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## NEW OPTICAL METHOD FOR THE MEASUREMENT OF THE AZIMUTHAL ANCHORING ENERGY OF NEMATIC LIQUID CRYSTALS

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**Abstract** We propose a simple symmetry based optical technique for the measurement of the azimuthal anchoring energy of nematic liquid crystals on solid substrates. It can be applied even in the case of strong anchoring and for arbitrarily large surface director deviations. The proposed technique is applied to measure the azimuthal anchoring energy of the nematic 5CB on obliquely evaporated SiO layers.

### INTRODUCTION

When in contact with a boundary surface or interface, a nematic liquid crystal is usually aligned - its surface director  $\mathbf{n}_s$  orients itself along some «easy» axis  $\mathbf{n}_{s0}$ , which depends on the surface properties. The easy axis is a local minimum of the surface orientational energy  $W_s(\delta\mathbf{n}_s)$ , where  $\delta\mathbf{n}_s = \mathbf{n}_s - \mathbf{n}_{s0}$  is the director deviation on the surface. In the case of small deviations ( $\delta\mathbf{n}_s^2 \ll 1$ ) the «anchoring» energy can be approximated as:

$$W_s(\delta\mathbf{n}_s) = 1/2 \delta\mathbf{n}_s \cdot \mathbf{A} \cdot \delta\mathbf{n}_s \quad (1)$$

where the tensor  $\mathbf{A}$  describes the strength and the anisotropy of the anchoring energy. Equation (1) can be further simplified assuming uniaxial symmetry of the anchoring. Then:

$$W_s(\delta\mathbf{n}_s) = 1/2 A \delta\mathbf{n}_s^2 \quad (2)$$

where  $A$  is an anchoring strength coefficient. Comparing the surface elastic constant  $A$  with the bulk one  $K$ , we obtain the de Gennes<sup>1</sup> extrapolation length  $L = K/A$ . For the weak anchorings  $L$  is of the order of one micron, while for the strong anchoring case it can be as short as 10 nm.

The simple approximation (2) usually fails due to the strong biaxiality of the tensor  $A$ , except for the trivial case of a homeotropic alignment, when  $n_{s0}$  is parallel to the surface normal  $N$  and the tensor  $A$  is intrinsically uniaxial. The simplest way to take into account the surface biaxiality is to assume that the main axes of the anchoring strength tensor are respectively in the zenithal plane (containing  $n_{s0}$  and  $N$ ) and perpendicular to it (i.e. along the azimuthal direction, perpendicular to both  $n_{s0}$  and  $N$ ). This decouples the zenithal and the azimuthal anchoring energies and for small deviations we obtain:

$$W_s = W_\theta(\delta\theta_s) + W_\varphi(\delta\varphi_s) = 1/2 A_\theta \delta\theta_s^2 + 1/2 A_\varphi \delta\varphi_s^2 \quad (3)$$

where  $\delta\theta_s = \theta_s - \theta_{s0}$  and  $\delta\varphi_s = \varphi_s - \varphi_{s0}$  are respectively the zenithal and the azimuthal surface director deviations (Figure 1). Two independent extrapolation lengths can be introduced now:  $L_\alpha = K_\alpha / A_\alpha$ , for  $\alpha = \theta, \varphi$ . Usually  $L_\varphi > L_\theta$ , corresponding to azimuthal anchoring weaker than the zenithal one.

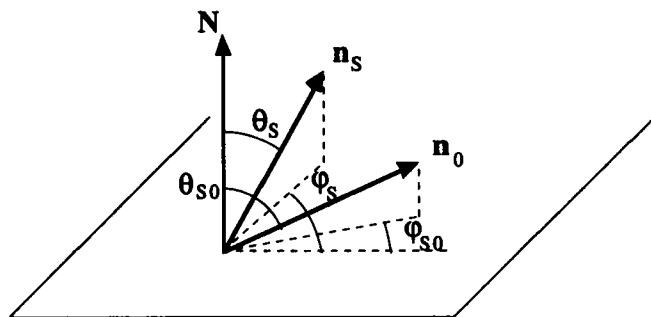


Figure 1: Definition of the zenithal ( $\theta_s, \theta_{s0}$ ) and the azimuthal ( $\varphi_s, \varphi_{s0}$ ) angles.

For the more general case of large surface director deviations the anchoring energy  $W_s$  becomes an arbitrary function of  $\theta_s - \theta_{s0}$  and  $\varphi_s - \varphi_{s0}$ . To simplify the problem we make the additional assumption that  $W_s$  can again be presented as a sum of two independent terms, the zenithal and the azimuthal anchoring energies:

$$W_s = W_\theta(\theta_s - \theta_{s0}) + W_\varphi(\varphi_s - \varphi_{s0}) \quad (4)$$

These energies are periodic functions of the corresponding angular parameters and can be expanded in Fourier series. Taking only the first term in the expansion gives us the simplest form compatible with the symmetry of the surface, proposed by Rapini and Papoular<sup>2</sup> for the special cases of planar and homeotropic alignments:

$$W_{\alpha} = 1/2 A_{\alpha} \sin^2(\alpha_s - \alpha_{s0}) \quad ; \quad \alpha = \theta, \varphi \quad (5)$$

However, the experimental studies have revealed that for some substrates the higher order terms in the surface energy cannot be neglected.<sup>3,4</sup>

Several experimental methods have been proposed so far for the measurement of the anchoring energy.<sup>3-9</sup> Usually, one applies a large bulk torque, opposite to the surface one. Then the equilibrium surface director orientation  $\mathbf{n}_s$  is measured, e.g. optically. This gives the surface torque as a function of the director deviation and integrating this function one obtains the anchoring energy (4) or at least the extrapolation length, if only small deviations data are available. This kind of measurements are relatively easy for the zenithal anchoring - large bulk torques can be created applying strong external fields (e.g. electric field) and the surface director deviation is detected using optical<sup>4,5,7-9</sup> or capacitive<sup>3</sup> techniques. The precision of the measurements is good enough even in the case of large deviations ( $\theta_s - \theta_{s0} \cong \pi/2$ ). In the azimuthal case some difficulties arise for large deviations - the strong bulk torques are much harder to obtain and only optical techniques can be used to detect the surface director. The data interpretation in this case is complicated, because the light propagation in the resulting strongly twisted nematic texture is far outside the waveguide Maugin's regime.

Here we propose a simple and direct technique to measure the azimuthal anchoring energy of nematic liquid crystals on solid substrates. It can be applied even in the case of strong anchoring ( $L \cong 50$  nm) and for arbitrarily large surface director deviations. To demonstrate the proposed technique, we present and discuss few measurements of  $W_{\varphi}(\delta\varphi_s)$  of the nematic pentylcyanobiphenyl (5CB) on obliquely evaporated SiO layers.

## **EXPERIMENTAL TECHNIQUE**

In our measurements we use a twisted nematic cell with variable thickness. The nematic is filled between the planar substrate under study and a counterplate - a large radius glass lens (Figure 2). The thickness of the nematic layer varies from zero (in the center of the sample) up to about 50 microns on the periphery. Moreover, a mechanical system enables

us to change the thickness in any fixed point of the sample just rolling the lens on the plate. The thickness  $D$  of the nematic layer is determined with good precision from the known radius of the lens and the measured distance  $r$  between the observed area and the point of contact between the plate and the counterplate.

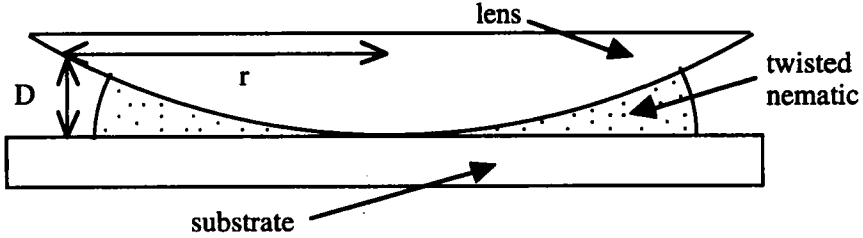


Figure 2: Geometry of the cell.

The lens surface is treated, e.g. by SiO evaporation, in order to induce a good uniform nematic alignment with the strongest possible anchoring. The zenithal angle  $\theta_{\ell 0}$  of the lens easy axis is chosen to be the same as the one of the studied plate  $\theta_{s0}$ . For simplicity we assume here also  $\theta_{s0} = \theta_{\ell 0} = \pi/2$ , i.e. planar alignment without pretilt on both the plate and the lens. All the formulae, however, remain unchanged in the more general case  $0 < \theta_{s0} = \theta_{\ell 0} < \pi/2$ , with only minor renormalization of the bulk elastic constant and the birefringence.

We chose the  $x$ -axis along the easy direction of the substrate under study ( $\varphi_{s0} = 0$ ) and we rotate the lens to obtain  $\varphi_{\ell 0} = \pi/2$ . The bulk twist angle  $\phi_b$  in the sample is now a function of the thickness  $D$ :  $\phi_b = \pi/2 - \delta\varphi_s - \delta\varphi_\ell$ , where  $\delta\varphi_s = \varphi_s - \varphi_{s0}$  and  $\delta\varphi_\ell = \varphi_\ell - \varphi_{\ell 0}$  are the thickness-dependent azimuthal deviations of the surface director (Figure 3). There is no external fields in our sample and the zenithal angle  $\theta = \theta_{s0} = \theta_{\ell 0}$  is constant throughout it. In result, the nematic is uniformly twisted and its free energy per unit area is:

$$F = \frac{1}{2} K_{22} \frac{\phi_b^2}{D} + W_s(\delta\varphi_s) + W_\ell(\delta\varphi_\ell) \quad (6)$$

where the first term is the integrated bulk energy contribution and  $W_s$  and  $W_\ell$  are the azimuthal surface anchoring energies (unknown arbitrary functions of the corresponding surface director deviations). From Equation (6) we obtain the torque's equilibrium equation:

$$M_S = M_l = \frac{K_{22}}{D} \left( \frac{\pi}{2} - \delta\varphi_S - \delta\varphi_l \right) \quad (7)$$

where  $M_i = \frac{d}{d\delta\varphi_i} W_i$ ;  $i = l, S$ , are the respective surface torques. From Equation (7), if we know  $\delta\varphi_S$  and  $\delta\varphi_l$  as functions of  $D$ , we obtain the surface torques. Integrating them we have finally:

$$W_S(\delta\varphi_S) = \int_0^{\delta\varphi_S} M_S(\alpha) d\alpha \quad (8)$$

To measure the surface director deviations we observe our sample under a polarizing microscope. The first step is to detect the easy axes on both plates. This can be done in the thickest region ( $D \approx 50 \mu\text{m}$ ), where the light propagation is in the waveguide Mauguin's regime and the surface director deviations are negligible, due to  $D \gg L_S, L_l$ , the anchoring extrapolation lengths. Rotating the polarizer ( $P_S$ ) and the analyzer ( $P_l$ ) up to complete extinction, we determine with good precision the easy axes orientations on both surfaces (Figure 3a).

Decreasing the thickness, the bulk torque applied on the surfaces increases, and the surface director deviations are no more negligible. If the sample remains thick enough ( $D > 5 \mu\text{m}$ ) to satisfy the Mauguin's conditions, we obtain again a complete extinction

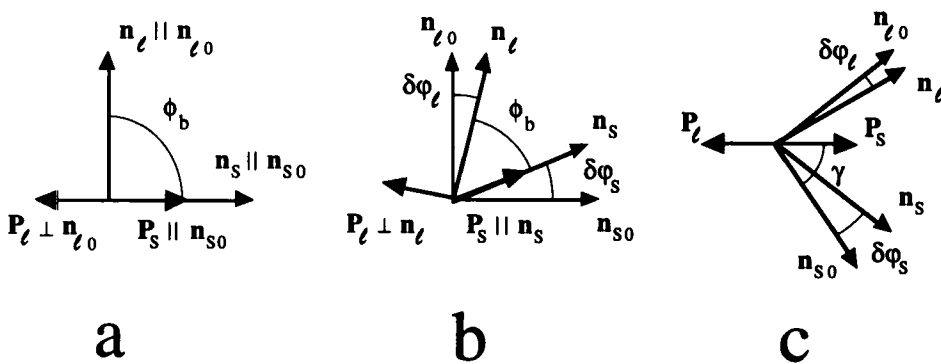


Figure3: Orientation of the polarizers and of the surface directors:

- a) - for infinitely thick cell; b) - for thick cell in the Mauguin regime;
- c) for our measurements at arbitrary thickness.

rotating the polarizers respectively at angles  $\delta\varphi_s$  and  $\delta\varphi_l$  (Figure 3b). This direct observation of the surface deviations has already been applied<sup>8,9</sup> to study the azimuthal anchoring. The domain of application of this simple technique is, however, very limited: only weak anchorings ( $L_s > 1 \mu\text{m}$ ) can be studied and only for small deviations from the easy axis ( $\delta\varphi_s \ll 1$ ).

To overcome this limitation we need to analyze the light propagation in thinner twisted cells. Several papers have treated this problem,<sup>10-12</sup> which is of great interest for the twisted nematic displays. Simple analytical expressions exist for the polarized light transmission:<sup>11</sup>

$$T = \left[ \cos b \cos(\alpha_l + \alpha_s) + \frac{\sin b}{\sqrt{1+a^2}} \sin(\alpha_l + \alpha_s) \right]^2 + \frac{a^2}{1+a^2} \sin^2 b \cos^2(\alpha_l - \alpha_s) \quad (9)$$

where  $\alpha_s$  is the angle between  $P_s$  and  $n_s$ ;  $\alpha_l$  is the angle between  $P_l$  and  $n_l$ ;  $a = \pi D \Delta n / (\phi_b \lambda)$ ;  $b = \phi_b \sqrt{1+a^2}$ ;  $\lambda$  is the light wavelength and  $\Delta n$  is the birefringence.

In principle, Equation (9) gives  $\delta\varphi_s$  and  $\delta\varphi_l$  from the transmission measurements at different wavelengths (or thicknesses, or polarizer orientations). In practice, this approach is quite difficult:  $T$  is an oscillating function of several parameters ( $\alpha_l$ ,  $\alpha_s$ ,  $\Delta n$ ,  $D$ ) and all of them must be measured or must be known from another experiment. Even slight error in the value of  $T$  or in one of these parameters can induce not only quantitative, but also qualitative errors in the deduced  $\delta\varphi_s$  and  $\delta\varphi_l$  values, due to jumps from one oscillation to another. Our numerical simulations and experiments have confirmed this difficulty: even the small errors in the transmission, due to the microscope depolarization, or in the thickness, due to the capillary forces induced change of  $D$  after filling the sample, lead to qualitatively wrong results for  $\delta\varphi_s$  and  $\delta\varphi_l$ .

We will now show how this problem can be avoided. We fix the polarizers at their positions of Figure 3a and we rotate the sample on the microscope stage at an arbitrary angle  $\gamma$ , like in Figure 3c. The transmission can be presented now in the form:

$$T(\gamma) = T_1 + T_2 \sin^2(2\gamma + \delta\varphi_l - \delta\varphi_s) \quad (10)$$

where the coefficients  $T_1$  and  $T_2$  are independent on  $\gamma$ . The transmission has a minimum for

$$\gamma = \gamma_{\min} = (\delta\varphi_s - \delta\varphi_l) / 2 \quad (11)$$

and this gives us directly the difference between the surface deviations. There is no error accumulation in this approach and we do not need to know *any* material parameters (e.g. the birefringence). The angle  $\gamma_{\min}$  can be easily measured with high precision on area as small as  $10 \times 10 \mu\text{m}^2$ . Only when  $T_2 \ll T_1$  (i.e. when the minimum of Equation (10) is very shallow) the precise measurement of  $\gamma_{\min}$  becomes delicate. To overcome this difficulty we rotate the output polarizer at right angle, i.e. parallel to  $\mathbf{n}_0$ . The transmission becomes:

$$T(\gamma) = T_1' + T_2' \cos^2(2\gamma + \delta\varphi_l - \delta\varphi_s) \quad (12)$$

The minimum of T is now obtained at:

$$\gamma = \gamma'_{\min} = \pi/4 - (\delta\varphi_s - \delta\varphi_l)/2 \quad (13)$$

Now the coefficients have changed and the new ratio  $T_2' / T_1'$  is more favorable. Usually the Equations (11) and (13) are sufficient to measure precisely  $\delta\varphi_s - \delta\varphi_l$  at any thickness. However, if necessary, one can change continuously the value of  $T_2$ , rotating the polarizers. This enables us to obtain at any given thickness the optimal precision of the measurement.

The astonishing simplicity of Equations (11) and (13) can be explained by symmetry arguments, without even using the formula (9) for the transmission. Our nematic film is uniformly twisted. Then the bissectrice  $\mathbf{b}$  of  $\mathbf{n}_l$  and  $\mathbf{n}_s$  (Figure 4a) is a twofold symmetry rotation axis for the sample. Rotating the sample *and* the polarizers at angle  $\pi$  around  $\mathbf{b}$  we obtain the situation sketched at Figure 4b. The transmission of the system is obviously

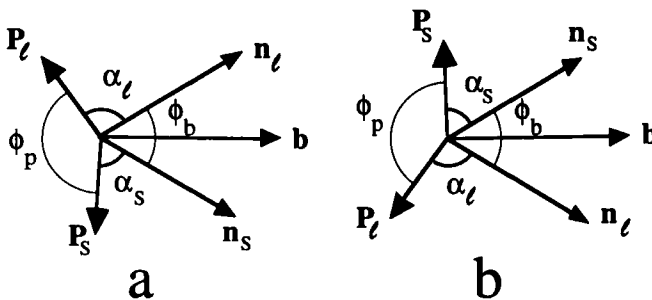


Figure 4: Symmetry transformation of the cell.



the same before and after the rotation, i.e.  $T$  do not change when we replace  $\alpha_l$  with  $\alpha_s$  and vice versa. If we fix all the other angular parameters ( $\phi_b$  and  $\phi_p$ ),  $T$  becomes an even function of  $\alpha_l - \alpha_s$  and, hence, has an extremum at  $\alpha_l = \alpha_s$ . This extremum of the transmission is obtained when the bissectrice of the polarizers coincides with  $\mathbf{b}$ . Equations (11) and (13) are particular cases of this more general symmetry property.

There is no more symmetry elements in our problem and  $\delta\phi_s - \delta\phi_l$  remains the only quantity which can be measured in this simple and direct manner. If one wants to obtain separately the deviations  $\delta\phi_s$  and  $\delta\phi_l$ , one needs to apply the Equation (9) and to deal with all the error accumulation problems explained above. To avoid this, we make at this stage the only restrictive assumption in the present paper: We suppose that the azimuthal anchoring is much stronger on the lens than on the substrate under study and we neglect  $\delta\phi_l$  in Equations (11) and (13). Obviously, our method cannot be then applied for the strongest anchorings. Nevertheless, this limitation remains the less restrictive one among all the existing methods for the measurement of the azimuthal anchoring strength.

## EXPERIMENTAL RESULTS AND DISCUSSION

Using the proposed technique we have measured the azimuthal anchoring strength at ambient temperature of the nematic 5CB on three anisotropic substrates. All of them were flat glass plates with SiO layers, evaporated at grazing incidence ( $\alpha_{ev}=75^\circ$ , thickness  $d_{ev}=40 \text{ \AA}$ ). This treatment is known<sup>13</sup> to give a moderately strong planar anchoring. In order to weaken farther the anchoring we have deposited before the evaporation a thin DMOAP silane layer on the plates 2 and 3 (dip coating for the plate 2 and spin coating for the plate 3, polymerization at  $110^\circ\text{C}$  for both of them). The counterplate is a large radius glass lens, also covered with SiO layer, evaporated under conditions known to give a very strong planar anchoring ( $\alpha_{ev}=60^\circ$ ,  $d_{ev}=150 \text{ \AA}$ ).

On Figure 5 we present the experimental results for  $\delta\phi_s(D)$ . With decreasing thickness the surface director deviation increases and for some critical thickness  $D_C$  we obtain  $\delta\phi_s(D_C) = \pi/2$ , i.e. the anchoring is completely broken. The critical thickness is of the same order of magnitude as the extrapolation length and  $D_C = L$  if the energy has a Rapini-Papoular form. We see from Figure 5 that  $D_C$  is longer for the silane treated plates 2 and 3: as expected, the anchoring energy is weaker on these plates.

The data on Figure 5 are obtained under the assumption that the lens azimuthal anchoring is infinitely strong. To test this assumption we have measured in the same way several plates with different anchoring strengths. We observe two kinds of behaviours of

these plates: Most of them give  $\delta\phi_S(D)$  dependences like those presented on Figure 5 -  $\delta\phi_S$  increases with decreasing thickness and the anchoring breaks at the critical thickness  $D_C$ , typically  $30 \text{ nm} < D_C < 200 \text{ nm}$ . A different behaviour has been observed for the few strongest anchoring substrates, e.g. a plate with SiO layer evaporated at the same conditions as the one on the lens. In this case no critical thickness is observed and  $\delta\phi_S - \delta\phi_\ell$  varies slowly or not at all with decreasing thickness. This behaviour is expected for  $\delta\phi_S \equiv \delta\phi_\ell$  (see Equation (11)), i.e. when the anchoring strength is almost the same on both plates. We estimate in this way the lens extrapolation length to be less than 30 nm. This gives us the practical limit for the strongest azimuthal anchoring which can be measured.

On Figure 6 we present the surface torques obtained from Equation (7) as a function of the surface director deviation  $\delta\phi_S$ . For small  $\delta\phi_S$  the surface torque is almost the same on the three plates, corresponding to an extrapolation length of about 80 nm. At large deviations, however, the silane treated substrates have weaker torques, especially the spin coated plate 3, which has a thicker silane layer.

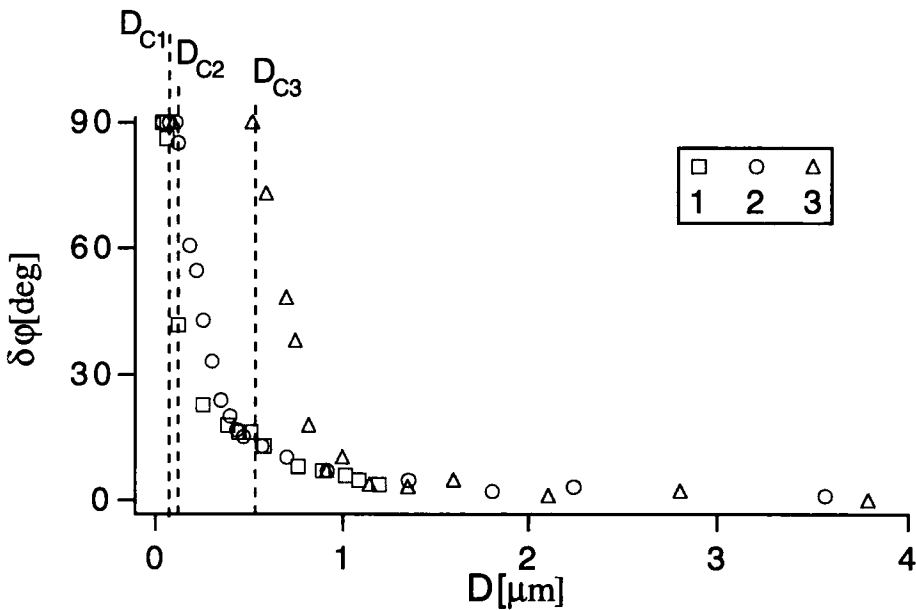


Figure 5: Thickness dependence of the surface director deviation.

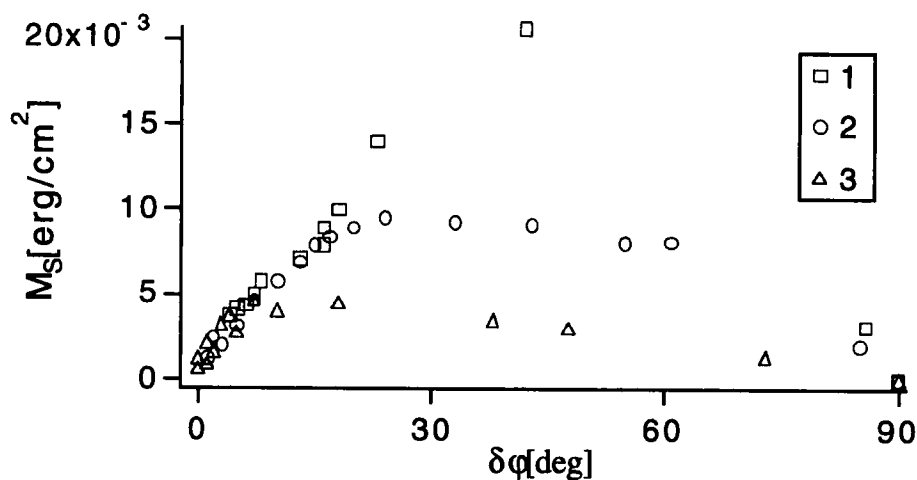


Figure 6: Surface torques on the substrates.

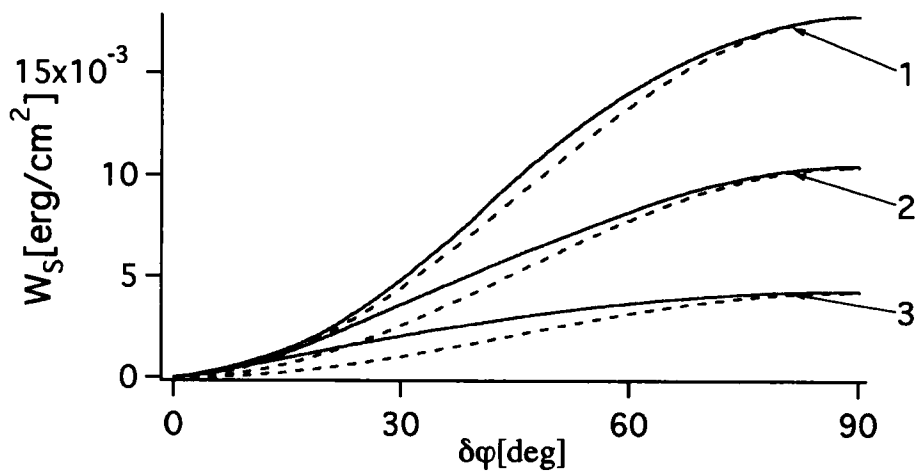


Figure 7: Azimuthal anchoring energy:  
solid lines - experimental results;  
dashed lines - fit with the Rapini-Papoular model.

On Figure 7 are presented the azimuthal anchoring energies of the three substrates. The solid lines are the experimental curves obtained by numerical integration of the torques

after interpolation, which gives an apparent smooth aspect. The dashed lines are the fits with the model of Rapini and Papoular. For small  $\delta\phi_s$  all the plates have approximately the same  $W_\phi(\delta\phi_s)$ . At larger deviations the curves separate and the energy barrier at  $\delta\phi_s=90^\circ$  is lower for the silane treated plates, in particular for the thicker silane coating plate 3. For all the three substrates the azimuthal anchoring energy deviates from the Rapini-Papoular form, the deviation being much stronger for the silane treated plates. Here we will not discuss in more detail these preliminary results, which are beyond the scope of the present contribution.

In conclusion, we propose a very simple and direct technique to measure the azimuthal anchoring energy of the nematics on solid anisotropic substrates. Our method is based on the symmetry properties of the twisted nematic cell and the data interpretation do not depend on any material parameters. The measurement is extremely simple and can be applied for moderately strong anchoring energies as well as for weak ones and for arbitrary large surface director deviations.

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