\sigma_1/dz)^2$ and $(d\sigma_2/dz)^2$ [15]. Furthermore, we can use the assumption of the occurrence of a deep S_{A_1} phase when the value of the order parameter σ_1 is sufficiently large and stable. Then we can neglect the term proportional to $(d\sigma_1/dz)^2$ and so the contribution to the free energy density caused by the layer inhomogeneity is given by

$$f_2 = K\left(\frac{d\sigma_2}{dz}\right)^2, \tag{10}$$

where K is analogous to an elastic constant. Thus, the free energy density in a polar liquid crystal layer with regard to the interaction between the molecules and the free surface is given by

$$f(z) = f_0(\sigma_1, \sigma_2(z)) + K\left(\frac{d\sigma_2}{dz}\right)^2 + (N/2) \sum_{s=\pm 1} G(z, s)P(z, s). \tag{11}$$

3. Free surface-induced S_{A_2} phase in a semi-infinite layer of a polar liquid crystal

Up to now we have not been interested in the thickness ($2L$) of the layer. We can consider two different cases, namely very thick layer ($2L \rightarrow \infty$) and a layer of finite thickness. In the first place let us investigate the former case when we need consider only one half of the layer adjoining the free surface. Because of the infinitely large thickness the properties of this half of the sample are completely independent of the second boundary surface ($z = 2L \rightarrow \infty$). In addition, for a very thick (semi-infinite) layer the properties of the sample in the bulk ($z = L$) can be considered as identical to those of an infinite homogeneous liquid crystal sample [1].

In order to obtain the total free energy of half of the sample per unit area of the free surface we must integrate expression (11) over z from 0 to L We have also to take into account that although the order parameter σ_2 is a function of z it cannot vary considerably within a distance of the order of a molecular length l, otherwise the definition of the order parameter given by equation (2) is not valid. Then, remembering that the characteristic decay length of the interaction between the molecules and the free surface is of the order of the molecular length we can obtain the contribution of such interactions to the total free energy of half of the layer as

$$F_1 = \int_0^L f_1(z)\,dz = -NkTg\Phi_0, \tag{12}$$

where

$$g = (2/V_1)\int_0^L G_0(z)\cos(2\pi z/2l)\,dz, \tag{13}$$

$\Phi_0 = \sigma_{20}/T^*$ and σ_{20} is the value of the parameter σ_2 at the free surface ($z = 0$), Finally the total free energy of half the layer per unit area of free surface is given by

$$(F/NkT) = \int_0^L \left[f'_0(\Psi_0, \Phi(z)) + K^*T^*\left(\frac{d\Phi}{dz}\right)^2 \right] dz - g\Phi_0' \tag{14}$$

where $\Psi_0 = \sigma_{10}/T^*$, σ_{10} is the value of the monolayer smectic order parameter (assumed to be homogeneous over the whole sample), $\Phi(Z) = \sigma_2(Z)/T^*$ and $K^* = K/NV_1$. Expression (14) is completely analogous to that for the free energy of a semi-infinite nematic layer in contact with a solid substrate [1]. The functional equation (14) must be minimized with respect to $\Phi(z)$ and Φ_0. Minimization with respect to $\Phi(z)$ with due regard for the homogeneity of the Φ order parameter in the bulk of the layer

$$\left.\frac{d\Phi}{dz}\right|_{z=L} = 0 \tag{15}$$

leads to

$$K^*T^*\left(\frac{d\Phi}{dz}\right)^2 = f'_0(\Psi_0, \quad \Phi(z)) - f'_0(\Psi_0, \Phi_b) \tag{16}$$

and

$$(F/NkT) = f'_0(\Psi_0, \Phi_b)L + 2\int_0^L [f'_0(\Psi_0, \Phi(z)) - f'_0(\Psi_0, \Phi_b)]\,dz - g\Phi_0 \tag{17}$$

where Φ_b is the value of the parameter Φ in the bulk of layer ($z=L$). Further, from (16) we find that

$$dz=\sqrt{(K^*T^*)}[f'_0(\Psi_0,\Phi(z))-f'_0(\Psi_0,\Phi_b)]^{-1/2}\,d\Phi \tag{18}$$

and hence

$$F/(NkT\xi_0\sqrt{T^*})=\frac{f'_0(\Psi_0,\Phi_b)L}{\xi_0\sqrt{T^*}}+2\int_{\Phi_b}^{\Phi_0}[f'_0(\Psi_0,\Phi)-f'_0(\Psi_0,\Phi_b)]^{1/2}\,d\Phi-\frac{g'}{\sqrt{T^*}}\Phi_0, \tag{19}$$

where

$$\xi_0=\sqrt{K^*} \quad \text{and} \quad g'=g/\xi_0.$$

Since the properties of the semi infinite layer in the bulk are identical to those of an infinite homogeneous sample at the same temperature, Φ_b in equation (19) is equal to zero (the S_{A_1} phase occurs in the bulk of the layer). The value of Ψ_0 can be obtained by minimization of the free energy density in equation (7) for the S_{A_1} phase (under the condition $\Phi=0$). The value of Ψ_0 obtained is

$$\Psi_0=4(\tfrac{1}{2}-T^*)^{1/2}. \tag{20}$$

It is easily seen that the first term in equation (19) describes the bulk contribution to the free energy of half of the layer and the other two terms give us the surface part of the free energy. Simple integration leads to the following expression for this surface part of the free energy:

$$\begin{aligned}(F/NkT\xi_0\sqrt{T^*})_{\text{surface}}=\frac{2}{3c_2}\{[(A_2-B\Psi_0)+C_2\Phi_0^2]^{3/2}\\ -(A_2-B\Psi_0)^{3/2}\}-\frac{g'}{\sqrt{T^*}}\Phi_0,\end{aligned} \tag{21}$$

Minimizing this expression with respect to Φ_0 we can obtain

$$\Phi_0^2=-\frac{16}{\alpha^3}\left[\left(T^*-\frac{\alpha}{2}\right)-\alpha(\tfrac{1}{2}-T^*)^{1/2}\right]+\left\{\frac{256}{\alpha^6}\left[\left(T^*-\frac{\alpha}{2}\right)-\alpha(\tfrac{1}{2}-T^*)^{1/2}\right]^2+\frac{16g'^2}{\alpha^4T^*}\right\}^{1/2}. \tag{22}$$

It is easily seen that this expression gives a non-zero value for Φ_0 at any temperature T^* (if $g'\neq 0$). In addition, we can verify that the substitution of equation (22) into equation (21) always leads to a negative value of the surface part of the free energy. Therefore, we can conclude that the existence of the bilayer S_{A_2} phase at the free surface of a thick (semi-infinite) polar liquid crystal layer with the S_{A_1} phase in the bulk is energetically favourable at any temperature. In other words the S_{A_2} phase always occurs at the free surface of a thick polar liquid crystal sample with a S_{A_1} phase. The appearance of the region of the bilayer smectic A phase at the free surface of such a sample does not have the character of a phase transition. The temperature T^* as well as the reduced interaction strength g' only influence the value of the surface bilayer smectic order parameter σ_{20}. The dependence of σ_{20} on the strength of the interaction between polar molecules and the free surface is shown in figure 2. The parameter $T_R^*=T^*-T_C^*)/T_C^*$ where T_C^* is the reduced temperature of the S_{A_1}–S_{A_2} second order transition in the bulk of a thick layer (at the chosen value of $\alpha=0{\cdot}3$ $T^*=0{\cdot}288$) is often used in papers on critical phenomena. As expected the bilayer smectic order parameter at the free surface

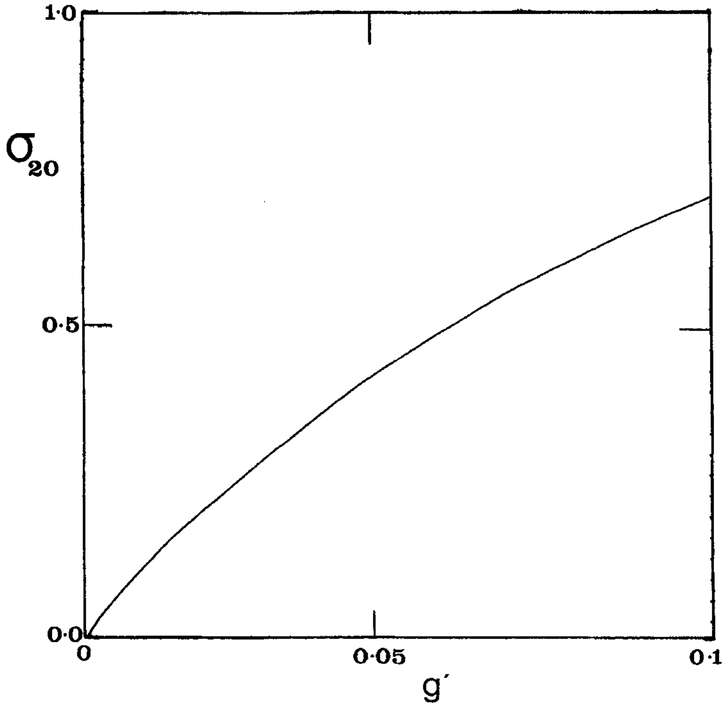

Figure 2. The dependence of the surface bilayer smectic order parameter σ_{20} on the strength of the interaction between polar molecules and the free surface. $\alpha=0{\cdot}3$; $T_R^*=0{\cdot}01$.

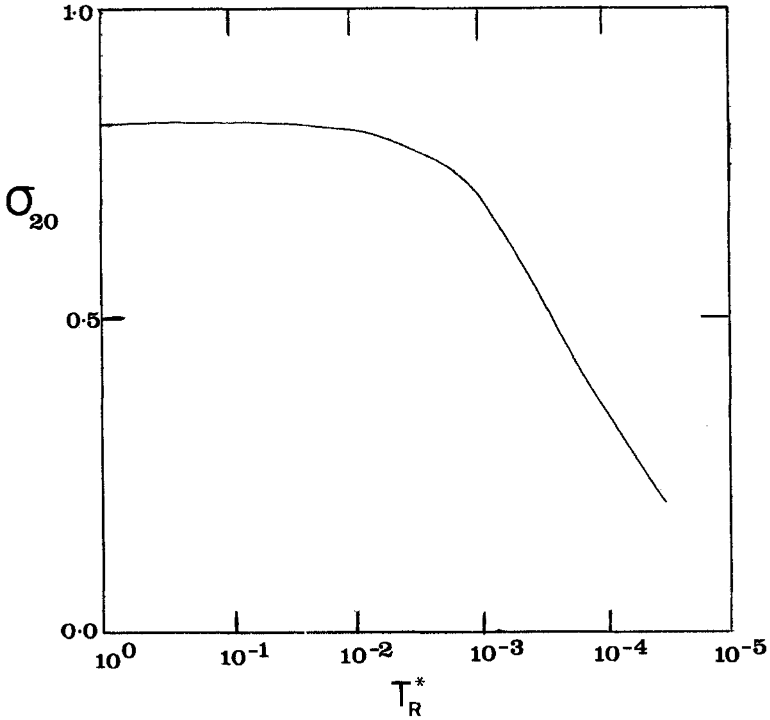

Figure 3. The temperature dependence of the order parameter σ_{20}. $\alpha=0{\cdot}3$; $g'=0{\cdot}1$.

is proportional to the strength of the interaction between the molecules and the free surface and at small values of g' the dependence of σ_{20} on g' has a linear character. The temperature dependence of σ_{20} at fixed interaction strength ($g'=0{\cdot}1$) is shown in figure 3. The bilayer smectic order parameter at the free surface increases with decreasing parameter T^*_R (i.e. approaching the temperature of the S_{A_1}–S_{A_2} transition) and achieves a sufficiently large value at the transition ($\sigma_{20}=0{\cdot}828$ at $T^*_R=0$). It should be noted that the saturated surface bilayer smectic order has been observed experimentally [17].

One of the most important characteristics of the phenomena considered is the depth of the surface S_{A_2} phase penetration into the bulk of the layer with a S_{A_1} phase. In order to determine this characteristic we can use equation (18) and after simple integration we obtain the following dependence of the bilayer smectic order parameter on the distance to the free surface

$$Z/\xi_{\parallel}=\tfrac{1}{2}\left\{\ln\frac{H_0-a_0}{H_0+a_0}-\ln\frac{H(z)-a_0}{H(z)+a_0}\right\}, \tag{23}$$

where

$$a_0=\left\{\frac{\alpha}{2}\left[\left(T^*-\frac{\alpha}{2}\right)-\alpha(\tfrac{1}{2}-T^*)^{1/2}\right]\right\}^{1/2},$$

$$H_0=\left[a_0^2+\frac{\alpha^4}{64}\Phi_0^2\right]^{1/2},$$

$$H(z)=\left[a_0^2+\frac{\alpha^4}{64}\Phi^2(z)\right]^{1/2},$$

and

$$\xi_{\parallel}=\xi_0\sqrt{(T^*/a_0)}$$

is the longitudinal correlation length of the S_{A_2} fluctuations in the vicinity of the S_{A_1}–S_{A_2} second order transition. Analysis of expression (23) leads us to the following results. When the temperature is sufficiently higher than that of the S_{A_1}–S_{A_2} second order transition in the liquid crystal bulk ($a_0^2\gg(\alpha^4/64)\Phi_0^2$) then expression (23) may be simplified and we can obtain a simple exponential dependence of the bilayer smectic order parameter on the distance to the free surface

$$\Phi(z)/\Phi_0=\sigma_2(z)/\sigma_{20}=\exp(-z/\xi_{\parallel}). \tag{24}$$

If the depth ξ_p of the surface S_{A_2} phase penetration into the bulk with a S_{A_1} phase is defined as the distance to the free surface at which the bilayer smectic order parameter is e times smaller than that at the free surface, than according to equation (24) this depth coincides with the longitudinal correlation length for S_{A_2} phase fluctuations in the S_{A_1} phase. However, in the vicinity of the S_{A_1}–S_{A_2} transition in the bulk (when $a_0^2\ll(\alpha^4/64)\Phi_0^2$) relation (23) leads us to a non-exponential dependence of the bilayer smectic order parameter on the distance to the free surface

$$\Phi(z)/\Phi_0=\sigma_2(z)/\sigma_{20}=\left[1+\frac{\alpha^2\Phi_0}{8\xi_0\sqrt{T^*}}z\right]^{-1}. \tag{25}$$

Thus, the exponential dependence for the bilayer smectic order parameter transforms into a non-exponential dependence with decreasing T^*_R (i.e. approaching the S_{A_1}–S_{A_2}

transition in the bulk sample) (see figure 4). It is clearly seen that the dependence given by equation (25) is sharper than the exponential dependence in equation (24). This theoretical result is in qualitative agreement with experimental observation of a non-exponential sharp decay of the bilayer smectic structure with the penetration into the bulk [17]. The dependence of the ratio $\xi_p/\xi_{\parallel}$ on T_R^* at various values of the strength of interaction between polar molecules and the free surface are shown in figure 5. It is seen that the larger strength of the interaction g' corresponds to a larger value of T_R^* (i.e. a higher temperature) at which this ratio begins to deviate from one (i.e. the dependence of the bilayer smectic order parameter on the distance to the free surface begins to deviate from an exponential dependence). A simple qualitative explanation of this fact is as follows. The derivation of the exponential decay of the smectic (as well as the nematic) order fluctuations is based on the assumption of their small value [23]. In this case the bilayer smectic order fluctuations are proportional to the surface bilayer smectic order parameter σ_{20}. The value of σ_{20} is proportional to the strength of the interaction between polar molecules and the free surface. Therefore, the larger g' is the sooner (at a higher temperature) σ_{20} achieves a value sufficient to violate the validity of the assumption which forms the basis of the derivation of the exponential decay of the bilayer smectic order fluctuations.

As for the absolute value of ξ_p, we can find from figure 5, for example, that at $g'=0{\cdot}01$ $\xi_p \approx \xi_{\parallel}$ at $T_R^*=0{\cdot}01$ and $\xi_p \approx 0{\cdot}8\xi_{\parallel}$ at $T_R^*=0{\cdot}001$. A typical value of $\xi_{\parallel}$ can be obtained from X-ray studies of the second order S_{A_1}–S_{A_2} transition in the binary

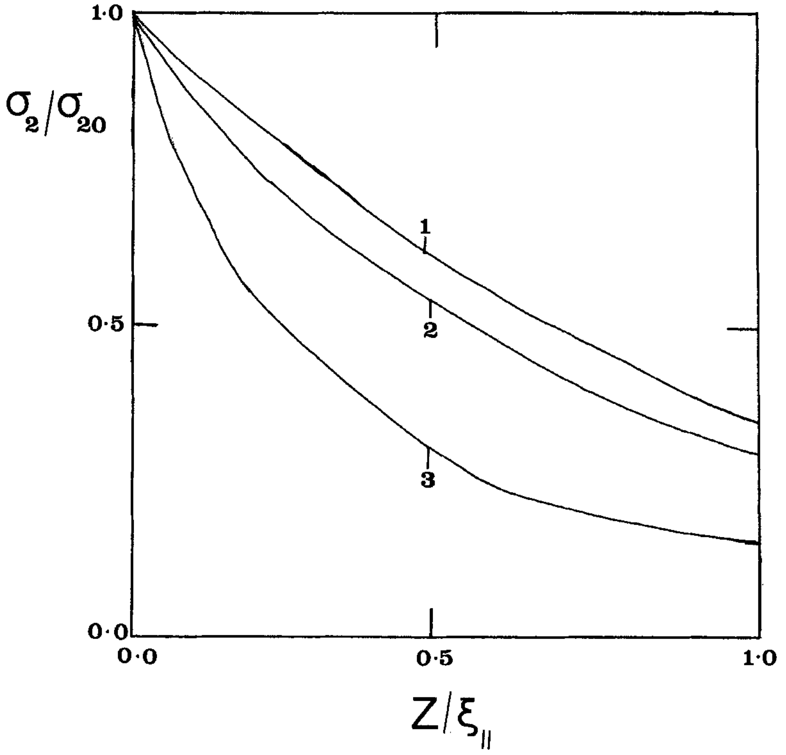

Figure 4. The dependence of the bilayer smectic order parameter σ_2 on the distance to the free surface at various values of T_R^*. $\alpha=0{\cdot}3$; $g'=0{\cdot}1$; $1-T_R^*=0{\cdot}1$; $2-T_R^*=0{\cdot}01$; $3-T_R^*=0{\cdot}001$.

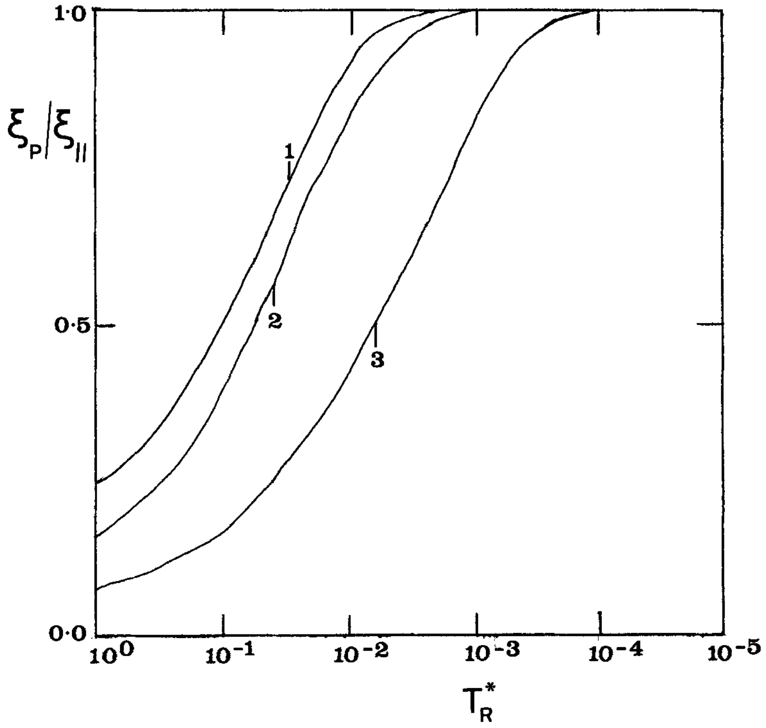

Figure 5. The dependence of the $\xi_p/\xi_\parallel$ ratio on T_R^* at various values of the strength of the interaction between the polar molecules and the free surface. $\alpha=0{\cdot}3$; $1-g'=0{\cdot}005$; $2-g'=0{\cdot}01$; $3-g'=0{\cdot}1$.

mixture of polar (DB6) and non-polar (TBBA) liquid crystals [24]. According to these data $\xi_\parallel \approx 90$ Å at $T_R^* = 0{\cdot}01$ (i.e. at a temperature about 4 K higher than that of the S_{A_1}–S_{A_2} transition) and $\xi_\parallel \approx 300$ Å at $T_R^* = 0{\cdot}001$. Hence $\xi_p = 90$ Å at $T_R^* = 0{\cdot}01$ and $\xi_p \approx 240$ Å at $T_R^* = 0{\cdot}001$. Since the thickness of the smectic A monolayer is about 30 Å [17, 18] we can conclude that at $T_R^* = 0{\cdot}01$ and $T_R^* = 0{\cdot}001$ the S_{A_2} phase forms about three and eight smectic monolayers, respectively, at the free surface of a polar liquid crystal with a S_{A_1} phase in its bulk. These theoretical results are in qualitative agreement with experiment [17, 18].

It should be added that the notion of the depth of the surface S_{A_2} phase penetration into the bulk with a S_{A_1} phase allows us to answer the question as to which real layers can be considered as semi-infinite. It is obvious that the liquid crystal layer can be considered as semi-infinite if its thickness $2L \gg \xi_p$. Then the properties of the layer in the bulk ($z = L$) are really identical to those of the infinite homogeneous sample.

4. Free surface-induced S_{A_2} phase in a freely suspended polar liquid crystal film

Now let us consider the case of a polar liquid crystal layer of finite thickness when the condition $2L \gg \xi_p$ is not valid. It is clear that in this case we cannot neglect the influence of the second boundary surface of the layer on its part adjoining the free surface. Also, we cannot assume the properties of the sample in the bulk ($z = L$) to be identical to those of an infinite homogeneous sample with a S_{A_1} phase (i.e. we cannot set $\sigma_{2b} = \Phi_b = 0$ and $d\Phi/dz|_{z=L} = 0$). In addition, we cannot divide the free energy of the layer into bulk and surface parts as we did for a semi-infinite layer.

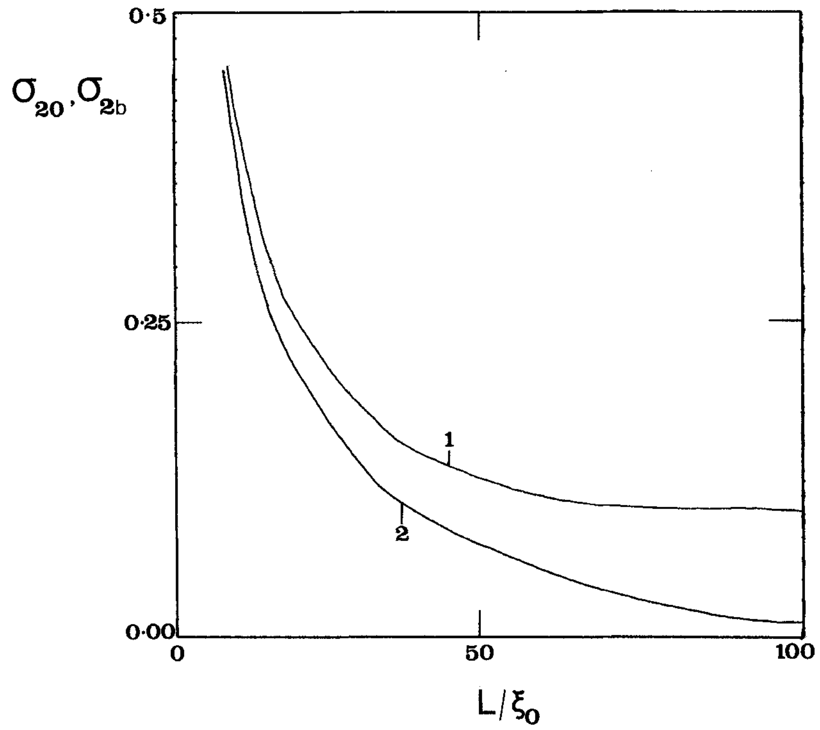

Figure 6. The dependence of the bilayer smectic order parameters σ_{20} and σ_{2b} on the thickness of a freely suspended film of polar liquid crystal $\alpha=0{\cdot}3$; $T^*_R=0{\cdot}01$; $g'=0{\cdot}01$. $1-\sigma_{20}$; $2-\sigma_{2b}$.

However, when the layer is freely suspended film, then all of these difficulties can be overcome. First, as both the boundary surfaces of the freely suspended film are identical free surfaces, then we need only consider half of the layer adjoining the free surface. Secondly, since the bilayer smectic order parameter has a maximum value at the free surfaces of the film then it must have a minimum value in the middle ($z=L$), and we can again use relation (15) which leads to expression (19) for the free energy of the half of liquid crystal layer considered. Now we must minimize this expression with respect to both Φ_0 and Φ_b because we cannot simply set $\Phi_b=0$ as we did for a semi-infinite layer. Minimization of equation (19) with respect to both Φ_0 and Φ_b leads to

$$\left.\begin{array}{l} 2[f'_0(\Psi_0,\Phi_0)-f'_0(\Psi_0,\Phi_b)]^{1/2}-\dfrac{g'}{\sqrt{T^*}}=0, \\ \text{and} \\ \dfrac{df'_0(\Psi_0,\Phi_b)}{d\Phi_b}\left\{1-\dfrac{\xi_0\sqrt{T^*}}{L}\displaystyle\int_{\Phi_b}^{\Phi_0}\dfrac{d\Phi}{[f'_0(\Psi_0,\Phi)-f'_0(\Psi_0,\Phi_b)]^{1/2}}\right\}=0, \end{array}\right\} \qquad (26)$$

which can only be solved numerically. After substitution of the values obtained for Φ_0 and Φ_b into expression (19) we must compare the free energy of half of the layer with the free energy per unit area of the free surface of an analogous half of the layer with a S_{A_1} phase ($F_{S_{A_1}}=NkTf'_0(\Psi_0,\Phi=0)\,L$). If expression (19) is smaller, than the free energy of the S_{A_1} phase then $\Phi_0\neq 0$ and $\Phi_b\neq 0$. For the opposite case $\Phi_0=\Phi_b=0$. It is obvious that the result obtained must depend not only on the strength of the interaction between the polar molecules and the free surface (g'), and temperature (T^*_R) for a semi-infinite layer, but also on the thickness of the freely suspended film (L). Typical dependences of both the surface σ_{20} and bulk σ_{2b} bilayer smectic order parameters on the thickness of the freely suspended film are shown in figure 6. It is seen that in very thin films ($L/\xi_0 \sim 10$) σ_{20} and σ_{2b} are practically identical and nearly four times larger than σ_{20} in a semi-infinite layer at the same values of g' and T_R^* (see figure 2). The values of both σ_{20} and σ_{2b} decrease and the difference between them increases with increasing thickness of the freely suspended film. In addition, when the ratio $L/\xi_0 \rightarrow \infty$, then $\sigma_{2b} \rightarrow 0$, and σ_{20} approaches the value of the surface bilayer smectic order parameter in a semi-infinite layer (i.e. the results obtained for freely suspended films of finite thickness approach those for a semi-infinite layer). Thus we can conclude that in sufficiently thick freely suspended films with a S_{A_1} phase the regions of the bilayer S_{A_2} phase always appear at the free surfaces. This free surface-induced S_{A_2} phase can completely occupy the sample with decreasing thickness of the freely suspended film (i.e. the S_{A_1} phase in all polar liquid crystal samples undergoes a transition to a S_{A_2} phase). The critical film thickness for such a transition can be estimated as follows. The film can be assumed to be completely occupied by the S_{A_2} phase if half of its thickness is equal to the depth of the surface S_{A_2} phase penetration into the bulk with a S_{A_1} phase. Then the bilayer smectic order parameter in the bulk σ_{2b} must be e times smaller than the surface bilayer smectic order parameter σ_{20}. It is seen from figure 6 that the corresponding value of L is about 80 ξ_0 at $g' = 0{\cdot}01$ and $T_R^* = 0{\cdot}01$. According to the results in [24] $\xi_0 \approx 2$ Å. Thus, the critical thickness of a freely suspended polar liquid crystal film is equal to about 320 Å, which corresponds to the thickness of about ten smectic monolayers. In other words, freely suspended films with a thickness of about 10 smectic monolayers can be completely occupied by the S_{A_2} phase at a temperature within the range of the S_{A_1} phase in a thick sample. It should be added that the S_{A_2} phase may not be observed at all in a thick sample, if, for example, the the S_{A_1}–S_{A_2} transition temperature is lower than that of crystallization. At present we have no information about the experimental observation of such phenomena. However, we should note that the appearance of smectic phases not existing in thick samples was observed experimentally in freely suspended films with a thickness of about 20 smectic monolayers [25]. Therefore, the experimental investigation of phase polymorphism in thin freely suspended films would be of particular interest.

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