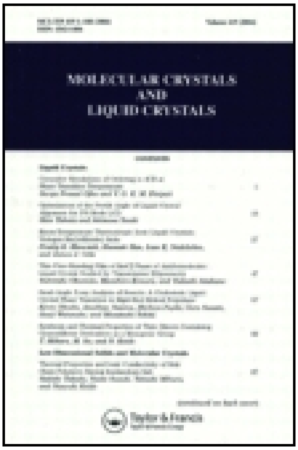

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Determination of the Surface Anchoring Energy of a Nematic Liquid Crystal by Polarization Azimuth Measurement

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1. INTRODUCTION

The anisotropic interfacial interaction between a nematic liquid crystal (LC) and the surface of a substrate is frequently described by the expression

$$f_s = W \cdot \sin^2 (\theta_s - \theta_o) \tag{1}$$

where f_s is the density of the free energy of the nematic LC at the surface, W the anchoring energy and θ_s the tilt angle with respect to the easy axis θ_o.[1]

Various methods have been devised for measuring the parameter W.[2–7] In all these cases the surface interaction is a small perturbation of bulk effects. Their separation is difficult and often leads to inaccurate results. This paper reports a method which allows a more direct determination of the surface tilt angle by an optical technique. Our method consists in the measurement of the polarization azimuth of the light transmitted through a plane parallel nematic LC sample.

The azimuth of polarization under certain conditions depends only on the orientation of the director near the substrate surface. By measuring the tilt angle in dependence on the strength of a distorting external magnetic field the anchoring energy can be calculated.

2. THEORY

2.1. Elastic Continuum Theory

We consider a homeotropically aligned nematic LC layer of thickness d sandwiched between two glass prisms which is deformed by an external magnetic field (Figure 1). The orientation of the director at a distance z from the wall at the side of incidence is described by the angle $\theta(z)$. It is governed by the elastic forces, the aligning actions of the cell surfaces and by the external magnetic field. We have the variation of the free energy

$$\delta F = \delta\left\{\int_V f(\theta, \theta')\, dV + \int_S f_s(\theta)\, dS\right\} = 0$$
$$\theta' = \frac{d}{dz}\theta \tag{2}$$

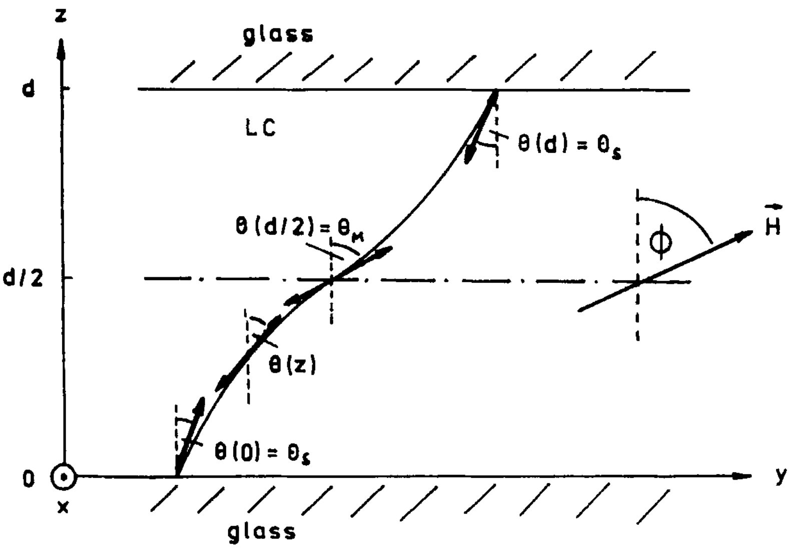

FIGURE 1 Profile of the director distribution deformed in the yz-plane.

F is the free energy of deformation in the volume and f the density of free energy with

$$f = \frac{1}{2}[(K_{11} \sin^2 \theta + K_{33} \cos^2 \theta)\, \theta'^2 - \mu\Delta\chi H^2 \cos^2(\Phi - \theta)] \quad (3)$$

K_{11} and K_{33} are the elastic constants, $\Delta\chi$ the anisotropy of the diamagnetic susceptibility, H the strength of the external magnetic field and Φ the angle between the magnetic field and the initial director orientation. S is the surface of the cell and V its volume. Using Equation (2) we get the equilibrium condition at the substrate surface

$$\frac{\partial f}{\partial \theta'} + \frac{\partial f_s}{\partial \theta} = 0 \quad (4)$$

and in the volume

$$\frac{\partial f}{\partial \theta} - \frac{d}{dz}\frac{\partial f}{\partial \theta'} = 0. \quad (5)$$

with Equation (3), (4) leads to

$$\frac{\partial f_s}{\partial \theta} = (K_{11} \sin^2 \theta_s + K_{33} \cos^2 \theta_s) \cdot \theta_s' \quad (6)$$

or with Equation (1) to

$$\frac{\partial f_s}{\partial \theta} = W \cdot \sin 2\theta_s \approx 2 \cdot W \cdot \theta_s. \quad (7)$$

If the elastic constants are known, the anchoring energy can be obtained from the slope of the $\partial f_s/\partial\theta$ -vs- θ_s plot. For the determination of the angle $\theta(z)$ we use a numerical method developed by Schmiedel et al.,[8] where initially an infinitely strong anchoring at the substrate surface is assumed. The weak anchoring can be taken into account by scaling the z-coordinate and fixing the z-origin at a point z_0 where

$$\theta(z_0) = \theta_s.$$

To evaluate the surface tilt angle we investigate its relation to the polarization azimuth of the light transmitted through an LC layer.

2.2. Light Propagation

When a divergent light beam passes through a plane parallel plate one can observe so-called fringes of equal inclination.[9,10] If the medium surrounding the plate is optically denser, the interference fringes leave the plate under refractive angles in the glass α smaller than the critical angle of total reflection. We have investigated the light propagation under the following assumptions:

a) The LC is distorted by the external magnetic field in a plane (yz-plane) perpendicular to the plane of incidence (xz-plane) (see Figure 1).

b) The incident light is linearly polarized in the plane of incidence.

c) The dielectric behavior of the uniaxially positive LC can be described by the tensor

$$\overleftrightarrow{\epsilon} = \begin{pmatrix} \epsilon_{xx} & 0 & 0 \\ 0 & \epsilon_{yy} & \epsilon_{yz} \\ 0 & \epsilon_{yz} & \epsilon_{zz} \end{pmatrix} \tag{8}$$

with

$$\begin{aligned} \epsilon_{xx} &= \epsilon_{\perp} \\ \epsilon_{yy} &= \epsilon_{\perp} \cos^2 \theta(z) + \epsilon_{\parallel} \sin^2 \theta(z) \\ \epsilon_{yz} &= (\epsilon_{\parallel} - \epsilon_{\perp}) \sin \theta(z) \cos \theta(z) \\ \epsilon_{zz} &= \epsilon_{\perp} \sin^2 \theta(z) + \epsilon_{\parallel} \cos^2 \theta(z) \end{aligned} \tag{9}$$

Here $\epsilon_{\parallel}$ and $\epsilon_{\perp}$ are the dielectric constants parallel and perpendicular to the optical axis, respectively.

d) We investigate the interference fringes leaving the LC near the critical angle of total reflection for the extraordinary wave. Its propagation inside the cell occurs almost parallel to the glass surfaces (x-axis).

For this wave the director configuration appears to be twisted, where the direction of the principal plane (containing the wave normal and the optical axis) varies with position. To begin with we apply the so-called quasi-adiabatic theorem (Mauguin limit). In the case of small deformations described by the inequality

$$\lambda \cdot (d\theta/dz) << 1 \tag{10}$$

a wave polarized in the principal plane (or perpendicular to it) remains linearly polarized and its plane of polarization rotates with the rotating principal plane.[11]

In this approximation the state of polarization of a wave refracted into the glass at the output side is determined only by the direction of the principal plane, or the director, at the surface of the LC. We obtain the following relation between the tilt angle θ_s and the azimuth of polarization β of the transmitted wave:[12,15]

$$\tan\beta = \tan\theta_s \frac{\bar{k}_x^2 + \bar{k}_{1z}\bar{k}_{2z}}{n_1\bar{k}_x}$$

$$\bar{k}_{1z}^2 = \epsilon_1 - \bar{k}_x^2;\ \bar{k}_{2z}^2 = \epsilon_\perp - \bar{k}_x^2 \tag{11}$$

$$\bar{k}_x^2 = \epsilon_1 \sin^2\alpha;\ k_{x,z} = \frac{\omega}{c}\bar{k}_{x,z};\ \epsilon_1 = n_1^2$$

n_1 is the refractive index of the glass and k_x and k_z are the components of the wave vector $\vec{k}$ in the glass (index 1) and in the LC (ordinary wave, index 2), resp.

To generate a wave in the LC that is linearly polarized in the principal plane we have to realize angles of incidence in the glass obeying the inequality

$$\epsilon_\perp < \epsilon_1\sin^2\alpha < \epsilon_\parallel. \tag{12}$$

This is the condition for the so-called single internal reflection of the extraordinary wave.[12] Ordinary waves can occur only as evanescent waves which cannot propagate through the LC plate. They cause, however, a phase shift

$$\tan\delta = -\frac{\sqrt{\bar{k}_x^2 - \epsilon_\perp}\sqrt{\epsilon_1 - \bar{k}_x^2}}{\bar{k}_x^2} \tag{13}$$

which is due to the imaginary z-component of the ordinary wave vector k_{2z} in Equation (11).

The transmitted light is therefore elliptically polarized and we have the following relation between the position of the ellipse of polarization γ and the tilt angle (see Figure 2)

$$\begin{aligned} \tan\theta_s &= a(\sqrt{1+b} - 1)\ ;\ a = (n_1/q)\cot 2\gamma \\ b &= q/(\bar{k}_x\cot^2 2\gamma)\ ;\ q = [\bar{k}_x^2(\epsilon_\perp + \epsilon_1) - \epsilon_\perp\epsilon_1]/\bar{k}_x^3 \end{aligned} \tag{14}$$

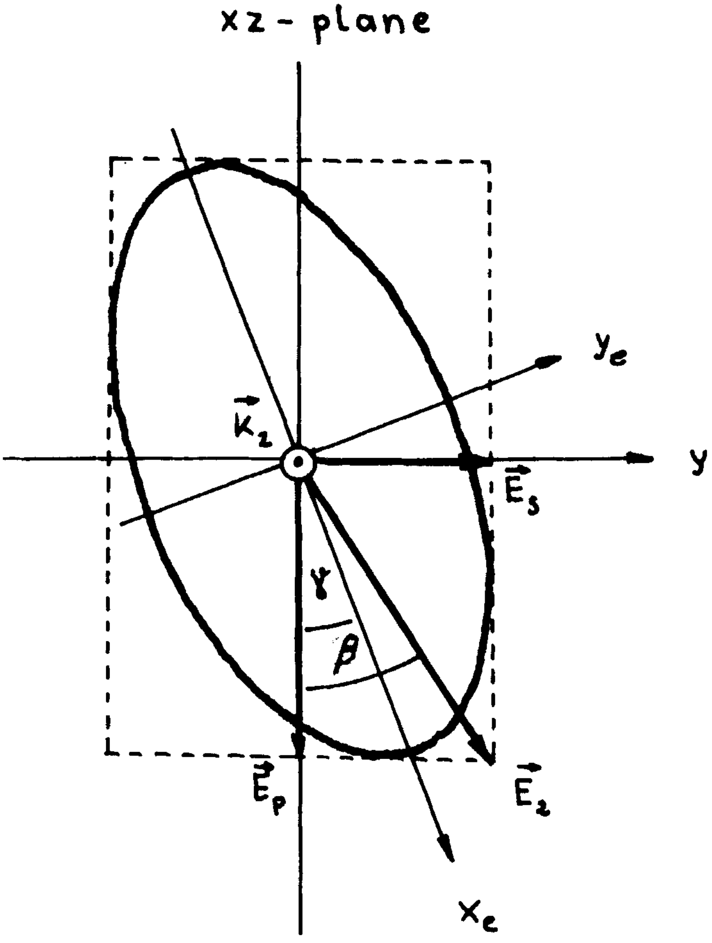

FIGURE 2 View against the direction of light propagation k_2 of the transmitted elliptically polarized wave in glass E_2. E_p and E_s are the components of the electric vector parallel and perpendicular to the plane of incidence, respectively. x_e and y_e denote the axes of the ellipse.

For $b << 1$ we obtain

$$\tan \theta_s = \frac{\tan 2\gamma}{2\sin \alpha} \tag{15}$$

The ellipticity of the light was always small in our experiment (less than 1%). Therefore γ can be comprehended as the azimuth of a linearly polarized wave.

Since Equation (14) is exactly valid only for a homogeneous tilt of the director $\theta(z)$ = const. now we have to account for the z-dependent director configuration. We regard the deformed LC layer as consisting of a sequence of sublayers each being homogeneously aligned. At each sublayer interface an exchange between both ordinary and extraordinary polarization states and incident and reflected waves, resp., takes place. However, the corresponding reflection and transmission coefficients at a given interface are of very different magnitudes. For infinitesimal small steps of the director orientation the transmission of waves with unchanged polarization states (t_{ee}, t_{oo}) remain the major processes which lead to guided waves if all other processes are neglected (Mauguin limit). They are followed by transmission and reflection processes with polarization changes (t_{eo}, t_{oe}, r_{eo} and r_{oe}). The smallest contributions due to reflections without polarization changes (r_{ee}, r_{oo}) will be neglected. Therefore we shall assume that an extraordinary wave is guided (t_{ee}) up and down between both LC-to-glass interfaces. These multiple reflections give rise to the observed interference fringes. On its way at each interface between consecutive sublayers a certain amount of the extraordinary wave is transmitted (upward by t_{eo}) or reflected (downward by r_{eo}) into an ordinary wave, resp., which then independently propagates further (t_{oo}). Since in our case k_{2z} is imaginary all ordinary partial waves are exponentially decaying. Therefore in the geometry presented here only those contributions arrive at the LC-to-glass interface which are excited within a small boundary layer of thickness $|k_{2z}|^{-1}$, *i.e.*, within the penetration depth of the ordinary wave. In the other case, *i.e.*, in the angular range of real k_{2z} contributions from all over the sample could reach the boundary and influence the

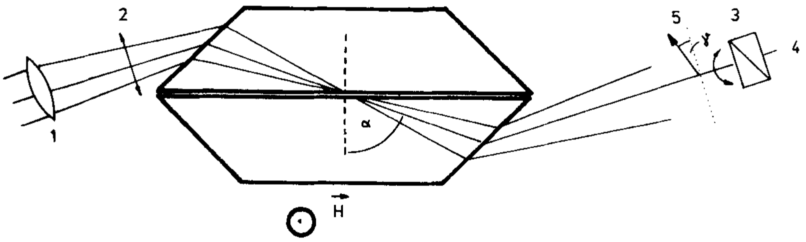

FIGURE 3 Schematic sketch of the experimental setup used for the generation and observation of the fringes of equal inclination
1 lens
2 divergent light beam linearly polarized in the plane of incidence
3 analyzer
4 photodetector
5 azimuth of polarization

polarization azimuth. Therefore a change of the polarization azimuth in general can be only used to indicate deformations of the whole sample.[14] Accounting for these assumptions and integrating all contributions we obtain by a repeated application of the method presented in Reference 15 instead of Equation (11) the following expression for the polarization azimut $\tilde{\beta}$

$$\mathrm{Tan}\,\tilde{\beta} = (n_o/\bar{k}_x)\frac{A \cdot \tan\theta_s + B \cdot \Delta\theta}{C - (n_o/\bar{k}_x)^2 D \cdot \Delta\theta \cdot \tan\theta_s} \tag{16}$$

where

$$A = \bar{k}_{1z}/\epsilon_1 + \bar{k}_{2z}/\epsilon_\perp \; ; \; B = 2\bar{k}_{1z}/\epsilon_1 + \bar{k}_{2z}/\epsilon_\perp$$

$$C = (\bar{k}_{1z} + \bar{k}_{2z})/n_1 n_o \; ; \; D = (2\bar{k}_{1z} + \bar{k}_{oz})/n_1 n_o$$

$$\Delta\theta = \frac{1}{|k_{2z}|} \cdot d\theta/dz \; ; \; \epsilon_\perp = n_o^2 \; ; \; \epsilon_\parallel = n_e^2$$

Thus the measurable polarization azimuth $\tilde{\beta}$ actually depends on both the surface tilt angle θ_s and the derivative $d\theta/dz$ which was assumed to be constant within the penetration depth $|k_{2z}|^{-1}$. The ellipticity of the transmitted light remains small as in the former case. Estimating the validity of Equations (11) and (16) it can be seen that Equation (11) is obeyed for $\Delta\,\theta << \theta_s$, *i.e.*, in the case of weak anchoring, whereas Equation (16) may be used up to $\Delta\theta \approx \theta_s$.

3. EXPERIMENTAL

For the investigation of the interference fringes of equal inclination we have devised an experimental setup that allows the deformation of an LC sample in a magnetic field as well as the determination of the position and the azimuth of polarization of the interference fringes (see Figure 3). The sample ($n_o = 1.4939$, $n_e = 1.6365$) is doped with 0.2% hexadecyl-trimethyl-ammonium-bromide (HTAB) to produce a homeotropic alignment and placed in a cell consisting of two glass prisms ($n_1 = 1.7205$) and spacers ($d = 21.6$ μm). The interference fringes are generated by illuminating the cell with a divergent laser

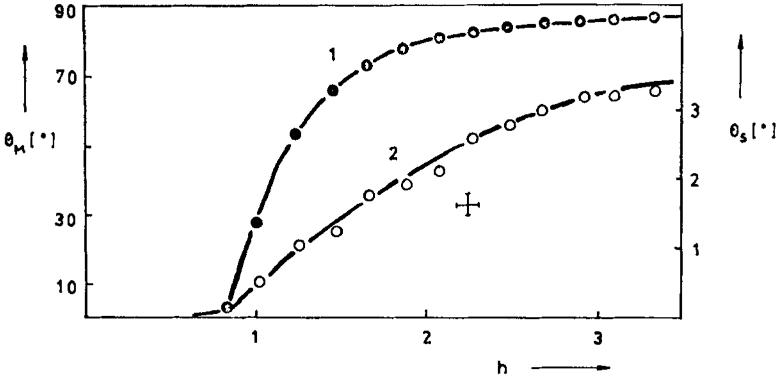

FIGURE 4 Dependence of the surface tilt angle (2) and the deformation angle θ(*d*/2) (1) (see Figure 1) on the reduced magnetic field $h = H/H_c$ (H_c-critical magnetic field)

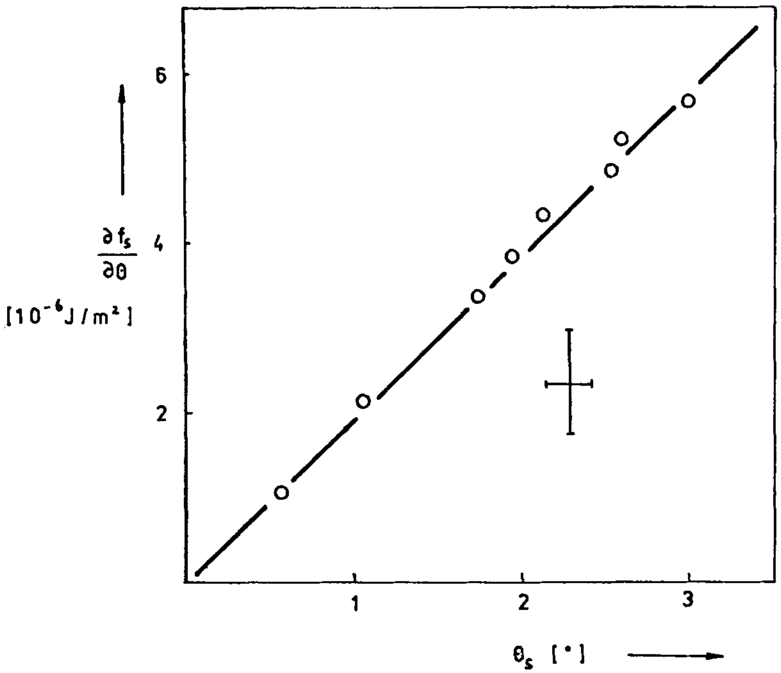

FIGURE 5 Dependence of the derivation of the surface free energy density on the surface tilt angle.

light beam (λ = 633 nm) polarized in the plane of incidence. The fringes are observed on a screen. Position and azimuthal angle are measured in magnetic fields up to 1.6 T (Φ = 88.4°). Measurements were performed at room temperature (24.5°C).

The azimuthal angles were determined by rotating an analyzer until the intensity of transmitted light is minimum. The tilt angle θ_s was obtained by varying the computed director distribution $\theta(z)$ until best agreement with Equation (16) was achieved. The dependence of θ_s on the reduced magnetic field strength h is depicted in Figure 4. Evaluating Equation (7) we get the anchoring energy $W = (6 \pm 1)$ 10^{-5} J/m^2 (Figure 5). If Equation (15) was used we would obtain $W = (1.8 \pm 0.7)10^{-5}$ J/m^2. This difference and our calculated director distribution with $\Delta\theta \approx \theta_s$ indicate that anchoring energies of the order of magnitude given above represent an upper limit to the applicability of the simple theoretical model used here. In general the study of the polarization azimuth, especially in the angular range of the so-called single internal reflection[12] is a simple and useful complement to other techniques for the study of anchoring properties. It is not limited to a certain range of surface tilt angles θ_s but only to a finite ratio $\Delta\theta/\theta_s$, *i.e.*, to finite values of W. Its applicability might be extended further by a more complete but also much more complicated theory.

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