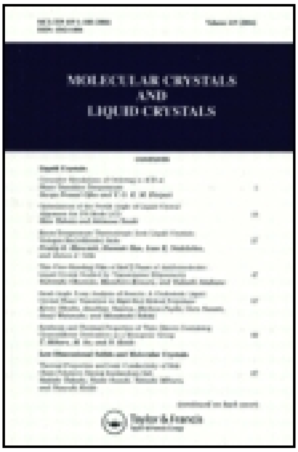

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Free Surface-Induced Bilayer Smectic A Structure in a Vicinity of Nematic-Monolayer Smectic A Transition in Polar Liquid Crystals

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Free Surface-Induced Bilayer Smectic A Structure in a Vicinity of Nematic-Monolayer Smectic A Transition in Polar Liquid Crystals

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Here a thick (semi-infinite) layer of polar liquid crystal having a free surface is considered. The temperature of the sample is assumed to be in the vicinity of the nematic (N)-monolayer smectic A (SA1) phase transition and considerably higher than the temperature of possible ("virtual") SA1-bilayer smectic A phase with long-range antiferroelectric order (SA2) transition. Therefore, the bilayer smectic ordering, induced by the interaction between polar molecules and the free surface of liquid crystal, decays much more rapidly with increasing distance to the free surface than the free surface-induced monolayer smectic ordering. Using this assumption the dependnence of both the monolayer and bilayer smectic order parameters on the temperature and the distance to the free surface are determined. It is shown that the latter dependence for the monolayer smectic order parameter has an approximately exponential character and the depth of the free surface-induced monolayer smectic A ordering penetration into bulk liquid crystal increases with the approaching of the *N*–SA1 transition point. At certain temperature below the *N*–SA1 transition point this penetration depth achieves an infinite value. The bilayer smectic order parameter also decays almost exponentially with increasing distance to the free surface. However it's magnitude and the depth of the bilayer smectic ordering penetration into bulk liquid crystal are practically independent of temperature. The results obtained are compared with the experiment.

Keywords: Surface, bilayer smectic structure, polar liquid crystals

1. INTRODUCTION

It is known that both a free surface and an interface between different media have a considerable influence on the properties of liquids and liquid crystals. For example, the liquid–solid substrate interface not only imposes some orientational order on the isotropic phase of liquids having a nematic phase[1–5] but also induces orientational ordering in non-mesogenic liquids.[6] Furthermore, in[7–11] it has been shown that the smectic A phase can be formed at both the free surface of nematic and nematic-solid substrate interface.

The influence of the surface on strongly polar liquid crystals consisting of molecules having end groups ($-$CN or $-NO_2$) with a large permanent dipole moment ($\sim$ 4 D), is particularly interesting. The point is that various types of smectic A phase, namely monolayer smectic A (SA1) with layer thickness d nearly equal to molecular length 1, partially bilayer smectic A (SAd) with $1 < d < 21$, and bilayer SA2 and S$\tilde{A}$ phases in which a monolayer smectic A structure coexists with bilayer structures ($d \simeq 21$) with long-range antiferroelectric order, occur in such liquid crystals[12,13]. The direct transitions between these smectic A phases (SA1–SA2, SA1–S$\tilde{\text{A}}$–SA2, SAd–SA2 etc.) have been observed.[12–14] Therefore, we can expect particularly interesting changes in the phase diagrams of such systems to be caused by the interaction between the mesogenic molecules and the surface.

X-ray studies show that several layers of the bilayer SA2 phase are formed at the free surface of polar liquid crystal which exhibits only a monolayer SA1 phase.[15] The theoretical description of this phenomenon has been offered in.[16] This description is based on both de Jeu and Longa's microscopic models for the SA1 and SA2 phases in polar liquid crystals[17] and Parson's idea of polar ordering of mesogenic molecules by a free surface.[18] It has been shown that the interaction between polar molecules and the free surface of liquid crystal results in the appearance of a surface-induced SA2 phase at any temperature within range of the existence of the SA1 phase in the bulk sample. However in[16] it assumes the occurrence of a deep SA1 phase when the value of the monolayer smectic order parameter is sufficiently large and stable. In reality the free surface-induced bilayer SA2 phase was observed in the vicinity of the nematic (N)–SA1 phase transition[15] when considerable fluctuations of the monolayer smectic order parameter occur.

The purpose of the present paper is to eliminate the above-mentioned contradiction between theory and experiment. The semi-infinite polar liquid crystal layer having a free surface is considered. The temperature of the sample is assumed to be in the vicinity of the second order N–SA1 transition in the bulk and considerably higher than the temperature of possible ("virtual") SA1–SA2 transition. In this temperature interval the longitudinal correlation length of the monolayer smectic order fluctuations is much larger than that of the bilayer smectic order fluctuations. Therefore the free surface - induced bilayer smectic order parameter must decay much more rapidly with increasing distance to the free surface than the free surface-induced monolayer smectic order parameter. Using this assumption the dependence of both the monolayer and bilayer smectic order parameters on the temperature and the distance to the free surface are determined. The magnitude of the surface monolayer smectic order parameter smoothly increases with decreasing temperature and it's decay with the distance to the free surface has an approximately exponential character. The depth of the free surface-induced monolayer smectic ordering penetration into the bulk of the liquid crystal increases with the approach of the N–SA1 transition point and achieves an infinite value at the certain temperature below this point. The bilayer smectic order parameter also decays almost exponentially with increasing distance to the free surface. However it's magnitude and the depth of the bilayer smectic ordering penetration into the bulk of the liquid crystal are practically independent of the temperature. The results obtained are compared with the experiment.[15]

2. FREE ENERGY OF A SEMI-INFINITE POLAR LIQUID CRYSTAL LAYER HAVING A FREE SURFACE

Let us consider a semi-infinite polar liquid crystal layer having a free surface. The temperature T is assumed to be in a vicinity of the second order N–SA1 phase transition and sufficiently higher than the temperature of possible SA1–SA2 transition. The latter transition can be considered as "virtual" if the SA1–SA2 transition temperature is lower than that of crystallization. For simplicity let us assume that the orientational order is perfect (the long axes of all the molecules are oriented parallel to the director $\vec{n}$). This assumption is reasonable because the observed N–SA1 transition temperatures in polar liquid crystals are considerably lower than those of the isotropic (I)–N transitions.[12, 14] The director $\vec{n}$ 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[17] in a mean field approximation the thermodynamic properties of an infinite and homogeneous sample of perfectly ordered polar liquid crystals having the SA1 and SA2 phases are completely described by the single particle distribution function

$$\rho(z,s) = 1 + 2\sigma_1 \cos(2\pi z/l) + 2s\sigma_2 \cos(2\pi z/2l) = A^{-1} \exp[-V(z,s)/kT] \tag{1}$$

where $V(z,s)$ is the single particle molecular field pseudopotential, A is the normalization constant, σ_1 and σ_2 are the coordinate independent monolayer and bilayer smectic order parameters respectively, which are defined by the self-consistent equations

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

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

s is the variable defining the molecular orientation ($s = +1$ for molecules with the dipole moment aligned parallel to the director $\vec{n}$ and $s = -1$ for molecules aligned in the opposite direction). When $\sigma_1 = \sigma_2 = 0$ then the nematic phase is found; when $\sigma_1 \neq 0$ and $\sigma_2 = 0$ then the monolayer SA1 phase depicted in Figure 1(a) is observed and finally, when $\sigma_1 \neq 0$ and $\sigma_2 \neq 0$ then we find the SA2 phase in which the monolayer smectic A structure coexists with bilayer smectic A structure with long range antiferroelectric order depicted in Figure 1(b).

If the pair potentials for the intermolecular interactions are assumed to be even functions of the distance between molecular centres, then the pseudopotential in Equation (1) can be represented in it's simplest form[19,20]

$$V(z,s) = -[V_1 \sigma_1 \cos(2\pi z/l) + s V_2 \sigma_2 (2\pi z/2l) \tag{4}$$

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

$$f_0 = (N/2)\frac{1}{2} \sum_{s=\pm 1} V(z,s) \rangle_s - NKT \langle ln P(z,s) \rangle_s \tag{5}$$

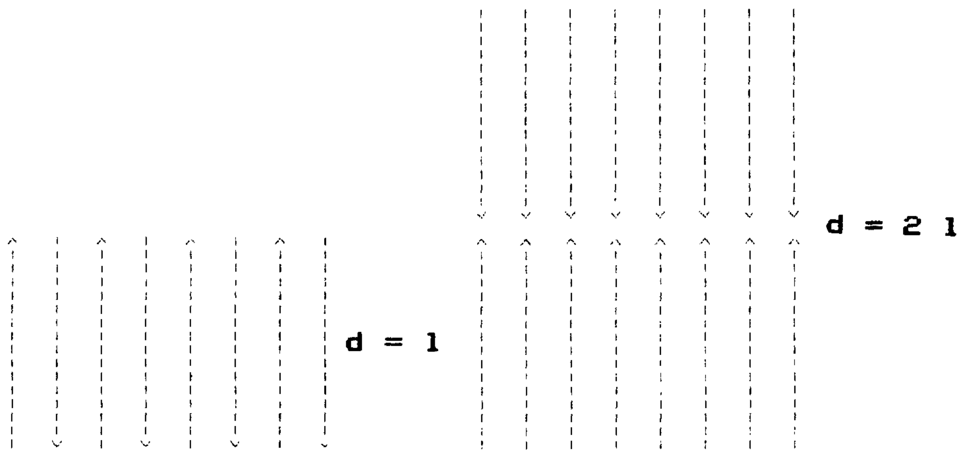

FIGURE 1 (a) - Monolayer SA1 phase ($d = 1$) (b) - Bilayer smectic A structure in a SA2 phase ($d = 2L$).

where N is the number density. For our convenience we can use the following Landau expansion of the free energy density (5) in a series of σ_1 and σ_2 parameters

$$f_0 = NKTf_0^1,$$

$$f_0^1 = A_1\psi^2 + A_2\varphi^2 - B\psi\varphi^2 + C_1\psi^4 + C_2\varphi^4 + \cdots \tag{6}$$

where $\psi = \sigma_1/t$, $\varphi = \sigma_2/t$, $A_1 = (1/2)(t-(1/2))$, $A_2 = (\alpha/2)(t-\alpha/2)$, $B = \alpha^2/8$, $C_1 = 1/64$, $C_2 = \alpha^4/64$, $\alpha = V_2/V_1$ and $t = kT/V_1$ is the reduced temperature.

Now let us take into account the interaction between the polar molecules and the free surface. In[15] it is assumed that the free surface not only imposes homeotropic orientation but also 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.[18] He supposed that the energy of interaction between the polar molecules and free surface is of the form $\gamma_0 - 1/2\,\gamma_1(\vec{n}\cdot\vec{v})^2 - \gamma_2(\vec{n}\cdot\vec{v})$, where γ_0 = constant, both γ_1 and γ_2 are the functions of the orientational order parameter Q and $\vec{v}$ is the unit vector normal to the free surface. If for simplicity we assume that the molecules interact with free surface due to the short-range forces and there is perfect orientational order, then such an interaction energy can be written as

$$g(z,s) = -G_1\delta(z) - sG_2\delta(z) \tag{7}$$

where the G_1 and G_2 are the interaction constants and $\delta(z)$ is a well known Dirac-function. It is easily seen from Equation 7 that the first surface layer ($z = 0$) 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

$$f_1 = \frac{1}{2} N \sum_{s=\pm 1} G(z,s) P(z,s) \tag{8}$$

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 (x,y) dependence of both σ_1 and σ_2 can be neglected. The layer inhomogeneity along the z-axis can be taken into account by adding to the free energy density (6) of a homogeneous sample the expression[13]

$$f_2 = K_1 \left(\frac{d\sigma_1}{dz}\right)^2 + K_2 \left(\frac{d\sigma_2}{dz}\right)^2 \tag{9}$$

where both K_1 and K_2 are analogous to the elastic constants. Thus, free energy density in a polar crystal layer with regard to the interaction between the molecules and the free surface is given by

$$f(z) = f_0(\sigma_1(z), \sigma_2(z)) + K_1 \left(\frac{d\sigma_1}{dz}\right)^2 + K_2 \left(\frac{d\sigma_2}{dz}\right)^2 + (N/2) \sum_{s=\pm 1} G(z,s) P(z,s) \tag{10}$$

Now we can use the assumption that the polar liquid crystal layer under consideration is semi-infinite (i.e. the layer thickness $2L \rightarrow \infty$). Because of the infinitely large thickness the properties of half of the layer adjoining the free surface are completely independent of the second boundary surface ($z = 2L \rightarrow \infty$) and we only need consider this half of the layer. In addition, for the 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. In order to obtain total free energy of half of the sample per unit area of the free surface we must integrate expressions (10) over z from O to L. The result of this integration is given by

$$(F/NKT) = \int_0^L \left[f_0'(\psi(z), \varphi(z)) + K_1^* t \left(\frac{d\psi}{dz}\right)^2 + K_2^* t \left(\frac{d\varphi}{dz}\right)^2 \right] dz - g_1 \psi_0 - g_2 \varphi_0 \tag{11}$$

where $g_1 = 2G_1/V_1$, $g_2 = 2G_2/V_1$, $K_1^* = K_1/NV_1$, $K_2^* = K_2/NV_1$, $\psi_0 = \sigma_{10}/t$, $\varphi_0 = \sigma_{20}/t$, σ_{10} and σ_{20} are the values of the monolayer and bilayer smectic order parameters, respectively, at the free surface ($z = 0$). It should be noted that expression (11) for the free energy of the semi-infinite polar liquid crystal layer having the free surface is analogous to that in our previous paper.[16] However, in[16] the terms $K_1^* t(d\psi/dz)^2$ and $-g_1\psi_0$ are omitted because of the assumption of the occurence of a deep SA1 phase when the value of the order parameter σ_1 is sufficiently large and stable (i.e. the value of σ_1 at the free surface is equal to that in the bulk).

3. SOLUTION OF EULER-LAGRANGE EQUATIONS IN A VICINITY OF THE SECOND ORDER *N*–SA1 PHASE TRANSITION

In order to determine the dependence of both ψ and φ smectic order parameters on the distance to the free surface z we must minimize the functional Equation (11) with respect to $\psi(z)$, $\varphi(z)$, ψ_0 and φ_0. This minimization leads to the following Euler-Lagrange equations and the boundary conditions:

$$2K_1^* t \frac{d^2\psi}{dz^2} = 2A_1\psi(z) - B\varphi^2(z) + 4C_1\psi^3(z), \tag{12}$$

$$2K_2^* t \frac{d^2\varphi}{dz^2} = 2A_2\varphi(z) - 2B\varphi(z)\psi(z) + 4C_2\varphi^3(z), \tag{13}$$

$$2K_1^* t \left.\frac{d\psi}{dz}\right|_{z=0} + g_1 = 0, \tag{14}$$

$$2K_2^* t \left.\frac{d\varphi}{dz}\right|_{z=0} + g_2 = 0, \tag{15}$$

It is very difficult to obtain the solution of these equations in the general case. However, we can use above-made assumption that the temperature of the liquid crystal layer is in the vicinity of the second order N–SA1 phase transition and considerably higher than the temperature of possible SA1–SA2 transition. In this temperature interval the longitudinal correlation length of the monolayer smectic order fluctuations ξ_1 is much larger than that of the bilayer smectic order fluctuations ξ_2. Since the characteristic decay length for the surface-induced smectic A phase is proportional to the longitudinal correlation length of the smectic order fluctuations, the bilayer smectic A structure must decay much more rapidly with distance to the free surface than the monlayer smectic A structure. Therefore we can divide half of the layer under consideration into two regions. In the first region adjoining the free surface the SA2 phase occurs ($\psi \neq 0, \varphi \neq 0$). The order parameter ψ decreases slowly and φ decays rapidly with distance to the free surface. In the second region the bilayer smectic order parameter φ is negligible and we can assume that only the monolayer smectic A structure occurs ($\varphi = 0$, $\psi \neq 0$). Furthermore, if the characteristic decay length ξ_L of the monolayer smectic order parameter is introduced then the $\psi(z)$ dependence is that of the ratio z/ξ_L. This ratio is a small value in the first region. Then the $\psi(z)$ dependence can be expanded in a series of (z/ξ_L) and we can restrict the linear term of this expansion. Consequently we can assume that in the first region of half of the layer under consideration the monolayer smectic order parameter $\psi(z)$ decreases linearly with the distance to the free surface. Using the assumptions made above let us solve Equations 12–15 for both first and second regions of the liquid crystal layer.

In order to determine the solution for the first region we must analyse Equation 13. At first let us estimate the magnitudes of the coefficients A_2, B and C_2. The necessary values of the parameter α and the reduced temperature t can be chosen from the phase diagram for the infinite and homogeneous polar liquid crystal sample. Such a phase diagram can be obtained by the minimization of the free energy density given by Equation 6. This minimization shows that when $\alpha > 0.8$ then the N–SA2 transition occurs and the phase sequence N–SA1–SA2 can be observed at $\alpha < 0.8$. The reduced temperature t_{NSA1} of the second order N–SA1 transition is equal to 1/2. Since the temperature of the polar liquid crystal under consideration is assumed to be in the vicinity of the N–SA1 phase transition and considerably higher than the temperature of possible SA1–SA2 transition, we must take $t \simeq 0.5$ and $\alpha < 0.8$. Let us set $\alpha = 0.5$. Then we obtain $A_2 = (\alpha/2)(t - (\alpha/2)) \approx 0.06$, $B = \alpha^2/8 \approx 0.03$ and $C_2 = \alpha^4/64 \approx 0.001$, i.e. $A_2 \sim B$ and $C_2 \ll A_2, B$. Hence, if the interaction between mesogenic molecules and the free surface is not "very strong" and the free surface-induced bilayer smectic order parameter φ is not too large ($\varphi < 1$) then the term $\sim C_2\varphi^3(z)$ in the right-hand side of Equation 13 can be neglected in comparison with two other terms. Further, since in the first region the parameter $\psi(z)$ varies slowly in comparison with the parameters $\varphi(z)$, we can perform a further simplification of Equation 13 by replacing $\psi(z)$ in the term $\sim\varphi(z)\psi(z)$ by it's average value in the first region $\bar{\psi} = (\psi_0 + \psi_b)/2$, where ψ_b is the value of the monolayer smectic order parameter ψ at the boundary between the first region and the second region. Then Equation 13 transforms to equation

$$K_2^* t \frac{d^2\varphi}{dz^2} = (A_2 - B\bar{\psi})\,\varphi(z) \tag{16}$$

which has a simple exponential solution

$$\varphi(z) = \varphi_0 \exp(-z/\xi_p) \tag{17}$$

where $\xi_p = [K_2^* t/(A_2 - B\bar{\psi})]^{1/2}$ is the characteristic decay length of the bilayer smectic order parameter $\varphi(z)$. Using the boundary condition (15) we obtain the value of the surface bilayer smectic order parameter φ_0

$$\varphi_0 = \frac{1}{2} g_2' [A_2 - B\bar{\psi}]^{-1/2} \tag{18}$$

where

$$g_2' = g_2/\xi_{02}, \quad \xi_{02} = \sqrt{K_2^*}.$$

In order to determine the solution for the second region we must multiply Equation 12 by $d\psi/dz$ and integrate the resulting equation with due regard for the condition $\varphi = 0$ and the homogeneity of the order parameter ψ in the bulk of the layer under consideration

$$\left.\frac{d\psi}{dz}\right|_{z=L} = 0 \tag{19}$$

This procedure leads to equation

$$\frac{d\psi}{dz} = -\frac{1}{\sqrt{K_1^* t}}\left[f_0^1(\psi(z), \varphi = 0) - f_0^1(\psi_v, \varphi = 0)\right]^{1/2} \tag{20}$$

where ψ_v in the value of the parameter ψ in the bulk of the layer. Using the above-mentioned definition of both first and second regions of the liquid crystal under consideration we can assume that the boundary between these regions is at the distance to the free surface similar to the characteristic decay length ξ_p of the bilayer smectic order parameter φ. Then we obtain from Equation 20 the following dependence of the monolayer smectic order parameter ψ on the distance to the free surface in second region:

$$Z = \xi_p + \xi_{01}\sqrt{t}\int_{\psi(z)}^{\psi_v} [f_0^1(\psi, \varphi = 0) - f_0^1(\psi_v, \varphi = 0]^{-1/2}\, d\psi, \tag{21}$$

where

$$\xi_{01} = \sqrt{K_1^*}.$$

Further, we can combine the assumption of linear dependence of the monolayer smectic order parameter ψ on the distance to the free surface in the first region

$$\left.\frac{d\psi}{dz}\right|_{z=\xi_p} = \frac{\psi_b - \psi_0}{\xi_p} = \left.\frac{d\psi}{dz}\right|_{z=0} \tag{22}$$

with the condition of the continuity of the derivative $d\psi/dz$ at the boundary between the first region and the second region

$$\left.\frac{d\psi}{dz}\right|_{z=\xi_p} = \frac{\psi_b - \psi_0}{\xi_p} = -\frac{1}{\sqrt{K_1^* t}}[f_0^1(\psi_b, \varphi = 0) - f_0^1(\psi_v, \varphi = 0)]^{1/2} \tag{23}$$

Using Equations 22 and 23 and the boundary condition (14) we can obtain the following equation with respect to the parameter ψ_b:

$$[f_0^1(\psi_b, \varphi = 0) - f_0^1(\psi_v, \varphi = 0)]^{1/2} = g_1'/2\sqrt{t} \tag{24}$$

where $g_1' = g_1/\xi_{01}$. The surface monolayer smectic order parameter ψ_0 can also be obtained from Equation 23

$$\psi_o = \psi_b + (\xi_{02}/\xi_{01})[f_0^1(\psi_b, \varphi = 0) - f_0^1(\psi_v, \varphi = 0)]^{1/2}[A_2 - B\bar{\psi}]^{-1/2} \tag{25}$$

Since the properties of the semi-infinite layer in the bulk are identical to those of an infinite homogeneous sample at the same temperature, both ψ_v and $f_0^1(\psi_v, \varphi = 0)$ in Equations 20, 21, 23–25 are equal to zero at the temperature above the N–SA1 transition point. At the temperature below the N–SA1 transition point the value of ψ_v can be obtained by minimization of the free energy density in Equation 6 for the SA1 phase (under the condition $\varphi = 0$). The value of ψ_v obtained is

$$\psi_v = 4(\tfrac{1}{2} - t)^{1/2} \tag{26}$$

and

$$f'_0(\psi_v, \varphi = 0) = -4(\tfrac{1}{2} - t)^2 \tag{27}$$

4. RESULTS OF NUMERICAL CALCULATIONS AND COMPARISON WITH THE EXPERIMENT

In order to obtain numerical solutions of Equations 17, 18, 21, 24 and 25 we must choose the magnitudes of the parameters g'_1, g'_2, ξ_{01} and ξ_{02} (the magnitude of the parameter α is chosen in Section 3). Since we have no evidence allowing us to determine these magnitudes, we arbitrarily set $g'_1 = g'_2 = 0.01$ and $\xi_{02}/\xi_{01} = 1$.

The temperature dependence of both the monolayer σ_{10} and bilayer σ_{20} smectic order parameters at the free surface is shown in Figures 2 and 3, respectively. The parameter $R = (t - t_{NSA1})/t_{NSA1}$ is often used in papers on critical phenomena. It is

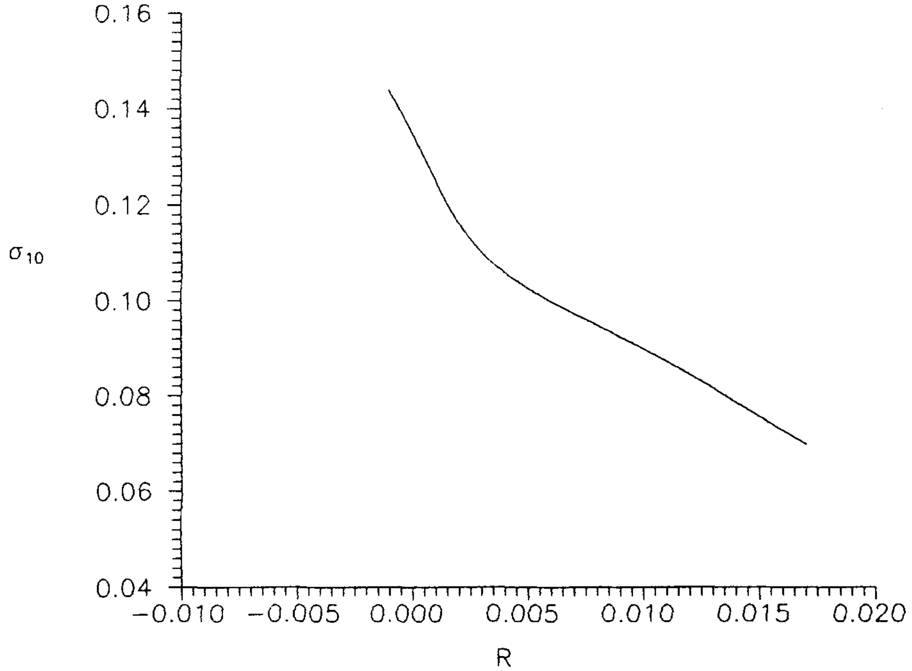

FIGURE 2 Temperature dependence of the surface monolayer smectic order parameter σ_{10}. $\alpha = 0.5$, $g'_1 = g'_2 = 0.01$, $\xi_{01} = \xi_{02}$.

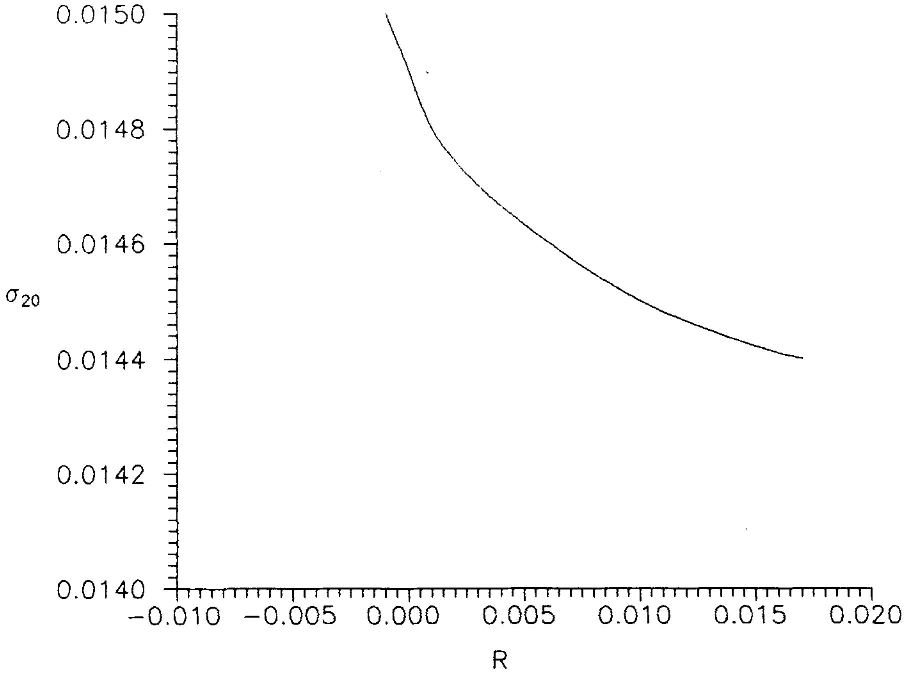

FIGURE 3 Temperature dependence of the surface bilayer smectic order parameter σ_{20}. $\alpha = 0.5$, $g'_1 = g'_2 = 0.01$, $\xi_{01} = \xi_{02}$.

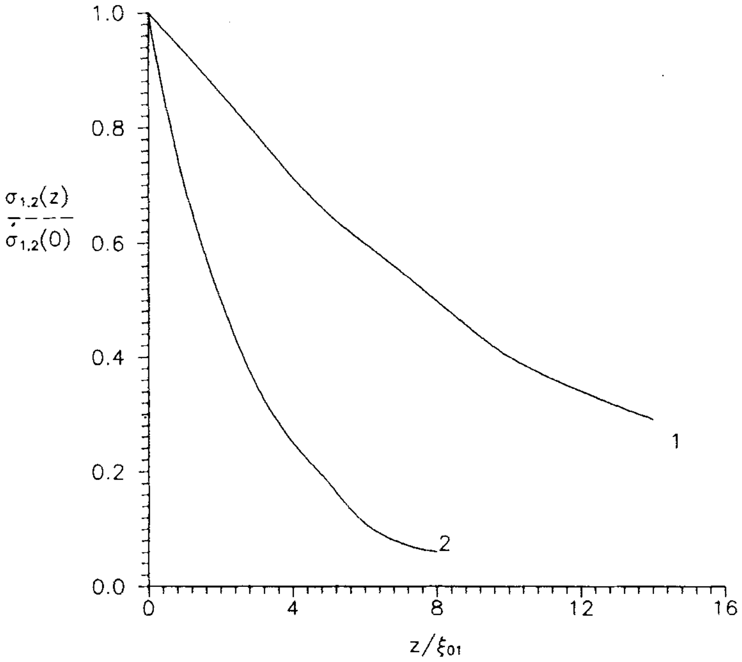

FIGURE 4 The dependence of both the monolayer σ_1 and bilayer σ_2 smectic order parameters on the distance to the free surface. $\alpha = 0.5$, $g'_1 = g'_2 = 0.01$, $\xi_{01} = \xi_{02}$, $R = 0.0166$. $1 - \sigma_1$; $2 - \sigma_2$.

seen that the monolayer smectic order parameter at the free surface smoothly increases with decreasing parameter R without any discontinuity at the N–SA1 transition point whereas the magnitude of the bilayer smectic order parameter at the free surface is practically independent of the temperature. Evidently this result is the consequence of the temperature of possible (or "virtual") SA1–SA2 phase transition which is considerably lower than that of the N–SA1 phase transition.

Typical dependence of both the monolayer and bilayer smectic order parameters on the distance to the free surface is shown in Figure 4. It is seen that both the monolayer and bilayer smectic order parameters decay almost exponentially with increasing distance to the free surface. As expected the bilayer smectic order parameter decreases much more rapidly than the monolayer smectic order parameter. It should be noted that the exponential decay of the free surface-induced monolayer smectic ordering in the nematic phase of the polar liquid crystal has been experimentally observed.[15] However, the decay of the free surface-induced bilayer smectic ordering has been found to be non-exponential. We assume that this contradiction between theory and experiment can be explained as follows. As is shown above the exponential decay of the antiferroelectric bilayer smectic ordering with the distance to the free surface is

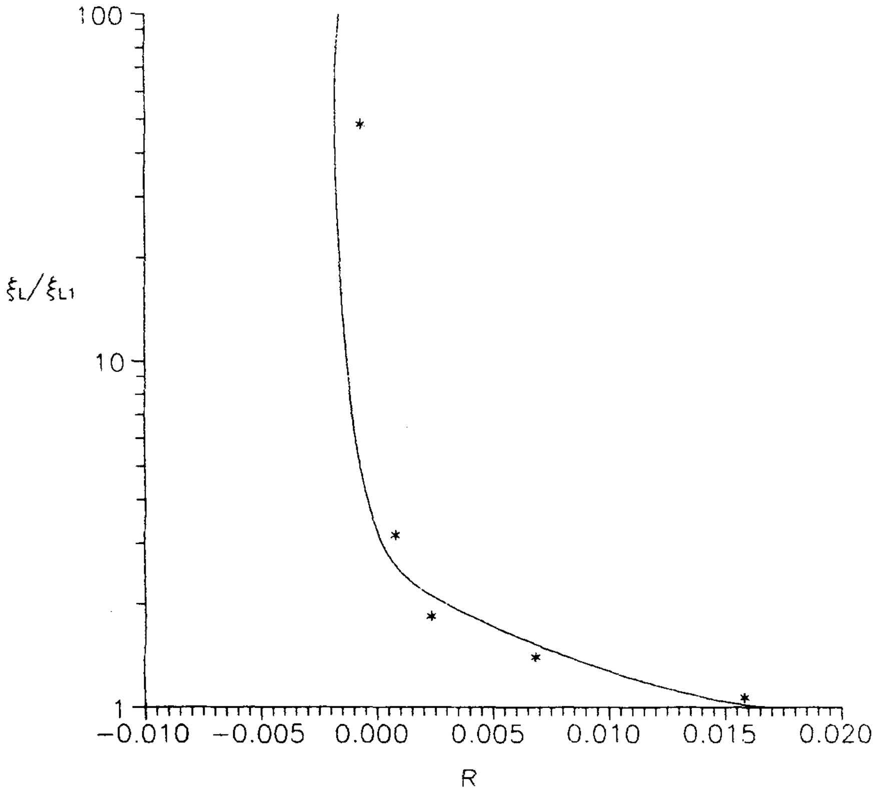

FIGURE 5 Temperature dependence of the ratio ξ_L/ξ_{L1}. $\alpha = 0.5$, $g'_1 = g'_2 = 0.01$, $\xi_{01} = \xi_{02}$. * — experimental points.[15]

a consequence of Euler-Lagrange Equation 13 when the bilayer order parameter φ is assumed as being not too large ($\varphi < 1$). As for the non-exponential decay of the free surface induced bilayer smectic ordering, it has been found [15] from an analysis of the X-ray reflectivity from the free surface based on the assumption of the saturation of the surface antiferroelectric ordering ($\sigma_{20} \sim 1$, $\varphi_0 = \sigma_{20}/t \sim 2$).

The most important characteristics of the phenomenon considered are the depths of the penetrations of the free surface induced monolayer and bilayer smectic A structures into the bulk of the liquid crystal layer. These depths can be assumed to be similar to the characteristic decay lengths ξ_L and ξ_P (i.e. the distances at which corresponding order parameters are e times smaller than those at the free surface) for the monolayer and bilayer smectic order parameters, respectively. Since we have no information about the absolute values of both the parameters ξ_{01} and ξ_{02}, it is reasonable to determine the magnitudes of the ratios ξ_L/ξ_{L1} and ξ_P/ξ_{P1}, where ξ_{L1} and ξ_{P1} are the depths of the penetrations of the monolayer and bilayer smectic A structures, respectively, into the bulk of the sample at a certain fixed temperature: for example, $R = 0.0166$ corresponding to one of the experimental points.[15]

The computed temperature dependence of both the ratios ξ_L/ξ_{L1} and ξ_P/ξ_{P1} is shown in Figures 5 and 6, respectively. It is seen that in the nematic phase ($R > 0$) the magnitude of the ratio ξ_L/ξ_{L1} smoothly increases with decreasing parameter R without any discontinuity at the N–SA1 transition point. Then in the smectic phase ($R < 0$) the magnitude of this ratio sharply grows up to an infinite value. The values of the ratio

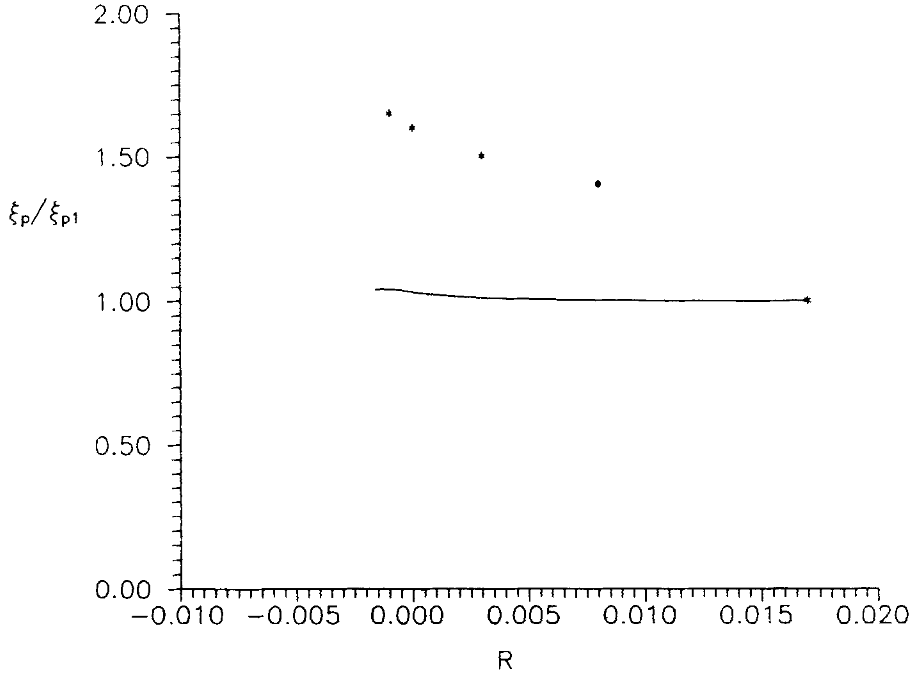

FIGURE 6 Temperature dependence of the ratio ξ_p/ξ_{p1}. $\alpha = 0.5$, $g'_1 = g'_2 = 0.01$, $\xi_{01} = \xi_{02}$. * – experimental points.[15]

ξ_L/ξ_{L1} determined from experiment[15] are also shown in Figure 5. It is easy to be convinced that the theoretical temperature dependence of the ratio ξ_L/ξ_{L1} is in qualitative agreement with the experiment. As for the computed temperature dependence of the ratio ξ_P/ξ_{P1} one can find from Figure 6 that this ratio is practically independent of the temperature in both the nematic and smectic phases. Though the experimental value of the ratio ξ_P/ξ_{P1} increases with decreasing parameter R (see Figure 6) this growth is very slow and we can again note the qualitative agreement between theory and experiment.

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