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Invited Lecture. Experimental studies of the anchoring energy of nematic liquid crystals

L. M. Blinov[a]; A. Yu. Kabayenkov[a]; A. A. Sonin[a]
[a] Institute of Crystallography, U. S. S. R. Academy of Sciences, Moscow, U.S.S.R.

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Invited Lecture

Experimental studies of the anchoring energy of nematic liquid crystals

by L. M. BLINOV, A. YU. KABAYENKOV and A. A. SONIN
Institute of Crystallography, U.S.S.R. Academy of Sciences, 117333 Moscow, Leninsky prospekt 59, U.S.S.R.

An analysis is given of experimental techniques for measuring the anchoring energy, W, of nematic liquid crystals with solid surfaces. Two novel methods for measuring W in homeotropically oriented samples are discussed. The first is based on the stabilization of the flexoelectric distortion by a magnetic field. In the second the thickness dependence of the phase delay for the light beam transmitted through a wedge-form cell with the hybrid orientation of a nematic should be measured. New experimental data on thickness and temperature dependences of the anchoring energy for homogeneously oriented 5CB are also presented. The anchoring energy was even measured for thin interface layers in the isotropic phase and its critical behaviour near the N-I transition is also discussed. New data were also obtained for the anchoring energy of nematics at crystalline surfaces.

1. Introduction

The orientational order of nematic liquid crystals results in the anisotropy of the surface free energy. The anisotropic part of the energy, F_{sa}, depends on a deviation of the director from the equilibrium position along the so-called easy axis of the substrate. We introduce a polar θ and azimuthal φ angle for the director deviation from the normal to the substrate and the easy axis, respectively. Then, the anisotropic part of the surface free energy may be presented by two independent functions expanded in a series in even powers of $\sin^{2n}(\theta, \varphi)$

$$\left.\begin{aligned} F_{sa}(\theta) &= \tfrac{1}{2} W_1^{\theta} \sin^2(\theta - \theta_0) + \frac{1}{2} \sum_{n=2}^{\infty} W_n^{\theta} \sin^{2n}(\theta - \theta_0), \\ F_{sa}(\varphi) &= \tfrac{1}{2} W_1^{\varphi} \sin^2(\varphi - \varphi_0) + \frac{1}{2} \sum_{n=2}^{\infty} W_n^{\varphi} \sin^{2n}(\varphi - \varphi_0). \end{aligned}\right\} \quad (1)$$

These equations are valid if $\varphi = \varphi_0$ or $\theta = \theta_0$, respectively. θ_0 and φ_0 are initial angular coordinates for the easy axis.

In the simplest case of small deviations of the director $\delta\theta = \theta - \theta_0 \to 0$, $\delta\varphi = \varphi - \varphi_0 \to 0$ (Rapini's approximation [1]) only the first terms are kept in expansion (1)

$$\left.\begin{aligned} F_{sa}(\theta) &= \frac{W_1^{\theta}}{2} \sin^2 \delta\theta, \\ F_{sa}(\varphi) &= \frac{W_1^{\varphi}}{2} \sin^2 \delta\varphi \end{aligned}\right\} \quad (2)$$

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and the parameters W_1^θ and W_1^φ are usually referred to as the polar and the azimuthal anchoring energies. For strong deviations of the director in a surface layer, when $\delta\theta$, $\delta\varphi \approx \pi/2$ the effective values of the anchoring energies are measured

$$\left.\begin{aligned} W_{\text{eff}}^\theta &= \sum_{n=1}^{\infty} nW_n^\theta, \\ W_{\text{eff}}^\varphi &= \sum_{n=1}^{\infty} nW_n^\varphi. \end{aligned}\right\} \tag{3}$$

According to a more sophisticated consideration [2] the values W_1^θ and W_1^φ are not independent and for small W_1 ($W_1 \ll 1\,\text{erg}\,\text{cm}^{-2}$) are of the same order of magnitude.

There are various experimental techniques for measuring the anchoring energy which may be divided into two different groups according to whether an external perturbating field is applied [3–15] or not [16–23]. In any case the kind of distortion of the director field in a surface layer is of great importance. In different experiments for the determination of W the parameters varied were (*a*) an optical technique (phase delay, total internal reflection, etc), (*b*) the nature of the external field (electric, magnetic), (*c*) surface treatment of substrates and (*d*) liquid-crystalline compounds (for details see the review [24]). Some literature values for W are collected in table 1. It is seen that the data obtained with different techniques are scattered over a wide range, from 10^{-5} to $1\,\text{erg}\,\text{cm}^{-2}$.

At the start of this work we had in mind two aims. First, we tried to find agreement between the values W^θ measured for different director distortions for the same nematics in contact with the same solid substrate. For this purpose, we have studied the classical nematogens 4-methoxybenzylidene-4′-*n*-butylaniline (MBBA) and 4-*n*-pentyl-4′-cyanobiphenyl (5CB) homeotropically oriented by glass substrates covered with chromium distearyl chloride (CDC). The molecular orientation was distorted by an electric or magnetic field (the Fredericks transition and the flexoelectric effect), by a static inhomogeneous orientation in a hybrid cell and by an acoustic excitation. As we shall see we managed to obtain the same order of magnitude for W_1^θ and W_{eff}^θ values from all such experiments.

Secondly, we wanted to advance our understanding of the phenomena at an interface between a nematic and a solid substrate and so we have made the following novel experiments:

(*a*) for planarly oriented layers of 5CB the anchoring energy W_{eff}^θ was studied as a function of temperature and layer thickness (dimensional effect);
(*b*) for the first time, the energy W_{eff}^θ was measured for the isotropic phase in contact with a glass plate treated to give planar nematic orientation;
(*c*) the azimuthal energy W_{eff}^φ was evaluated for a nematic oriented by a freshly cleaved NaCl crystal with two equivalent easy directions. In the same experiment the effect of the orientational bistability was observed which is due to the field-induced switching of the director between the two easy directions, i.e., between two equivalent energy minima.

In the following section we give the results of our experiments.

2. Experimental techniques for measuring the anchoring energy

We now discuss specific features of the various methods for measuring the anchoring energy.

Table 1. Some literature data on the anchoring energy of nematics.

Reference	Nematic	Method of orientation	Method of evaluating W	W/erg cm^{-2}
1	2	3	4	5
		(*a*) Homeotropic orientation		
[3]	5CB, MBBA	Clean or covered with In_2O_3 glass + *n*-silanes, lecithin etc	Magnetic threshold field for the Freedericksz transition	W_1^θ: 10^{-3}–10^{-2}
[4]	MBBA	Not mentioned	Electric threshold field for the Freedericksz transition	W_1^θ: 10^{-2}
[5]	MBBA	Glass covered with SnO_2 + lecithin	Electron threshold field for the Freedericksz transition	W_1^θ: 10^{-3}
[6]	MBBA	Clean or covered with SnO_2 glass + chromium distearyl chloride	Electric threshold field for the Freedericksz transition; flexoelectric effect	W_1^θ: $> 0{\cdot}1$ $< 10^{-3}$
[7]	MBBA	Clean or covered with SnO_2 glass + cetyltrimethyl-ammonium bromide	Electric threshold field for the Freedericksz transition; flexoelectric effect	W_1^θ: 10^{-3}–10^{-5}
[8]	MBBA	Clean glass + dodecyltrimethyl-ammonium chloride	Magnetic threshold field for the Freedericksz transition	W_1^θ: 10^{-2}
[9]	MBBA	Clean or covered with SnO_2 glass + Cr + lecithin	Measurement of the surface tilt angle induced by the electric field above the threshold for the Freedericksz transition (attenuated total internal reflection method)	W_{eff}^θ: 10^{-2}
[13]	MBBA and other nematic mixtures	Clean glass + hexadecyl amine	Magnetic saturation field for the Freedericksz transition	W_{eff}^θ: 10^{-2}

Table 1 (*continued*).

Reference	Nematic	Method of orientation	Method of evaluating W	W/erg cm^{-2}
1	2	3	4	5
		(*b*) Planar orientation		
[3]	(except the first paper) 5CB, MBBA	Clean or covered with In_2O_3 glass + *n*-silanes, lecithin etc	Magnetic threshold field for the Freedericksz transition	W_1^0: 10^{-3}–10^{-2}
[10]	5CB	Clean glass + Au + SiO_2	Measurements of the surface tilt angle induced by the electric field above the threshold for the Freedericksz transition (attenuated total internal reflection method)	W_{eff}^0: 10^{-1}
[11]	Not mentioned	Not mentioned	Measurements of the surface tilt angle induced by the electric field above the threshold for the Freedericksz transition (attenuated total internal reflection method)	W_{eff}^0: 10^{-1}
[14]	MBBA	SiO oblique evaporation	Electric saturation field for the Freedericksz transition	W_{eff}^0: 10^{-2} (in the vicinity of T_{NI})
[15]	MBBA	SiO oblique evaporation	Direct measurement of the mechanical torques in a deformed nematic	W_{eff}^{φ}: 10^{-3} (in the vicinity of T_{NI})

[16]	4-*n*-octyl-4′-ethoxytolane	Nematic in ethylene-terephtalate pores (the pores sizes were between 40 and 2000 Å)	Measurements of T_{NI} change produced by pores	W_{eff}^{0}: I
[17]	6CB	SiO oblique evaporation	Nematic hybrid orientation (attenuated total internal reflection method)	W_{eff}^{0}: 10^{-3}
[20]	MBBA	Slight rubbing of a clean or silane covered glass	Nematic hybrid orientation (polarization-optical method)	W_{eff}^{0}: 10^{-3}
[21]	MBBA	SiO oblique evaporation	The domains with hybrid director orientation (attenuated total internal reflection method)	W_{eff}^{0}: 10^{-3}
[22]	MBBA	Clean glass + carbon film	Observation of surface defects	W_{eff}^{φ}: 10^{-4}
[23]	MBBA and other nematic mixtures	Rubbing a clean glass; glass covered with polyvinyl alcohol and other surfactants	Light scattering of thermal director fluctuations	W_{1}^{0}: 10^{-3}–10^{-4}

2.1. *Threshold field for the Freedericksz transition*

It is well known [25] that a finite value for the anchoring energy W_1^θ results in a thickness dependence of the voltage threshold for the Freedericksz transition $U_F = E_F d$ (E_F is the threshold electric field, d is the thickness of the nematic layer). For a homeotropically oriented nematic we have

$$\frac{E_F}{E_{FO}} = \frac{d}{d + 2b}, \tag{4}$$

for $d \gg b$, where $b = K_{33}/W_1^\theta$ is an extrapolation length,

$$E_{FO} = (\pi/d)\sqrt{(4\pi K_{33}/\varepsilon_a)}$$

is the threshold field for $W_1^\theta \to \infty$, K_{33} and ε_a are the band elastic modulus and the dielectric anisotropy, respectively. In our experiments both electric and magnetic fields were used. For the magnetic case $\varepsilon_a E^2/4\pi$ in equation (4) should be replaced by $\chi_a H^2$ where χ_a is the diamagnetic anisotropy. Measurement of thickness dependences $E_F d(d)$ and $H_F d(d)$ and comparison of the experimental data with a set of theoretical curves (4) calculated for varied values of W_1^θ allow the anchoring energy to be determined.

2.2. *Saturation field for the Freedericksz transition*

At sufficiently strong fields saturation of the Freedericksz transition, that is complete reorientation of the director, occurs. The saturation field E_{sat} for the initial planar orientation of a nematic is [13, 26]

$$\operatorname{cth}\left[\frac{\pi}{2}\frac{E_{sat}}{E_{FO}}\left(\frac{K_{11}}{K_{33}}\right)^{1/2}\right] = \frac{\pi K_{33}}{W_{eff}^\theta d}\frac{E_{sat}}{E_{FO}}\left(\frac{K_{11}}{K_{33}}\right)^{1/2}. \tag{5}$$

Here

$$E_{FO} = (\pi/d)\sqrt{(4\pi K_{11}/\varepsilon_a)},$$

K_{11} is the splay elastic modulus. Thus, the experimental data on E_{sat} allow the energy W_{eff}^θ for planarly oriented samples to be calculated. Our measurements were carried out on 5CB with a rather high value of $\varepsilon_a \approx 10$ which corresponds to a low value of E_{FO} and so the saturation fields were fairly low. This technique may be used (and has been used) for measuring the anchoring energy even in the isotropic phase. A planarly oriented quasi-nematic layer near a solid boundary is birefringent even at temperatures higher than the transition temperature, T_{NI} [27–29]. For $\varepsilon_a \gg 0$ a sufficiently strong field reorients surface quasi-nematic layers and the birefringence disappears. The anchoring energy may be estimated by using the balance condition for surface and electric torques (per unit area) acting on the director

$$W_{eff}^\theta = \frac{\varepsilon_a E_{sat}^2 \xi(T)}{8\pi}, \tag{6}$$

where

$$\xi(T) = \xi_0(T - T_{NI}^*)^{-1/2}$$

is the temperature dependent correlation length which is identical to the thickness of the surface quasi-nematic layer and ξ_0 is a bare length [30, 31]. The field, $E = E_{sat}$, is easily detected by observation of the distortion of a shape of an oscillogram of the optical response to the sinusoidal electric field exactly as for the nematic phase [32].

The saturation of the Freedericksz transition may also be used to estimate the azimuthal anchoring energy $W_{\mathrm{eff}}^{\varphi}$ of a nematic oriented along an easy direction of a cleaved crystal. Applying an external field perpendicular to the easy direction in the layer plane the director can be forced to overcome the potential barrier and to take a new position along the second easy axis. The height of the potential barrier, equivalent to the anchoring energy $W_{\mathrm{eff}}^{\varphi}$, is calculated from the critical field required for complete director reorientation considered as a saturation field of the Freedericksz transition, see equation (5).

2.3. *Flexoelectric effect*

A finite anchoring energy W_1^{θ} opens the possibility to observe the flexoelectric effect in homeotropically oriented nematics. The induced birefringence $\overline{\Delta n}$ averaged over the cell thickness is calculated for $\varepsilon_a = \theta$ from [33]

$$\frac{\overline{\Delta n}}{E^2 d^2} = c\,(1 + d/2b)^{-2}. \tag{7}$$

Here

$$c = (1/24)\, n_{\perp}(1 - n_{\perp}^2/n_{\parallel}^2)\, e_{33}^{*2}/K_{33}^2,$$

$n_{\perp}$ and $n_{\parallel}$ are the principal refractive indices, and e_{33}^{*} is the flexoelectric coefficient including the surface polarization. Comparison of the experimental thickness dependences of the ratio $\overline{\Delta n}/E^2 d^2$ with theoretical curves (see equation (7)) calculated for various anchoring energies allows the extrapolation length b and energy W_1^{θ} to be determined. It should be noted that the character of the distortion of the director field is quite different from the Freedericksz transition and the flexoelectric effect. The maximum deviation of the director from the normal takes place in the middle of the layer in the former case and at the boundaries in the latter. This makes a comparison of the results for the two measurements more meaningful.

2.4. *The flexoelectric effect stabilized by a magnetic field*

We have developed a new technique for the determination of the anchoring energy W_1^{θ} of homeotropically oriented nematics based on the investigation of the flexoelectric distortion stabilized by a magnetic field [34]. Such a technique allows us to avoid measurement of the thickness dependence of the birefringence, that is the experiments are simplified. Moreover, the magnetic field squeezes the distortion from the bulk into the surface regions which essentially improves the sensitivity of the optical technique to surface phenomena, see figure 1(*a*). In this case, instead of thickness d a new variable appears, namely, the magnetic field strength, H, stabilizing the homeotropic orientation. Now equation (7) for the reduced birefringence $\overline{\Delta n}/E^2 d^2$ is transformed [34] to

$$\frac{\overline{\Delta n}}{E^2 d^2} = \tfrac{3}{2} c \left(\frac{sh\, d/\eta}{d/\eta} - 1\right)\left(\frac{d}{2b}\, sh\, \frac{d}{2\eta} + \frac{d}{2\eta}\, ch\, \frac{d}{2\eta}\right)^{-2}. \tag{8}$$

Here $\eta = \sqrt{(K_{33}/\chi_a)}/H$ is the magnetic coherence length, and the condition $\varepsilon_a E^2/4\pi \ll \chi_a H^2$ must be fulfilled. Measurement of the parameter $\overline{\Delta n}/E^2 d^2$ for fixed values of E as a function of H allows the energy W_1^{θ} to be found from equation (8).

In the experiment two small glass prisms were attached to a liquid crystal cell (see figure 1(*b*)) and this arrangement was placed into the gap of an electromagnet. In this

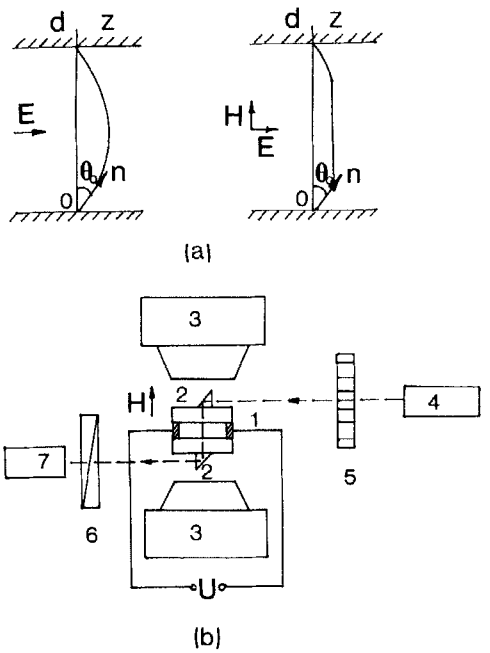

Figure 1. Determination of the anchoring energy by measurement of the flexoelectric effect stabilized by a magnetic field: (*a*) nematic director distribution geometry; (*b*) scheme of experiment: 1, nematic specimen; 2, glass prisms; 3, electromagnet poles; 4, He–Ne laser; 5, modulator; 6, polarizator; 7, photodiode.

case the magnetic field was parallel to both the light beam and the director; the electric field was applied to the nematic using in-plane electrodes.

Unfortunately, both the flexoelectric techniques described here require preliminary knowledge of the values of the flexo-coefficient e_{33}^{*} which are known only to within an order of magnitude [35].

2.5. *Homeoplanar (hybrid) nematic orientation*

We now discuss the technique for the determination of W_{eff}^{θ} for a homeotropically oriented nematic originally proposed by Chigrinov [18]. This method is based on measurement of the thickness dependences of the averaged birefringence in a wedge-shaped nematic sample with a hybrid orientation (planar at one boundary and homeotropic at the other). If the anchoring energy of the nematic at the planar boundary is considerably more than that at the homeotropic one, $(W_{\text{eff}}^{\theta})_{\text{p}} \gg (W_{\text{eff}}^{\theta})_{\text{h}}$ then, for $d < d_{\text{c}}$, where

$$d_{\text{c}} = K_{11}/(W_{\text{eff}}^{\theta})_{\text{h}}, \tag{9}$$

the transition occurs from the hybrid into the total planar orientation. The average birefringence $\overline{\Delta n}$ for $d \leqslant d_{\text{c}}$ is equal to $\overline{\Delta n}_{\text{p}} = n_{\parallel} - n_{\perp}$. For $d > d_{\text{c}}$ $\overline{\Delta n}$ depends on the thickness according to [18]

$$\overline{\Delta n} = \overline{\Delta n}_{\infty}(1 + K_{33}/d(W_{\text{eff}}^{\theta})_{\text{h}}). \tag{10}$$

Here $K_{33}/d(W_{\text{eff}}^{\theta})_{\text{h}} \ll 1$, and $\overline{\Delta n}_{\infty}$ is the birefringence of the hybrid cell for $d \to \infty$. In the opposite case $(W_{\text{eff}}^{\theta})_{\text{p}} \ll (W_{\text{eff}}^{\theta})_{\text{h}}$ and $K_{33} > K_{11}$ the transition occurs from the hybrid into the total homeotropic structure [19].

Thus, there are three possibilities to estimate W_{eff}^{θ}:

(*a*) from the critical thickness d_c, (see equation (9));

(*b*) from the thickness dependence of $\overline{\Delta n}$, (see equation (10));

(*c*) from the thickness dependence of the pyroelectric effect induced by a heat pulse in a hybrid nematic cell [36].

2.6. *Determination of W_1^{θ} for a homeotropically oriented nematic using acoustic excitation*

The low frequency acoustic excitation of a fluid in a flat capillary result in oscillations of the Poiseuille shear flow. For a homeotropically oriented nematic these oscillations distort slightly the initial orientation [37]. The profile of the director distribution over the layer thickness can be calculated from experimental data on the phase delay for light transmitted through the capillary and data on the total internal reflection at the interface between the nematic and a glass prism, with a large refraction index. On the other hand the profile can be calculated theoretically [9] for various anchoring energies W_1^{θ}. From a comparison of the two profiles the energy W_1^{θ} for a homeotropically oriented nematic can be found.

All of our measurements were carried out using a polarizing microscope and a simple polarization technique based on a He–Ne laser. The phase delay $\Delta\phi$ was calculated from the intensity of light transmitted through a cell placed between crossed nicols:

$$I = I_0 \sin^2 2\beta \sin^2 \frac{\Delta\phi}{2}. \tag{11}$$

Here I_0 is the intensity of light for maximum transmission, β is an angle between the polarizer axis and the director (either initial or induced).

3. Experimental results for homeotropically oriented nematics

3.1. *Determination of W^{θ} for nematics homeotropically oriented by glass substrates treated with surfactants*

As a surfactant we have used mainly a solution of chromium distearyl chloride (CDC) in isopropanol (concentration 0·4 wt per cent). Other surfactants such as lecithin and Langmuir-Blodgett films of stearic acid were also used. The cell thickness was measured by means of the interferrimetric method with a precision of 5–10 per cent. For our measurements, we used empty cells (filled with air). The same method was employed to measure the angle of the wedge-shaped cells. The anchoring energy was measured by the five techniques described previously [34, 37–39]. The results are shown in table 2. In all cases the anchoring energy W^{θ} is of the order of 10^{-3}–10^{-2} erg cm^{-2} for both MBBA and 5CB. It should be noted that overestimation [6] of W_1^{θ} from the Freedericksz transition data resulted from a low accuracy of the measurements of $E_F d$ for thin nematic layers ($d \lesssim 10\,\mu$m). Underestimated values of W_1^{θ} from data on the flexoelectric effect [6, 7] resulted from too low a magnitude of the flexoelectric coefficient and the thickness dependence of the reduced ratio $\overline{\Delta n}/E^2 d^2$ not being taken into account in earlier measurements. Using equation (7) and all old [6, 7] and new results for MBBA we obtained $W_1^{\theta} \approx 10^{-3}$–$10^{-2}$ erg cm^{-2}, dependent on the layer thickness according to a logarithmic law, see figure 2. The same logarithmic dependence was also demonstrated for planarly oriented 5CB [32], see figure 4. Here the problem of the thickness dependence of the anchoring energy appears for the

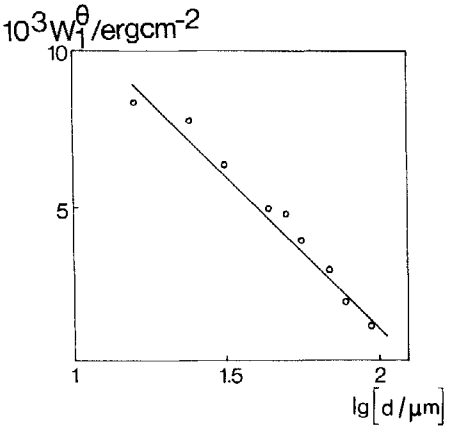

Figure 2. Thickness dependence of the anchoring energy W_1^θ for a homeotropic MBBA layer.

first time and requires special theoretical consideration. For example, the $W(d)$ dependence can possibly be understood in terms of the surface flexoelectric polarization or order-electricity [40].

3.2. *Determination of W_1^θ for nematics homeotropically oriented by crystalline substrates*

A layer of a nematic with thickness up to 200 μm can be oriented homeotropically by polished crystalline surfaces of low symmetry (e.g. by crystal cuts of $LiNbO_3$ or Al_2O_3 with surface symmetry 1) [41]. In this case no surfactant is needed. The anchoring energy W_1^θ of nematics homeotropically oriented by $LiNbO_3$ cuts was estimated from measurement of both the threshold magnetic field for the Freedericksz transition and the flexoelectric effect, see table 2. The magnitude of W_1^θ for the crystalline cuts is the same order as that for glass substrates treated with surfactants.

4. Experimental results for planarly oriented nematics including data on the isotropic phase

4.1. *Determination of W_{eff}^θ for planar nematic layers in contact with glass plates*

Planar orientation was achieved by unidirectional rubbing of the glass substrates covered with transparent SnO_2 layers. Such substrates induce surface quasi-nematic layers existing within a certain temperature range of the isotropic phase near the phase transition T_{NI} and into the nematic phase [27–29]. The temperature dependence of the phase delay, $\Delta\phi/2$, of the transmitted light beam are shown in figure 3. The thickness of the surface layer can be estimated from

$$l = \frac{\Delta\varphi}{2}\frac{\lambda}{2\pi\overline{\Delta n}_p}, \tag{12}$$

where λ is the wavelength of light ($\lambda = 0{\cdot}633\,\mu$m), $\overline{\Delta n}_p = n_\parallel - n_\perp$ ($\overline{\Delta n}_p \approx 0{\cdot}17$ for 5CB) is the birefringence of the nematic phase in the vicinity of T_{NI}. This thickness, $l \approx 40$–100 Å, depends on the anchoring energy of a nematic at the interface with glass, that is on the order parameter or a quasi-nematic layer at the surface. With increasing temperature the thickness, l, decreases and at a certain temperature the

Table 2. Our experimental results on nematic anchoring energy (room temperature).

Reference	Nematic	Method of orientation	Method of evaluating W	W/erg cm^{-2}
		(*a*) Homeotropic orientation		
[38]	5CB, MBBA	Clean or SnO_2 covered glass + CDC;	Electric and magnetic threshold fields for the Freedericksz transition;	W_1^θ: $1–5 \times 10^{-2}$
	MBBA	Clean glass + CDC	Flexoelectric effect	$10^{-3}–10^{-2}$
[34]	MBBA	Clean glass + CDC	Flexoelectric effect stabilized by a magnetic field	W_1^θ: 10^{-2}
[37]	5CB	Clean glass + CDC	Acoustic excitation of nematic layer	W_1^θ: 8×10^{-3}
[40]	5CB, MBBA	$LiNbO_3$ substrates (surface symmetry-1)	Magnetic threshold field for the Freedericksz transition;	W_1^θ: 10^{-2};
	MBBA		flexoelectric effect	5×10^{-3}
[39]	5CB, MBBA	Clean or SnO_2 covered glass + CDC	Homeoplanar nematic orientation	W_{eff}^θ: $3–5 \times 10^{-2}$
		(*b*) Planar orientation		
[32]	5CB	Rubbing a SnO_2 film	Electric saturation field for the Freedericksz transition	W_{eff}^θ: 1
[40]	5CB	NaCl crystal (001) surface	Electric saturation field for the Freedericksz transition (effect of orientational bistability)	W_{eff}^φ: 0·1
[39]	5CB, MBBA	Rubbing a clean glass	Homeoplanar nematic orientation	W_{eff}^θ: $3–6 \times 10^{-3}$

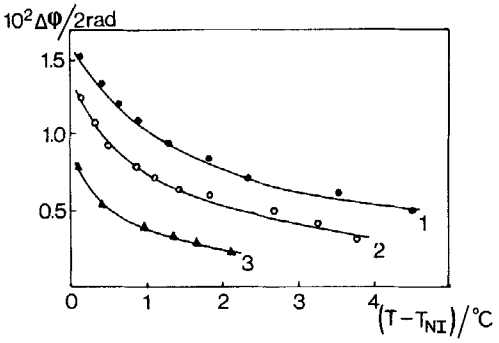

Figure 3. Temperature dependence of the phase delay of the transmitted light wave for nematic cells of varied thickness and anchoring energy: 1, $d = 4{\cdot}95\,\mu$m, $W_{\text{eff}}^{\theta} = 1{\cdot}85\,\text{erg cm}^{-2}$ (●); 2, $d = 14{\cdot}7\,\mu$m, $W_{\text{eff}}^{\theta} = 1{\cdot}34\,\text{erg cm}^{-2}$ (○); 3, $d = 30{\cdot}2\,\mu$m, $W_{\text{eff}}^{\theta} = 0{\cdot}96\,\text{erg cm}^{-2}$ (▲).

quasi-nematic layers disappear. The order of magnitude for l and its temperature dependence agree with the corresponding behaviour of the correlation length ξ for nematic fluctuations in the isotropic phase [30, 31].

The anchoring energy of 5CB in the nematic and isotropic phases was calculated from the measurements of the A.C. voltage (frequency $f = 1$ kHz) resulting in the total reorientation of the director in the surface layers from the initial planar into the homeotropic position (the saturation field for the Freedericksz transition, see equation (5)). The experimental error for E_{sat} was about 5–10 per cent. The calculated values for W_{eff}^{θ} at room temperature $W_{\text{eff}}^{\theta} \approx 1\,\text{erg cm}^{-2}$ prove to be in accord with data on the thickness dependence of the threshold of the Freedericksz transition, see tables 1 and 2. It was also found that W_{eff}^{θ} decreases with increasing thickness of the nematic layer for homeotropic orientation. At smaller thicknesses, $d \lesssim 25\,\mu$m the dependence $W_{\text{eff}}^{\theta}(d)$ is close to logarithmic, however, for rather thick cells, $d \gtrsim 10\,\mu$m it is closer to hyperbolic, see figure 4. In the range $d = 10$–$25\,\mu$m both dependencies are overlapped. The interesting question arises as to what are the values W_{eff}^{θ} extrapolated to almost zero and infinite thicknesses. The extrapolation of the curve $W_{\text{eff}}^{\theta}(d)$ to the thickness of one monolayer of a planarly oriented nematic, $d_0 = 5$ Å, gives a figure $W_0 \approx 3\,\text{erg cm}^{-2}$ comparable with the difference between the surface tensions of the nematic and the substrate. The extrapolation of the same dependence to infinite thickness appears to give a correct value for the anchoring energy $W_{\infty} \approx 0{\cdot}6\,\text{erg cm}^{-2}$ of the semi-infinite nematic medium.

For the isotropic phase the anchoring energy in the surface layers was estimated from equation (6) with two surface layers taken into account

$$W_{\text{eff}}^{\theta} = \frac{E_{\text{sat}}^2 l \varepsilon_a}{8\pi} \tag{13}$$

and $\varepsilon_a \approx 10$ taken for the nematic phase. The temperature dependence of the saturation voltage was measured for several cells differing in their thickness, see figure 5. The calculated values for the anchoring energy are shown in figure 6, the corresponding data for the elastic modulus $K_{33}(T)$ and the dielectric anisotropy $\varepsilon_a(T)$ for 5CB were taken from literature [42, 43]. It is easily seen from figure 6 that the anchoring energy depends critically on temperature near the phase transition T_{NI}. Further, the thickness dependence of W_{eff}^{θ} in the isotropic phase is absent as shown in a separate

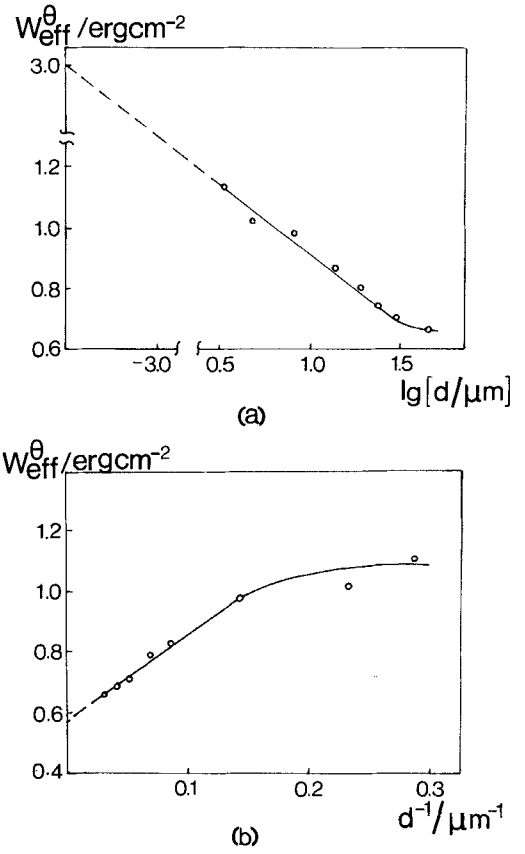

Figure 4. The anchoring energy W^{θ}_{eff} for a planar 5CB layer as a function of the cell thickness using logarithmic (*a*) and hyperbolic (*b*) scales ($T = 23 \pm 1$°C).

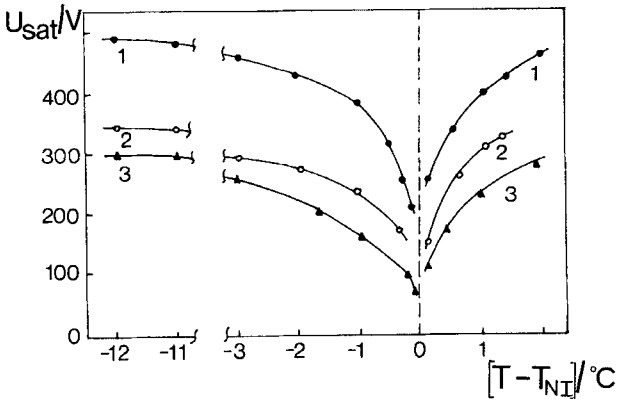

Figure 5. Temperature dependences of the saturation voltage U_{sat} for the Freedericksz transition ($U_{sat} = E_{sat}(d)$): 1, d = 30·2 μm (●); 2–24·0 μm (○); 3, 13·7 μm (▲).

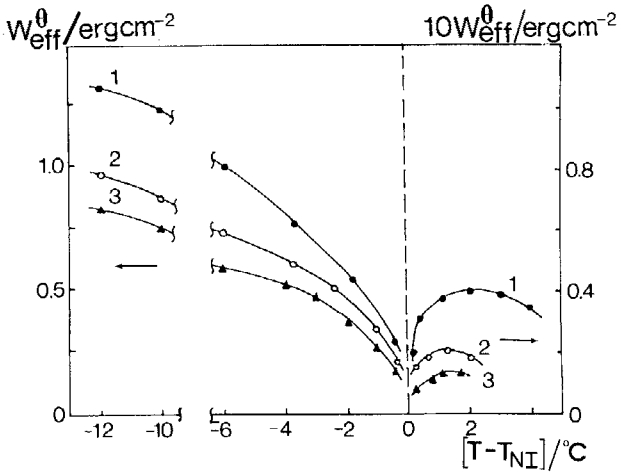

Figure 6. Temperature dependence of the anchoring energy W^{θ}_{eff} for the nematic and isotropic phases of 5CB: 1, d = 14·7 μm (●); 2, 30·2 μm (○); 3, 24·0 μm (▲).

experiment when the thickness was varied for the same glass substrates. Thus, the apparent thickness dependence of W^{θ}_{eff} seen in figure 6 has to be associated with the slightly different surface treatment of the different cells. For some incident reasons our cells with different thickness have different anchoring energies in the nematic phase and these energies define values of the surface order parameter in the isotropic phase. A careful theoretical analysis of the $W^{\theta}_{eff}(T)$ curves in the vicinity of T_{NI} requires the temperature behaviour of the correlation length [31] to be taken into account. This analysis will be carried out in the near future. At this stage we would like only to point to the correlation between the W^{θ}_{eff} values in both the phases.

Thus, rubbing a glass surface covered with SnO_2 provides rather high values of $W^{\theta}_{eff} \approx 1\,erg\,cm^{-2}$. At the same time we managed to obtain smaller values of W^{θ}_{eff} for clean glass plates without any coating (SnO_2 or polymeric) slightly rubbed in one direction. If a such glass plate is combined with an other treated with surfactant to form a wedge-shaped cell filled with MBBA or 5CB the transition from the hybrid into the homeotropic orientation occurs in the narrow part of the cell. Estimation of W^{θ}_{eff} for the planar boundary of the cell from the critical thickness of the transition, (see equation (9) with K_{11} substituted for K_{33}) results in a value of the order of $10^{-3}\,erg\,cm^{-2}$ in accord with some published data, see tables 1 and 2. Thus, the anchoring energy for planarly oriented layers may be varied within the range from 1 to $10^{-3}\,erg\,cm^{-2}$ while the anchoring energy for different homeotropically oriented layers is of the same order of magnitude, 10^{-2}–$10^{-3}\,erg\,cm^{-2}$.

4.2. *Determination of the azimuthal energy* W^{φ}_{eff} *for a nematic planarly oriented by a cleaved crystal of NaCl*

Until now we have discussed the polar anchoring energy W^{θ}. The azimuthal energy W^{φ}_{eff} at an interface between a nematic and an anisotropic crystal substrate may also be evaluated [41]. For this purpose 5CB was placed between two fresh surfaces (001) of NaCl. In accord with [44, 45] in this case there are two easy axes, that is two energy minima for the director at each interface along the [110] and [1$\bar{1}$0] crystal axes, see figure 7. Their combinations result in four types of planarly oriented and twist

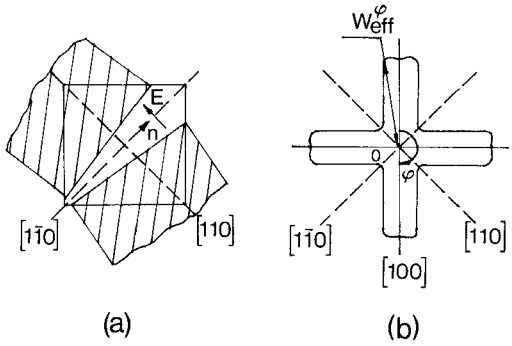

Figure 7. Evaluation of the azimuthal anchoring energy, W_{eff}^{φ}, for a 5CB layer on a NaCl crystal surface: (*a*) scheme of experiments showing NaCl surface, and aluminium electrodes; (*b*) qualitive dependence of the 5CB surface energy on the NaCl surface upon angle φ, determining the director orientation on a cleavage plane.

domains in the cell. We have also observed some additional local minima along the [100] and [010] directions [41, 44] which influence the kinetics of the director reorientation.

As already noted, the electric field from two in-plane electrodes can switch the director of 5CB from one surface minimum to the other and reorient domains initially oriented perpendicular to the field. Hence, orientational bistability can be realized. Considering the reorientating field to be equal to the saturation field of the Freedericksz transition, see equation (5), we can estimate the height of the potential barrier separating the two easy directions for the director orientation. This height is equivalent to the azimuthal anchoring energy. Its value $W_{eff}^{\varphi} \approx 0{\cdot}1\,erg\,cm^{-2}$ for NaCl surfaces is one order of magnitude smaller than the polar energy W_{eff}^{θ} for a nematic planarly oriented by an isotropic substrate, see table 2.

The value of W_{eff}^{θ} for a NaCl surface can be estimated only as below $W_{eff}^{\theta} > 10^{-2}\,erg\,cm^{-2}$ since the critical thickness for the transition from the hybrid into the total planar orientation in a wedge-shape cell is less than $1\,\mu m$, see equation (9).

5. Conclusion

In conclusion, this paper demonstrates the possibilities for measuring the anchoring energy using a variety of novel techniques, namely from the threshold and saturation fields of the Freedericksz transition in nematic and surface quasi-nematic layers, from the flexoelectric effect with and without a stabilizing magnetic field, from the phase delay of light transmitted through hybrid cells, from the acousto-optical effect and field-induced bistable director switching between easy directions on crystalline substrates. Typical values of the anchoring energy vary in the range 10^{-3}–$10^{-2}\,erg\,cm^{-2}$ for homeotropically oriented nematics and 10^{-3}–$1\,erg\,cm^{-2}$ for planarly oriented nematics. For the first time the anchoring energy has been measured in the isotropic phase and its critical behaviour observed near the transition into the nematic phase.

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