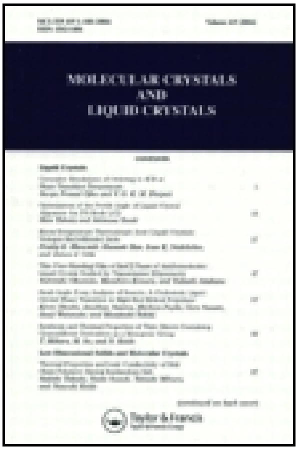

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Surface Induced Alignment Transition in a Nematic Layer with Symmetrical Boundary Conditions

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Surface Induced Alignment Transition in a Nematic Layer with Symmetrical Boundary Conditions

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The inner surfaces of a cell of conventional type were covered with an SiO_x aligning layer evaporated at an angle $\alpha = 60°$ and subsequently treated with lecithin in order to achieve symmetrical boundary conditions. The alignment of a nematic liquid crystal layer with negative dielectric anisotropy ($\Delta\varepsilon < 0$) was found to be homeotropic below a critical temperature T_c (low temperature range). Above that particular temperature the homeotropic alignment abruptly transforms into a planar one, which remains with increasing temperature up to the clearing point T_{NI} (high temperature range). The alignment transition was found to be reversible, and is attributed to a packing change of the lecithin layer with the temperature. A simple model based on the different temperature dependence of the anchoring strengths $W_H(T)$ and $W_P(T)$, characterizing the homeotropic and planar alignment respectively, is proposed to explain the surface induced alignment transition.

INTRODUCTION

During the last two decades a lot of theoretical and experimental work was devoted to the liquid crystal-solid surface interactions. The interest stems from the practical importance of the subject, as the alignment of liquid crystal molecules and their anchoring, playing an essential role in the functioning of liquid crystal display (LCD) devices, are caused by those interactions.

It is well known that by oblique evaporation and rubbing techniques a uniform parallel ($\theta = 0°$) or tilted parallel ($\theta < 45°$) alignment could be achieved,[1] whereas a perpendicular (homeotropic) ($\theta = 90°$) is obtained by covering the solid surface with a proper surfactant.[2–5] A certain combination of these techniques results in a tilted homeotropic alignment ($45° < \theta < 90°$).[6–8] The initial tilt and the strength of molecular anchoring at the solid surface have been known to be the most important characteristics of the liquid crystal-solid surface interaction. Their dependence on the surface treatment and chemical structure of liquid crystal materials have been a subject of intensive investigations since many years. These quantities also appear to be temperature dependent. In some cases, due to different reasons, the temperature change provokes a transition from one kind of alignment to the other (the so-called alignment transition) in a reversible manner. Most of the known cases were recently reviewed.[9]

The goal of the present work was to investigate experimentally and theoretically the case of a reversible alignment transition from a low temperature homeotropic alignment to a high temperature planar one in a nematic cell with symmetrical boundary conditions.

EXPERIMENTAL

In the experiments described below, a cell of conventional sandwich type, with symmetrical boundary conditions and with a gap of 12 μm kept by Mylar spacers, was used. On the inner surface of the glass substrates covered by ITO, an aligning layer of SiO_x was evaporated at angle $\alpha = 60°$ with respect to the substrate normal. As well known, the layer assures a unidirectional planar alignment of most liquid crystal materials.[10] On top of SiO_x a very thin layer of lecithin was deposited by means of dipping (Figure 1). The liquid crystal material used in the experiments was ZLI 2806 (Merck) with a negative dielectric anisotropy ($\Delta\varepsilon < 0$) and with wide nematic range ($-30°C < N \leq 99.5°C$). The nematic liquid crystal material was introduced into the cell in the isotropic phase under vacuum and slowly cooled down to room temperature. The sample was mounted in a Mettler FP 52 hot stage

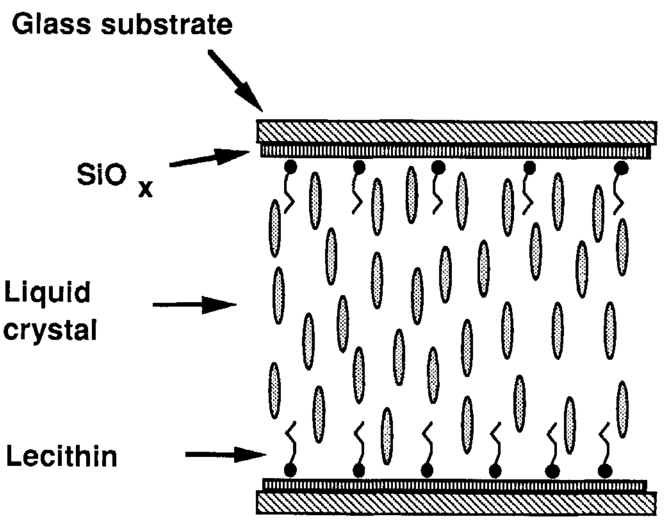

FIGURE 1 Cross-section of the experimental cell. The inner surfaces of the cell were covered by SiO_x evaporated at $\alpha = 60°$ and subsequently treated with lecithin to assure symmetrical boundary conditions. The alignment of the liquid crystal layer at temperatures, below some critical temperature T_c, is homeotropic i.e. in the low temperature range ($T < T_c$) the aligning force of SiO_x is suppressed effectively by the lecithin layer.

and the temperature controlled to within 0.1 degree accuracy. The investigations on the liquid crystal alignment and electro-optical characteristics were carried out using a Zeiss Photomicroscope III Pol. Below a critical temperature T_c (in the low temperature range), the alignment of liquid crystal molecules was found to be uniform and homeotropic ($\theta = 90°$). On heating, reaching T_c the director rapidly reoriented from homeotropic into planar alignment. The critical temperature T_c was found to be 93.5°C i.e. several degrees below the clearing point T_{NI}. Due to inhomogeneity of the lecithin layer, the transition began at different points of the cell and quickly spread over the whole cell area with increasing temperature in the high temperature range ($T_c \leq T < T_{NI}$). The alignment transition is demonstrated in Figure 2. In the black areas the alignment is homeotropic whereas in the bright ones it is planar. The regions with planar alignment (white spots) rapidly grew at the expense of the homeotropic regions (black spots) with increasing temperature above T_c. The transition to the planar state becomes complete at between 0.2 and 0.4 degrees above T_c. On lowering the temperature, the reverse transition from planar to homeotropic alignment took place with a small hysteresis (about 0.3 degrees). In the low temperature range, where the alignment is homeotropic, the sample exhibited an ECB (electrically controlled birefringence) effect, on applying an electric field. The electro-optic characteristics of the sample are given in Figure 3. From these one can define the critical temperature T_c at which the surface induced alignment transition from homeotropic to planar takes place. At that particular temperature the threshold voltage U_F for the Freedericksz transition appears to be zero. A certain increase of the molecular thermal fluctuations at T_c was observed.

THEORETICAL

Let us consider a nematic slab of thickness d with initial homeotropic alignment at room temperature, assuming symmetrical anchoring conditions at both walls $z_0 = -d/2$ and $z_1 = d/2$ (c.f. Figure 4). The idea is to describe the alignment of the nematic slab as a function of temperature, when the alignment appears as a result of superposition of two competitive preferred states, homeotropic and planar, characterized by anchoring strengths $W_H(T)$ and $W_P(T)$, whose easy directions coincide with the axes z and x respectively (c.f. Figure 4). Moreover, W_H and W_P are playing a role of probability coefficients for arising of the relevant alignments.

1. Orientational Transition Without Electric Field

The distortion free energy of the nematic slab in the one-elastic constant approximation ($K = K_{11} = K_{22} = K_{33}$) can be written as:

$$F = \frac{1}{2}\frac{K}{d}\int_{-\frac{1}{2}}^{\frac{1}{2}} \theta'^2\, d\eta + \frac{1}{2}\left\{W_H \sin^2\left(\theta_0 - \frac{\pi}{2}\right) + W_P \sin^2\theta_0 + W_H \sin^2\left(\theta_1 - \frac{\pi}{2}\right) + W_P \sin^2\theta_1\right\} \quad (1)$$

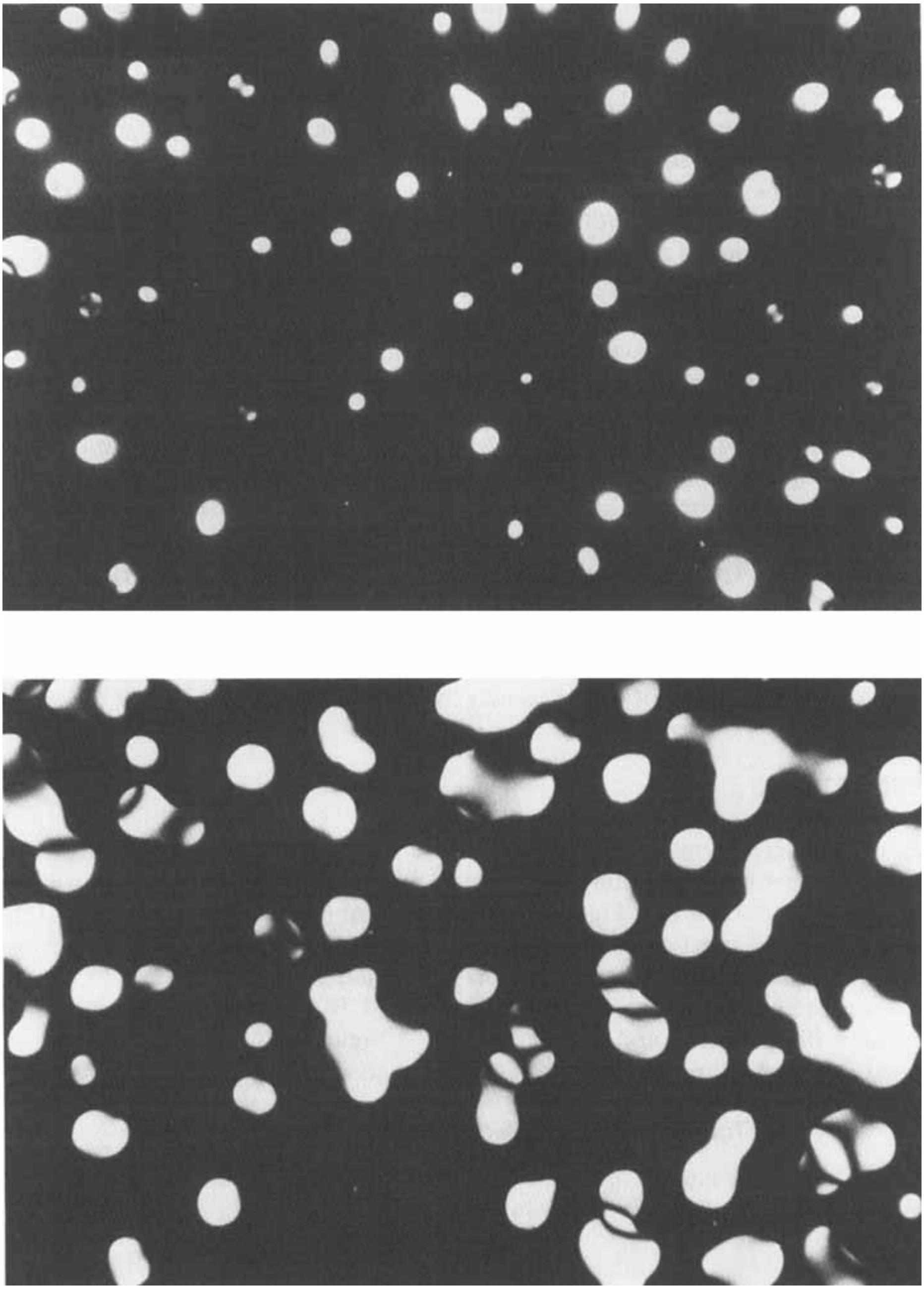

FIGURE 2 Orthoscopic observation of the surface induced alignment transition in a cell of thickness 12 μm, filled with ZLI 2806 ($\Delta\varepsilon < 0$) at three temperatures in the range $T_c \leqslant T < T_{NI}$ (T_1 = 93.5°C; T_2 = 93.7°C; T_3 = 93.9°C). In the dark regions the alignment is homeotropic whereas in the bright ones it is planar.

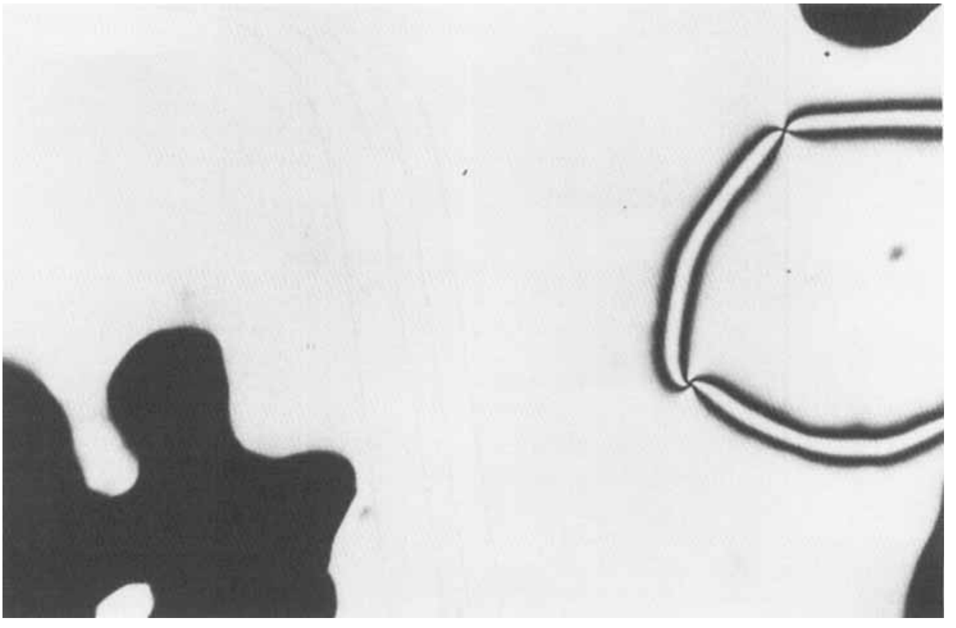

FIGURE 2 (*Continued*)

Where $\eta = z/d$ is the reduced coordinate, normal to the cell walls, $\theta(\eta)$ is the local tilt angle with respect to the walls, $\theta' = d\theta/d\eta$, $\theta_0 = \theta(-1/2)$ and $\theta_1 = \theta(1/2)$. In the symmetrical case, i.e. if a symmetrical treatment of the surfaces is assumed and thus $\theta_0 = \theta_1$, the reduced free energy reads:

$$G \equiv \frac{2Fd}{K} = \int_{-\frac{1}{2}}^{\frac{1}{2}} \theta'^2 \, d\eta + \left(\frac{2d}{K}\right)\{W_H \cos^2\theta_1 + W_P \sin^2\theta_1\} \quad (2)$$

The standard procedure gives for the Euler-Lagrange equation

$$\theta'' = 0 \quad (3)$$

and for the boundary condition

$$\theta_1' - L^{-1} \sin 2\theta_1 = 0 \quad (4)$$

where $L^{-1} = (W_H - W_P)\, d/K$ is the reciprocal reduced effective extrapolation length for the homeotropic alignment with respect to the planar one. This means that the observable is the effective anchoring strength $(W_H - W_P)$. The general solution of (3) is

$$\theta = c_1\eta + c_2 \quad (5)$$

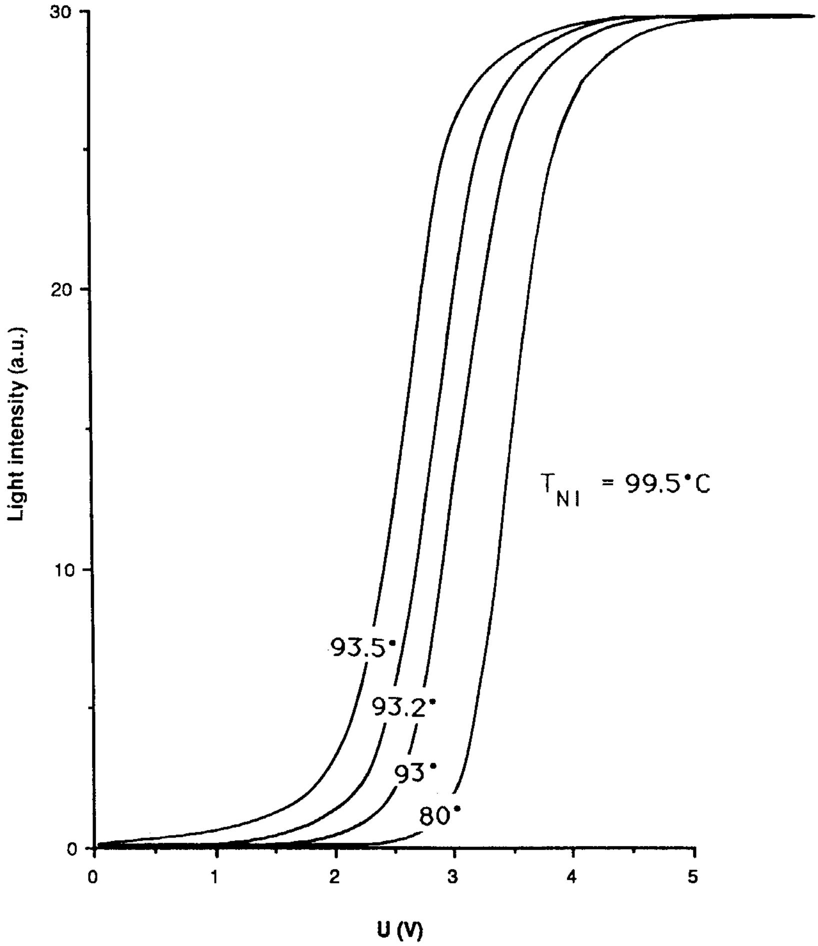

FIGURE 3 Electro-optical characteristics of the experimental cell at different temperatures. At the critical temperature $T_c = 93.5°$ the threshold voltage for the Freedericksz transition U_F becomes zero. At that temperature the alignment begins to deviate from the homeotropic without any applied electric field.

but physically, according to the surface treatment, only the even solution $\theta = c_2$ is of importance. Thus the boundary condition (4) writes

$$L^{-1} \sin 2c_2 = 0 \tag{6}$$

and the tilt angle θ, assuming a constant distortion over the whole cell, can only be either $\theta = 0$ or $\theta = \pi/2$, if $L^{-1} \neq 0$. But if $L^{-1} = 0$ (meaning $W_H = W_P$), the tilt angle θ is undetermined. On the other hand, at uniform tilt angle distribution across the sample, the free energy is given just by surface contribution

$$F = (W_H - W_P) \cos^2\theta + W_P \tag{7}$$

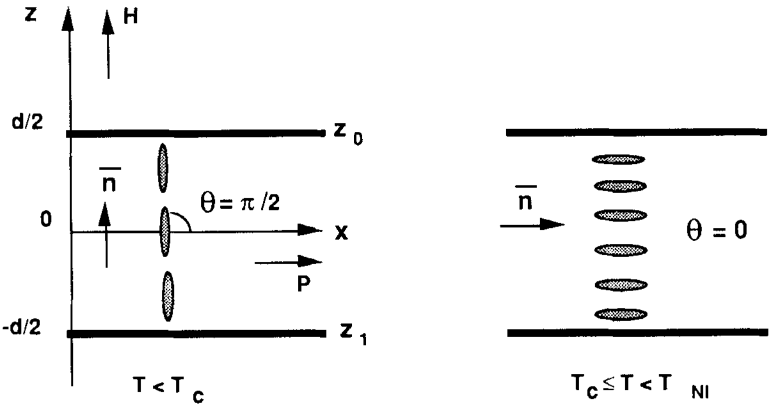

FIGURE 4 Director configuration in the low and high temperature range, and reference co-ordinate system used in our analysis. H and P are the two easy directions relevant to the homeotropic and planar alignment, respectively.

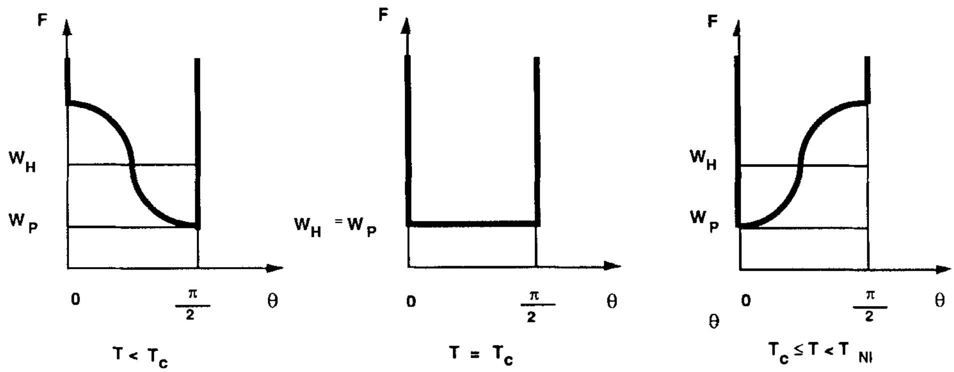

FIGURE 5 Tilt angle θ dependence of free energy F at three temperatures: 1) Below T_c (low temperature range), 2) At $T = T_c$, 3) Above T_c (high temperature range).

Thus, $W_H > W_P$ implies $\theta = \pi/2$ (homeotropic alignment), whereas $W_H < W_P$ implies $\theta = 0$ (planar alignment) (c.f. Figure 5). Moreover, if $W_H = W_P$, any alignment becomes unstable i.e. an orientational instability arises. As it was mentioned above, up to several degrees below the clearing point T_{NI} the temperature dependence of W_H resembles that of the square order parameters S^2,[11] whereas W_P is fairly constant with the temperature except in the range $T_{NI} - 1°C \leqslant T < T_{NI}$, where W_P is approaching zero quickly.[12,13] Thus, since W_H and W_P possess a quite different temperature dependence, it is enough to have a temperature behaviour of the anchoring coefficients like that depicted on Figure 6 to obtain a surface induced orientational transition from homeotropic to planar alignment. The transition occurs at a certain temperature T_c, several degrees below the clearing point T_{NI}, where $W_H(T_c) = W_P(T_c)$. On cooling, the reverse transition will take place without any hystheresis. Anyway, the transition does not appear to be of second order, since just two values of the order parameter θ are possible, and they

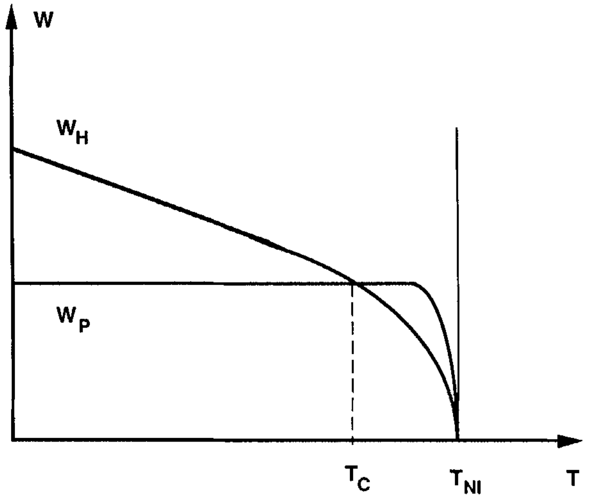

FIGURE 6 Idealized temperature dependence of W_H and W_P extracted from References 11–13. At the critical temperature T_c, the anchoring strengths W_H and W_P, relevant to homeotropic and planar alignment, become equal. Thus, at that particular point a preferred orientation does not exist any more. The alignment produced by the surface becomes unstable.

simply interchange through a degenerate instability their role of energetical extremals (c.f. Figure 5).

2. Orientational Transition Under an Applied Electric Field

A Freedericksz transition occurs at temperature $T < T_c$ in the nematic slab with negative dielectric anisotropy ($\Delta\varepsilon < 0$) when an electric field is applied along the preferred direction of the initial alignment, homeotropic in our case. It is of special interest to study the phenomenon close to T_c. As will be seen, both the critical E_c and saturation E_s fields appear to be dependent on the reduced effective extrapolation length L, in the absence of any hystheresis.

Let us assume, for simplicity, that the local field is identical to the applied one. Then the electrical reduced free energy g_E has to be added in Equation (2)

$$g_E \equiv \xi^{-2} \sin^2\theta \tag{8}$$

where

$$\xi^{-2} \equiv -\frac{\Delta\varepsilon E^2 d^2}{4\pi K} \tag{9}$$

is the reduced reciprocal square electric coherence length. Hence, the Euler-Lagrange equation becomes:

$$\theta'' - \left(\frac{\xi^{-2}}{2}\right) \sin 2\theta = 0 \tag{10}$$

with the same boundary condition given by equation (4). In order to approach the critical point for the Freedericksz transition, it is necessary to linearize equation (10) as a function of $\varphi = \pi/2 - \theta$, the tilt angle with respect to the z-axis (c.f. Figure 4), in the limit $\varphi \rightarrow 0$. Linearizing equation (10) in the limit $\theta \rightarrow 0$, we approach the saturation of the transition.

In two cases we obtain:

$$\varphi'' + \xi^{-2}\varphi = 0$$

$$\theta'' - \xi^{-2}\theta = 0 \tag{11}$$

with the linearized boundary conditions

$$\varphi_1' + 2L^{-1}\varphi_1 = 0$$

$$\theta_1' - 2L^{-1}\theta_1 = 0 \tag{12}$$

The even solution is

$$\varphi = A\cos(\xi^{-1}z) \tag{13}$$

close to the threshold, and

$$\theta = a\cosh(\xi^{-1}z) \tag{14}$$

close to the saturation.

Substituting equation (13) and (14) into the boundary conditions (12) we obtain two generalized forms of the Rapini-Papoular equation, i.e.:

$$\left(\frac{\xi_c^{-1}}{2}\right)\tan\left(\frac{\xi_c^{-1}}{2}\right) = L^{-1}$$

$$\left(\frac{\xi_s^{-1}}{2}\right)\tanh\left(\frac{\xi_s^{-1}}{2}\right) = L^{-1} \tag{15}$$

valid for $W_H \geqslant W_P$. Otherwise, $\xi_c^{-1} = \xi_s^{-1} = 0$ as one can expect. From equation (15) we can see that $E_c < E_s$ but the difference $E_s - E_c$ dimishes as the difference $W_H - W_P$ does. Moreover, if the homeotropic anchoring is strong ($W_H \rightarrow \infty$) the well known results[14] $\xi_c = \pi$ and $\xi_s \rightarrow \infty$ are derived. Furthermore, approaching the surface unstable alignment ($W_H \rightarrow W_P$) $\xi_c \rightarrow \xi_s \rightarrow \infty$. Close to the surface alignment instability, it is possible to expand in equation (15) the circular and hyperbolic tangents in MacLaurin series of their arguments, obtaining

$$\xi_c^{-2} = 4L^{-1}\left(1 - \frac{L^{-1}}{3}\right)$$

$$\xi_s^{-2} = 4L^{-1}\left(1 + \frac{L^{-1}}{3}\right) \tag{16}$$

The parabolic character of the inverse square reduced coherence lengths (proportional to the square of relevant fields) as a function of the reduced inverse effective extrapolation length (proportional to $W_H - W_P$) is depicted on Figure 7. It is evident that both critical fields are approaching zero likewise $(W_H - W_P)^{1/2}$ does, a behaviour similar to a second order phase transition, where $(W_H - W_P)$ plays the role of an order parameter in the Freedericksz transition considered above.

DISCUSSION

In the absence of external fields, due to the existence of a long range orientational order in the liquid crystals, the director **n** is oriented along a direction, the position of which depends on the crystal-solid surface interactions. As the investigations show, the character of liquid crystal alignment is influenced strongly by the chemical nature of the liquid crystal, the physico-chemical properties of the solid surface and the temperature. The homeotropic alignment in our experiments was achieved by covering the SiO_x layer with a thin lecithin layer, so that the alignment forces produced by SiO_x were fully suppressed (c.f. Figure 1). A model explaining the alignment properties of lecithin monolayers was proposed by Hiltrop and Stegemeyer,[15] where the surface packing density of the lecithin molecules and temperature play a crucial role. According to their model only a loosely packed lecithin layer (see Figure 8) is able to orient effectively the liquid crystal molecules in a uniform homeotropic alignment. Obviously, that situation is realized in our sample when the temperature is below T_c, i.e., in the low temperature range. However, when the temperature increases above T_c, the lecithin layer loses the aligning properties, probably due to a certain change of surface packing with temperature, leading to a reorientation of the tails of lecithin molecules from the normal to parallel position in respect to the substrate (c.f. Figure 9), and thus the aligning

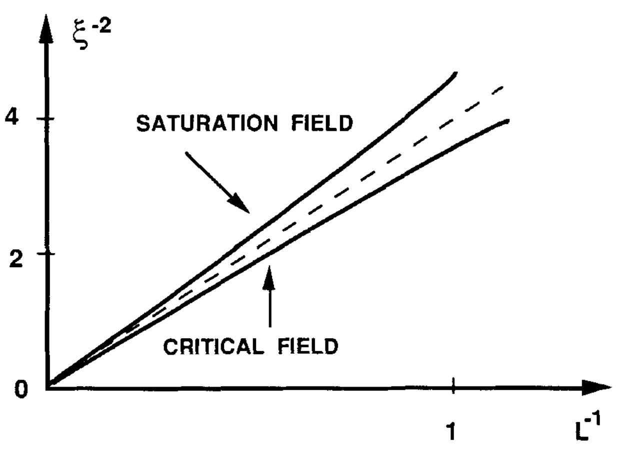

FIGURE 7 Inverse square reduced coherence lengths ξ_c and ξ_s (proportional to the square of relevant fields E_c (critical) and E_s (saturation)) as a function of inverse reduced effective extrapolation length (proportional to $W_H - W_P$).

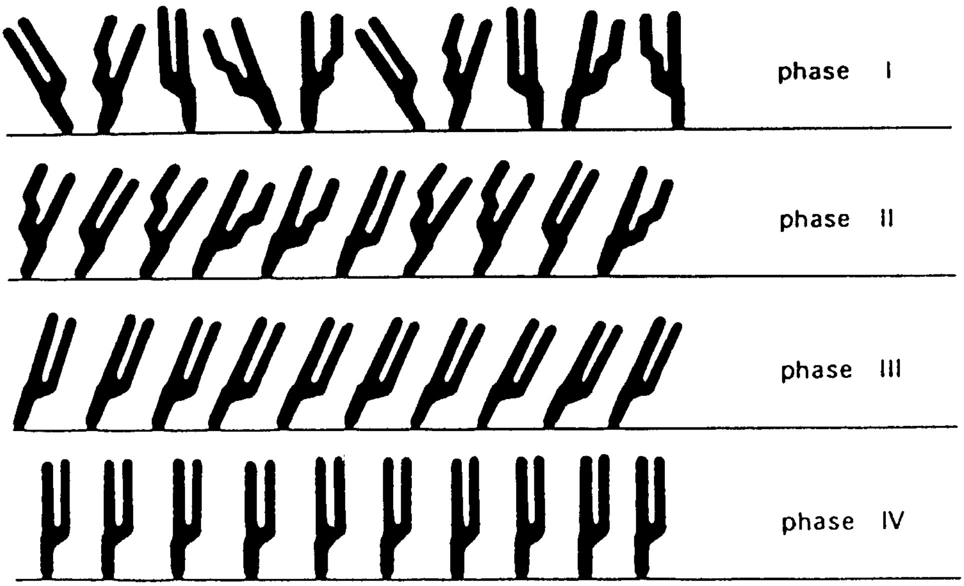

FIGURE 8 Sketch of the phases of lecithin monolayer; I. isotropic, II. sm C, III. tilted crystalline and IV. normal crystalline (from Reference 15). Only the loosely packed layer in the isotropic phase is able to produce a homeotropic alignment, because it contains holes allowing liquid crystal molecules to penetrate in the monolayer and to orient themselves in such a manner. The phase transition of the lecithin from I phase to the more ordered phases II, III and IV causes a tilted homeotropic orientation of the liquid crystal.

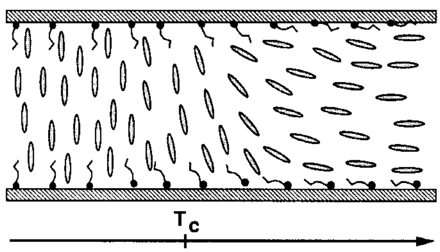

FIGURE 9 The average orientation of lecithin tails in respect to the solid surface normal considerably changes, approaching a position parallel to the surface, when the temperature increases above T_c.

properties of SiO_x become predominant. We are thus dealing with a surface induced alignment transition. In a preceding paper we studied a similar situation where the liquid crystal chromatography effect results in a gradient in the surface density of lecithin layer and thus causes a transition to planar alignment in the region with lower surface density.[7] Evidently, in the higher temperature range, the temperature change affects the surface packing in a similar way, changing it as the temperature increases above T_c. Consequently, in such a manner the alignment of nematic liquid crystal layer could be driven reversely by the temperature from homeotropic to planar, when a thin lecithin layer is deposited on SiO_x, i.e., a surface induced alignment transition will take place.

In addition, the diminishing value of U_F with increasing temperature up to T_c (see Figure 3) clearly shows a softening of surface anchorage strength when the solid surface is treated with lecithin. Moreover, the observed increase of the amplitude of molecular thermal fluctuations at that particular point indicates that the alignment produced by the surface becomes unstable i.e. when the condition $W_H = W_P$ is achieved.

In conclusion, we outline that a simple phenomenological model gives a considerably simplified description of the observed alignment transition, without taking into account the temperature dependence of the elastic constant ratio K_{11}/K_{33} (Reference 10), and without assuming any interaction between the competitive torques, acting along the two easy directions.[16,17] In a complete description, the elastic anisotropy, flexoelectricity and order electricity close to the substrate, should be taken into account.

Acknowledgments

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