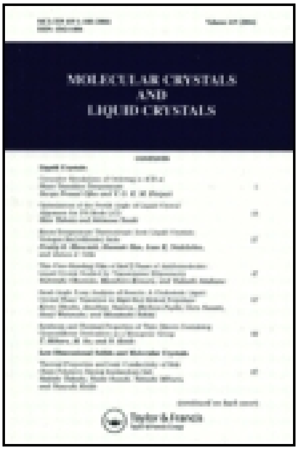

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Surface Order in Nematics[†]

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Interfaces have been studied between a liquid crystal and either glass or an evaporated SiO_x (60°) layer. Experimental results are discussed from both residual birefringence measurements in the isotropic phase and studies of the influence on the director of an in-plane magnetic field at the phase transition from isotropic to nematic. These data show that on pyrex an ordered interfacial layer exists while on SiO_x (60°) a multidomain structure is present at the surface. Comparison with literature data from nematic phase experiments shows that additional experiments with the isotropic phase and at the phase transition are vital for an understanding of the interfacial phenomena leading to liquid crystal anchorage.

INTRODUCTION

In general the orientation of a liquid crystal is characterized by two parameters. The first is the angle θ which the director makes with the macroscopic surface and which is called the tilt angle. The second is the direction in the plane of the surface. This direction is mostly defined as the angle ϕ which the director makes with a direction of preference $\mathbf{d}$ imposed by treatment of the surface.

The existence of tilt angles has been known for about a decade both at the free surfaces of certain liquid crystals and at specific liquid crystal-solid interfaces. Later on it was discovered that tilt angles could vary as a function of temperature. The influence of the surface structure on the observed tilt angle variation is discussed in a future publication.[1]

In this paper attention is paid to the in-plane behavior of the liquid crystal, the ϕ dependent part of the interfacial energy. This interfacial

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energy, which is mostly referred to as "torsional surface anchorage," represents the energy barrier against in-plane rotation of the director at the surface. The results of a number of measurements of this anchorage energy in the nematic phase have been compiled by Cognard.[2] The values for glass and SiO_x (60°)—silicon monoxide evaporated at 60° to the surface perpendicular—are reproduced in the first two columns of Table I. From these data in Table I it appears that the interfacial energy is probably somewhat larger for SiO_x (60°) than for a rubbed glass plate. Cognard states that those "anchoring energies" are due to periodic surface irregularities, such as grooves.

Our measurements of the residual birefringence in the isotropic phase[3] indicate, however, that there is a rather large difference in the interfacial order S_s above the clearing point between rubbed pyrex glass and SiO_x (60°). Below, the basic idea of this type of measurement is discussed briefly and it is indicated how interfacial energies can be obtained from the S_s values. This is done in Section I. In Section II studies are described of how pyrex glass and SiO_x (60°), which behave similarly in the nematic phase and differently in the isotropic phase, do behave at the phase transition. These qualitative results are essential for an understanding of the differences between the interfacial layers on both materials. A short discussion and the conclusions are given in Section III.

I. RESIDUAL BIREFRINGENCE IN THE ISOTROPIC PHASE

If the interface with the confining solid introduces some extra order in a planar liquid crystal layer it has been observed[3,4] that when the liquid crystal is heated to its isotropic phase there still exists an ordered layer near the surface. This has been visualized in Figure 1. As indicated, the residual, ordered layer is still birefringent ($\Delta n \neq 0$) and hence an optical phase shift δ must be observed. This shift depends on the order at the surface S_s, the layer thickness h and the profile of $S(z)$ in the layer, where the latter two depend on temperature. The expression for δ can be written as

TABLE I

Interfacial energies (Jm^{-2}) for in-plane rotation

	Cognard[2]		This work	
Material	experimental	calculated	F_s	S_s
Glass	10^{-6}, 10^{-4} 7×10^{-6}	8×10^{-5}	10^{-5}	0.1
SiO_x (60°)	10^{-3}	5×10^{-4}	0.0	0.0

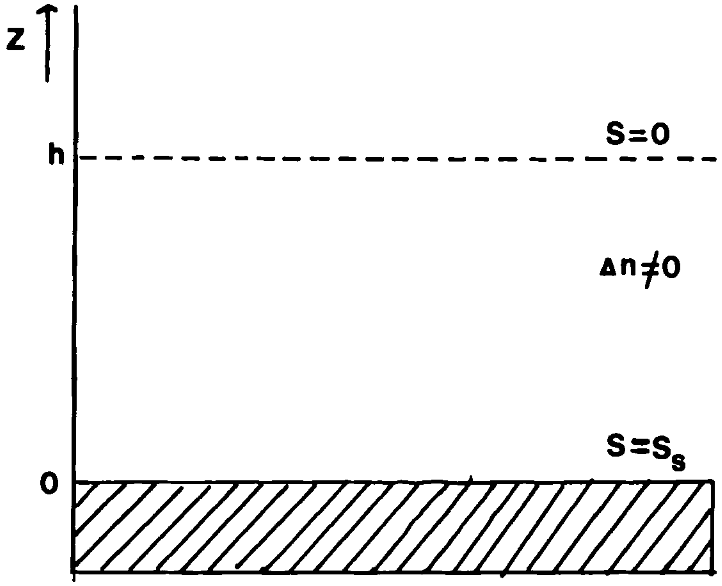

FIGURE 1 Schematic of the interfacial layer between a solid and a liquid crystal.

$$\delta = \delta^{0} \int_{0}^{h} S(z)\,dz \qquad (1)$$

with $S(0) = S_s$ and $S(h) = 0$.

The explicit dependence of $S(z)$ can be obtained for small values of S through a Landau-de Gennes expansion of the bulk free energy F_s in terms of the order parameter

$$F(S) = \int_{0}^{h} \left[f(S) + \frac{1}{2} L \left(\frac{dS}{dz} \right)^{2} \right] dz \qquad (2)$$

with

$$f(S) = \frac{1}{2} a (T - T^{*}) S^{2} - \frac{1}{3} b S^{3} + \frac{1}{4} c S^{4} \qquad (3)$$

where a, b, c and L are Landau parameters, and T^{*} is the minimum temperature for stability of the isotropic phase.

As has been shown by Tarczon and Miyano,[4] an explicit expression for $S(z)$ and hence for δ dependent on $T - T_c$ and S_s can be obtained. This enables one to obtain a value of S_s from an adaptation of the experimentally observed variations of δ as a function of $(T - T_c)$.

Analogous to the procedure applied by Gannon and Faber,[5] an expression for the surface free energy has been obtained as a function of S_s.[6] Therefore the total free energy of the interfacial layer has been expressed as

$$F_t = -F_s(S_s) + F(S) \tag{4}$$

where $F_s(S_s)$ represents the surface term. Minimization of $F(S)$ with respect to S leads to

$$F_t = -F_s(S_s) + \int_0^{S_s} [2Lf(S)]^{1/2}\, dS \tag{5}$$

via the Euler-Lagrange equation for $F(S)$. Minimization of F_t with respect to S_s then supplies a criterion for minimum free energy at the surface

$$\frac{dF_s(S_s)}{dS_s} = [2Lf(S_s)]^{1/2} \tag{6}$$

A possible choice for F_s is $F_s(S_s) = p \cdot S_s$. This is justified *e.g.* by considering the van der Waals surface interaction terms.[7] Introduction of this expression in Eq. (6) and subsequent solution for F_s leads to a value for p of

$$p = [2Lf(S_s)]^{1/2} \tag{7}$$

A block diagram of the experimental setup is given in Figure 2. A polarized, expanded, laser beam traverses the cell with the residual birefringence. The quarter wave plate behind it makes the elliptically polarized light linearly polarized again and the rotating analyzer then enables a 2δ signal measurement.[3] An example of the δ on T dependence is given in Figure 3 for 7CB on rubbed pyrex. The corresponding values of S_s and that

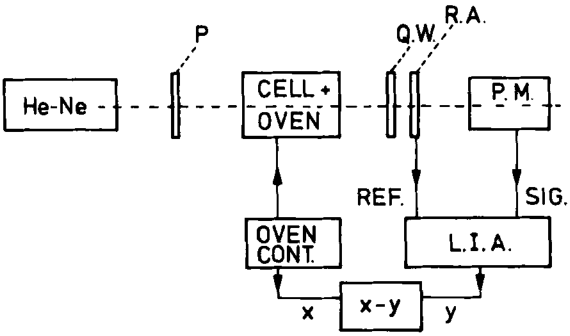

FIGURE 2 Block diagram of the experimental setup to measure optical phase shifts. He-Ne denotes a He-Ne laser, P a polarizer, R. A. a rotating analyzer, Q. W. a quarter wave plate, P. M. a photomultiplier, L. I. A. a lock-in amplifier and x-y an X-Y recorder.

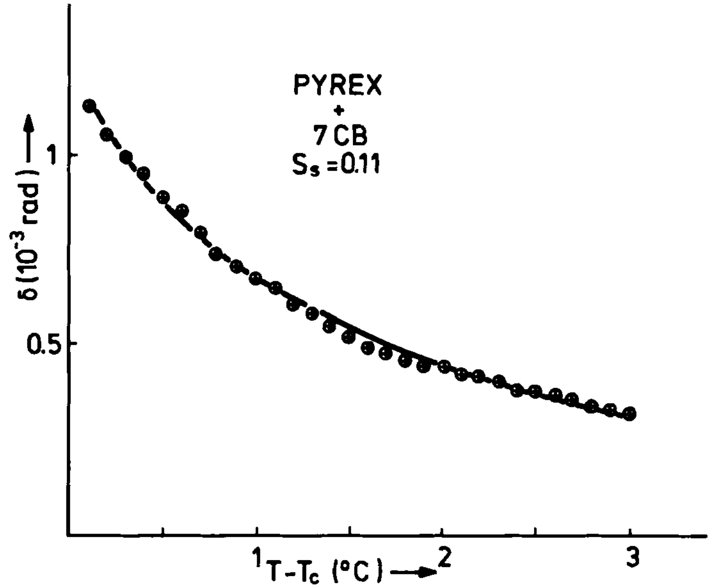

FIGURE 3 Experimental points and theoretical curve for the optical phase shift δ of 7CB on pyrex, as a function of $T - T_c$.

for 7CB on SiO_x (60°) are also in Table I. In the calculation, the values of $T^* = 313.8$ K, $T_c = 315.2$ K, $a = 0.21\ 10^6\ \mathrm{Jm^{-3}K^{-1}}$, $b = 3.3\ 10^6\ \mathrm{Jm^{-3}}$, $c = 8.1\ 10^6\ \mathrm{Jm^{-3}}$ and $L = 2 \times 10^{-11}$ N have been used.[8]

These values for S_s and the corresponding ones for F_s are presented in the third and fourth columns of Table I. Our value of F_s for pyrex glass is of the same order of magnitude as those given by Cognard. For SiO_x (60°), however, it is zero because $S_s = 0$. On such a SiO_x layer, an ordered, oriented interfacial layer is no longer present above T_c.

II. INFLUENCE OF A MAGNETIC FIELD ON THE DIRECTOR AT OR SLIGHTLY BELOW T_c

In order to get a better insight into the origin of the differences between SiO_x (60°) and pyrex glass in the isotropic phase concerning their interfacial liquid crystal layers, the influence of a magnetic field on the director at temperatures near T_c has been studied.

In all three experiments the sample is 20 μm thick and the applied external magnetic field H is in the surface plane.

In a first experiment, unrubbed, clean pyrex plates are used as a sample holder. This cell is filled with isotropic 7CB and cooled in a magnetic field of about 1 tesla. A homogeneous texture is obtained with **n** $\|$ **H**. The sample is birefringent above T_c with $S_s \approx 0.1$. The orientation remains after removal of the field. It is stable against heating up to $T_c + 10°C$ and in the nematic phase is unaltered by application of **H** in another direction.

In a second experiment, rubbed, pyrex surfaces are used with parallel directions of rubbing **d**. Cooling of this sample with $H \perp d$ leads to a rotation of **n** at the surface over a few degrees. The sample, however, is still homogeneous and its stability is comparable to that of the first sample. The surface order in the isotropic phase $S_s \approx 0.1$.

In a third experiment, surfaces coated with SiO_x (60°) are used with parallel directions of preference **d**. Cooling of the sample with $H \perp d$ leads to a multidomain structure, which disappears upon removal of the field because the sample relaxes to **n** $\|$ **d**.

III. DISCUSSION AND CONCLUSIONS

From the residual birefringence measurements, it appears that on rubbed or unrubbed-pyrex glass an ordered interfacial layer can exist above T_c. This is not influenced by external fields $H \approx 1$ tesla applied to the nematic phase. This means that on untreated pyrex too, a rotational barrier for the director exists. The value of $F_s = 10^{-5}$ J/m^2 which is obtained from residual birefringence measurements is of the same order as the rotational barriers in the nematic phase reported in literature. The above facts strongly suggest that the rotational barrier of the director at a pyrex surface is not due to surface irregularities, but to the ordered interfacial layer.

The experiments on SiO_x (60°) reveal a different type of interfacial layer. Absence of order S_s above T_c is probably due to the existence of a microdomain structure at the surface. Within a domain, orientational order may exist, but the average over many domains which is obtained due to the 5 mm laser spot yields no net birefringence above T_c (see also Ref. 1). Cooling through T_c in a magnetic field favors some of the domains at the cost of others which results in a domain structure in the nematic phase on a larger scale. Removal of the field makes the situation with **n** $\|$ **d** the more favorable again, and the domains disappear from the sample. Actually the anchoring of the bulk is not at the surface but in the transition layer in which the liquid crystal adapts itself to the surface domains. So it is improbable that an external field can provide the torsion to change the surface domain structure. This brings about some doubts concerning literature values[2] for rotational barriers of about 10^{-3} J/m^2. Unfortunately, the reference from which Cognard states to have taken the figure does not contain any figures on "torsional anchoring," neither on SiO_x nor on any other material.

(Ryschenkow and Kleman[9]; note also that the *in-plane azimuth*[9] becomes an *out-of-plane azimuth* in Ref. 2.)

Furthermore, the different interfacial layers on SiO_x and pyrex also make it impossible to compare the "calculated" values from Ref. 2 with each other or with experimental data.

Concluding, it can be said that on pyrex the bulk material is anchored *via* an ordered interfacial layer while on SiO_x the bulk is anchored in the inhomogeneous, transition layer in which the bulk adapts to the surface domain structure.

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