Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

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To cite this Article Faetti, S. , Nobili, M. and Schirone, A.(1991) 'Experimental measurement of the azimuthal anchoring energy function at a SiO-nematic interface', Liquid Crystals, 10: 1, 95 — 100

To link to this Article: DOI: 10.1080/02678299108028232

URL: http://dx.doi.org/10.1080/02678299108028232

Liquid Crystals, 1991, Vol. 10, No. 1, 95–100

Experimental measurement of the azimuthal anchoring energy function at a SiO–nematic interface

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(*Received 22 October 1990; accepted 18 January 1991*)

The functional form of the azimuthal anchoring energy, i.e. the anisotropic part of the interfacial free energy, at the interface between the nematic liquid crystal 4-*n*-pentyl-4′-cyanobiphenyl and an obliquely evaporated SiO substrate is measured for the first time by using a reflectometric method. The anchoring energy function is obtained by measuring the director rotation on the interface caused by an external magnetic field ranging from 0 to 2·3 T. The dependence of the anchoring energy on the director azimuthal angle is found to be well fitted by the function $W_a(\varphi) = W_a \sin^2 \varphi$ in agreement with the predictions of the Berreman model for the anchoring at a grooved interface.

1. Introduction

In recent years there has been a growing interest in the physical interactions at interfaces [1]. Particular interest has been focused on the interfacial properties of nematic liquid crystals [2–7]. An important parameter that characterizes the interfacial behaviour of a nematic is the anchoring energy function which corresponds to the anisotropic part of the interfacial free energy. Let us consider the interface between a nematic and a solid substrate lying on the *xy* plane. The average orientation of molecules at the interface is represented by a unit vector **n**, called the director, which makes the polar angle θ with the *z* axis orthogonal to the interface and the azimuthal angle φ with the *x* axis. At equilibrium and in the absence of external orienting torques the interfacial anisotropic free energy is minimized if the director is aligned along a well-defined *easy axis* defined by the two easy angles θ_O and φ_O. In the presence of external surface torques, the director is displaced from the easy axis to reach a new equilibrium position (θ, φ) where the external torque is balanced by the anchoring surface torque which the substrate exerts on the director. The work per unit surface area which must be spent to reach the new equilibrium angles is given by a function $W(\theta, \varphi)$ which is called the anchoring energy function. A review of experimental methods to measure $W(\theta, \varphi)$ can be found in [5]. Unfortunately in most of the experiments the anchoring is strong and thus, only the shape of the anchoring energy function near the equilibrium point $(\theta \approx \theta_O, \varphi \approx \varphi_O)$ can be explored; this is given by the approximate parabolic form

$$W(\theta, \phi) = \frac{W_a}{2}(\phi - \phi_O)^2 + \frac{W_p}{2}(\theta - \theta_O)^2, \qquad (1)$$

where W_a and W_p are the azimuthal and polar anchoring energy coefficients, respectively. This difficulty can be overcome if the anchoring is weak [8], if very high

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magnetic fields ($\approx 10\,\mathrm{T}$) are available [9] or if an electric field is applied to a nematic having a large dielectric anisotropy [10, 11].

In recent years some authors have succeeded in measuring the θ dependence of the anchoring energy function (polar anchoring energy) for $\varphi = \varphi_0$ by using different optical or capacitive methods [8–11] in the two cases of homeotropic director alignment ($\theta_0 = 0$) [9] and of homogeneous planar alignment ($\theta_0 = \pi/2$) [8, 10, 11]. In all of these experiments the authors found that the polar anchoring energy function $W(\theta) \equiv W(\theta, \varphi_0)$ cannot be represented by the simple phenomenological Rapini form [12] whilst it is satisfactorily described by a function of the kind

$$W(\theta) = \frac{W_1}{2}\sin^2(\theta - \theta_0) + \frac{W_2}{4}\sin^4(\theta - \theta_0), \tag{2}$$

where the anchoring coefficients W_1 and W_2 depend on the kind of surface treatment of the substrate. In the special case of an obliquely evaporated SiO substrate at 60° ($\theta_0 = \pi/2$) Yokoyama and Van Sprang [10] found $W_1 = 3{\cdot}9 \times 10^{-5}\,\mathrm{J/m^2}$ and $W_2 = -1{\cdot}8 \times 10^{-5}\,\mathrm{J/m^2}$. More recently Barbero *et al.* [13] have reanalysed all of these experimental results and showed that flexoelectricity, ordoelectricity and second order elasticity of nematic [14–16] can largely affect the experimental results. Therefore new detailed experimental investigations are needed.

A different behaviour concerns the azimuthal anchoring energy function $W(\varphi) \equiv (W(\theta_0, \varphi)$ for which we can easily show that flexoelectricity, ordoelectricity, and second order elasticity [13] do not play any role. In this paper we report for the first time our measurements of this function over the whole range $[0 < \varphi < \pi/2]$ at the interface between the nematic 4-*n*-pentyl-4′-cyanobiphenyl (5CB) on an obliquely evaporated SiO substrate [17]. The azimuthal anchoring energy coefficient has been recently measured by our group by using a torsion pendulum technique, and has been found to decrease significantly as the temperature approaches the nematic–isotropic transition T_{NI} of 35·3°C [18].

2. Experimental

In the present experiment we chose the evaporation conditions and the temperature of the nematic in such a way as to have a very weak anchoring energy [19]. 5CB was purchased from BDH Chemicals and used without further purification. The SiO layer had a thickness of 25 Å (tested by using the standard procedure of measuring the resonance frequency of a control plate) and it was obtained by evaporating 99·8 per cent purity SiO (BALZERS BD 481 293-T) on a glass plate at an incidence angle of 60° with respect to the plate normal. The evaporation molybdenum source (BALZERS BD 482048) was 40 cm from the glass plate, the residual pressure in the evaporation bell-jar was $\sim 10^{-6}$ Torr and the evaporation rate was $\sim 0{\cdot}2$ Å/s.

The reflectometric experimental technique used to measure $W(\varphi)$ has already been described [20]. The nematic sample was sandwiched between two SiO treated glass plates separated at the ends by two mylar spacers having different thickness (130 μm and 260 μm) in such a way as to make a wedge. The glass plates too are wedge shaped with a wedge angle of 0·4°. Under these conditions the laser beams reflected from various interfaces can be easily separated one from the other. The nematic was enclosed in a thermostatic box which ensures a temperature stability better than ±0·02°C and lies between the two polar expansions of a Brucker electromagnet giving a magnetic field up to 2·35 T. A 5 mW He–Ne laser beam was polarized by a polarizer and impinged at almost normal incidence ($\theta_i < 1°$) on the nematic layer. The laser beam reflected from the first SiO–nematic interface passes through a crossed analyser and was collected by a photodetector. For a uniformly aligned nematic sample (a monodomain) the light intensity after the analyser is given by

$$I=I_0\sin^2[2(\delta-\varphi)], \tag{3}$$

where δ is the angle between the polarizer axis and an x axis in the SiO plane and φ is the azimuthal angle between the director and the x axis at the interface. Let us assume that the x axis coincides with the easy axis at the SiO–nematic interface ($\varphi_0=0$). If a magnetic field B, widely exceeding the Freedericks threshold value B_c ($B_c\sim0{\cdot}015$ T), is switched on, the director tends to align parallel to the magnetic field everywhere in the nematic but in a thin layer close to the SiO–nematic interface. The balance of surface torques for $B\gg B_c$ is given by

$$\frac{\partial W(\varphi)}{\partial\varphi}=\sqrt{(K_{22}\chi_a)}B\sin(\beta-\varphi), \tag{4}$$

where β is the angle which the magnetic field makes with the easy axis, K_{22} is the twist elastic constant and χ_a is the diamagnetic anisotropy. Therefore the anchoring torque and thus, the azimuthal anchoring energy $W(\varphi)$, can be obtained by measuring the surface director angle φ as a function of the intensity of the magnetic field. The surface director angle φ is obtained by measuring the intensity of the reflected beam for a given value of the angle δ between the polarizer and the easy axis (see equation (3)). In the present experiment we use $\delta=-22{\cdot}5°$.

We point out that equation (3) has been deduced by assuming a homogeneous director orientation all over the nematic layer, whilst a director twist occurs near the interface when the magnetic field is switched on. By using a numerical procedure [21] we found that, in the range of temperatures used in our experiment, the maximum contribution to the reflected intensity due to the director distortion is always smaller than 0·5 per cent of the I_0 intensity shown in equation (3), (see also [20]). Therefore the effect of the director distortion can be neglected and the azimuthal director angle φ at the interface can be directly obtained by using equation (3) once the values of I_0, δ and I are measured. We point out that this measurement does not require the knowledge of the optical refractive indices of the nematic. This is an important advantage of this experimental method because the refractive indices of the nematic near the interface are not known parameters.

Figure 1 shows the azimuthal director angle versus the magnetic field B for a value of the temperature near the transition temperature T_{NI} of 5CB. The angle β between the magnetic field and the easy axis was chosen to be 88·5°, in order to avoid the occurrence of domain-like director patterns [22]. By substituting these experimental values together with the known values of the product $K_{22}\chi_a$ [18] on the right hand side term in equation (4) we find the azimuthal anchoring torque as shown in figure 2. Finally the azimuthal anchoring energy function $W(\varphi)$ is obtained by numerical integration of the surface anchoring torque of figure 2 as shown in figure 3. The full lines in figures 2 and 3 correspond to the best fits of the experimental results with respect to the anchoring energy function

$$W(\varphi)=\frac{W_1}{2}\sin^2\varphi. \tag{5}$$

We note the good agreement between the experimental results and the theoretical dependence of equation (5). Therefore, as far as the azimuthal anchoring is concerned, no correction to the simple Rapini expression is needed.

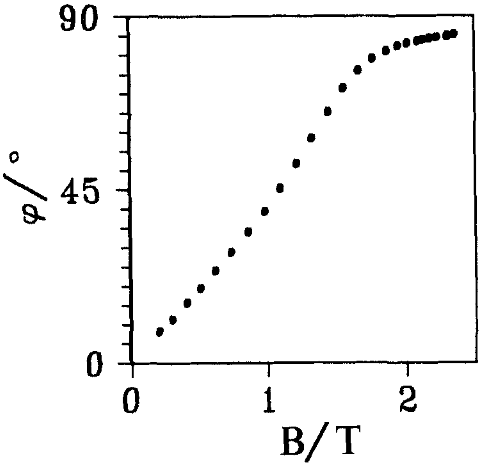

Figure 1. Azimuthal director angle at the SiO–nematic interface of 5CB versus the magnetic field at a temperature near the nematic–isotropic transition temperature T_{NI} of 35·3°C. The magnetic field makes an angle β of 88·5° with the easy axis and $T_{NI}-T=0\cdot14$°C.

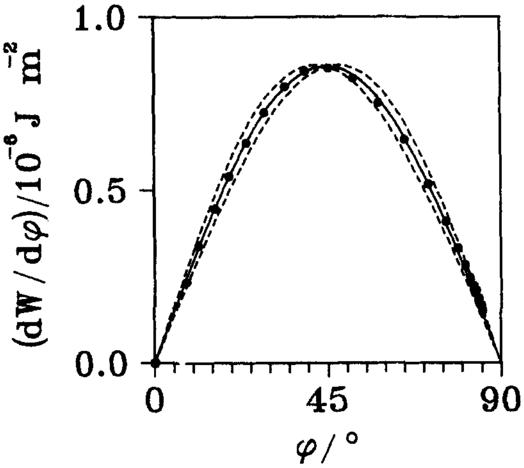

Figure 2. The azimuthal anchoring torque versus the azimuthal angle φ of the director at the interface with respect to the easy axis for $T_{NI}-T$ of 0·14°C. The azimuthal anchoring torque is calculated by substituting the experimental values of φ given in figure 1 in equation (4) and setting $\beta=88\cdot5$°. The value of the product $K_{22}\chi_a$ is that of [18]. The full line corresponds to the best fit of the experimental data to equation (4) with $W_1=1\cdot715\times10^{-6}$ J/m^2. The two dashed lines show the effect of adding to right-hand side of equation (5) a new contribution of the kind $W(\phi)\approx(W_2/4)\sin^4(\varphi)$ with $W_2=\pm1\cdot715\times10^{-7}$ J/m^2 ($W_2/W_1=10$ per cent).

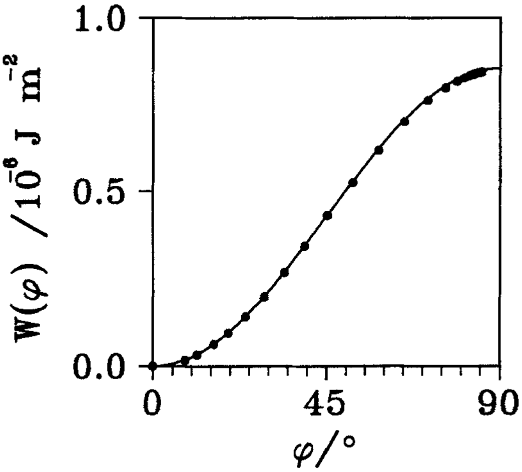

Figure 3. The azimuthal anchoring energy function $W(\varphi)$ versus the azimuthal angle φ for $T_{NI}-T=0{\cdot}14°C$ as deduced by numerical integration of the full points in figure 2. The full line corresponds to the functional dependence of equation (5) with $W_1=1{\cdot}715\times10^{-6}\,J/m^2$.

3. Discussion and conclusions

The azimuthal anchoring energy of nematic at the SiO–nematic interface is usually interpreted in terms of the Berreman mechanism [23] for anchoring at a grooved interface. In fact the experimental observation of the SiO surface by using electron microscopy clearly indicates that the SiO surface is not flat but consists of a periodic pattern of parallel grooves aligned along a given a axis. The characteristic wavelength of this pattern is of the order of 100–200 Å. According to the Berreman model, the elastic interactions between molecules near the interface favour the director alignment parallel to the x axis. By making the simplifying assumptions that the elastic constants of the nematic have the same values ($K_{11}=K_{22}=K_{33}$) and the local tilt angle of the SiO surface is small, Berreman obtained the functional dependence given by equation (5). The Berreman model has recently been generalized in order to account for the presence of a finite value of the polar anchoring energy [24] at the interface and for the presence of a reduced surface nematic order near the interface [18]. Both these contributions can greatly modify the value of the azimuthal anchoring coefficient but not the φ dependence of the anchoring energy. Therefore our experimental results seem to support the validity of the Berreman mechanism to explain the azimuthal anchoring at the SiO–nematic interface.

In a recent paper Yokoyama *et al.* [25] showed that the presence of an interfacial inhomogeneity of the order parameter produces an extra contribution both to the polar and to the azimuthal anchoring energy. Unfortunately Yokoyama *et al.* restricted their analysis to the case of near equilibrium conditions (see equation (1)) and thus no comparison between their theoretical results and our experimental results can be made.

In conclusion in this paper we have measured, for the first time, the complete azimuthal anchoring function at the SiO–nematic interface. In contrast with what occurs for polar anchoring [8–11], we have found that the experimental results do fit well with the simple Rapini form of equation (5) which has been predicted by Berreman for the azimuthal anchoring energy function at a grooved interface.

This research was supported in part by Ministero della Pubblica Istruzione (Italy) and by Consiglio Nazionale delle ricerche (Italy). The authors acknowledge C. Domenici for his useful help.

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