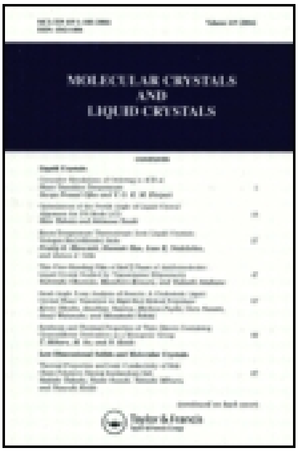

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Determination of the Nematic Liquid Crystal (NLC)-Substrate Interaction Potential by Means of Semiempirical Method of Self-Consistent Director Field

Jozef Żmija [a] , Jerzy Kędzierski [a] , Zbigniew Raszewski [a] , Jolanta Rutkowska [a] & Jerzy Zieliński [a]
[a] Institute of Technical Physics WAT, 01-489, Warsaw, Poland
Version of record first published: 24 Sep 2006.

To cite this article: Jozef Żmija , Jerzy Kędzierski , Zbigniew Raszewski , Jolanta Rutkowska & Jerzy Zieliński (1994): Determination of the Nematic Liquid Crystal (NLC)-Substrate Interaction Potential by Means of Semiempirical Method of Self-Consistent Director Field, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 251:1, 243-253

To link to this article: http://dx.doi.org/10.1080/10587259408027207

Mol. Cryst. Liq. Cryst. 1994, Vol. 251, pp. 243–253
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

DETERMINATION OF THE NEMATIC LIQUID CRYSTAL (NLC)-SUBSTRATE INTERACTION POTENTIAL BY MEANS OF SEMI-EMPIRICAL METHOD OF SELF-CONSISTENT DIRECTOR FIELD

JÓZEF ŻMIJA, JERZY KĘDZIERSKI, ZBIGNIEW RASZEWSKI,
JOLANTA RUTKOWSKA, JERZY ZIELIŃSKI
Institute of Technical Physics WAT, 01-489 Warsaw, Poland

Abstract A semi-empirical method is proposed for determination of the nematic liquid crystal-substrate interaction potential. Employing results of the dielectric constant ε and phase shift δ measurements, presented for 4-trans-4'-n-hexyl-cyclo-hexyl-isothiocyanatobenzene (6CHBT) and applying the self-consistent director field method, interaction potentials (6CHBT- polyimide) and (6CHBT-lecithin) have been estimated.

INTRODUCTION

In practical applications, as well as for research purposes, nematic liquid crystals (NLCs) are placed in thin flat parallel cells. Limiting surfaces are made of solids (glass + electrodes + ordering films). In such systems, limiting cell surfaces influence NLC orientation. Physical and chemical properties of NLC surfaces have been the subject of many original studies and review papers[1,2,4-14].

In our paper we would like to present a semi-empirical method for determining potential of interaction between a NLC and an orientating surface. For this purpose we consider a nematic layer, placed between two limiting planes, located at $z = -d/2$ and $z = d/2$, respectively. In order to simplify the problem and draw attention we assume that the director $\vec{n}$ may change in the $\Pi(x,z)$ plane.

Total free energy per unit area is written as [4,5]

$$\Im(\theta) = \int_{-d/2}^{+d/2} F(\theta, \theta_{,z})dz + F_{s1} + F_{s2} \tag{1}$$

where: $\Im(\theta)$ - total free energy of the system per unit area
$F(\theta, \theta_{,z})$ - bulk density of free energy, $\theta_{,z} = d\theta/dz$.
F_{s1} and F_{s2} - surface energy due to anchoring on the walls

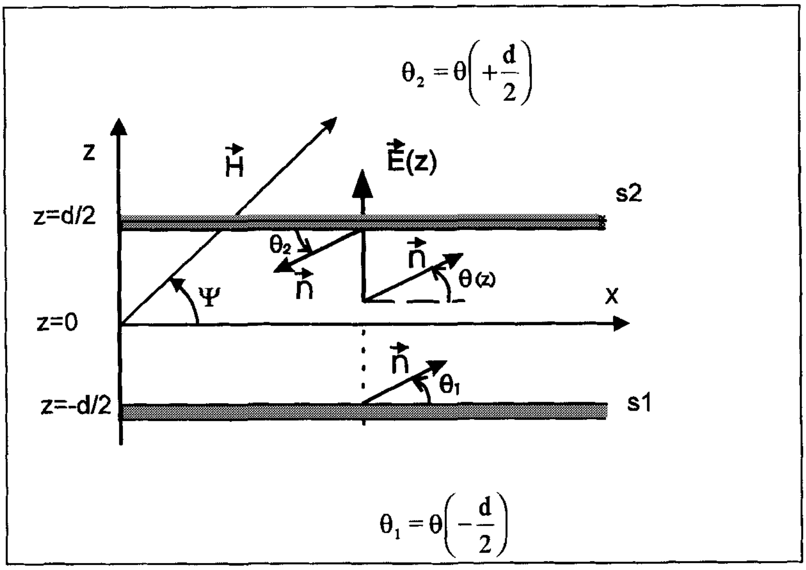

FIGURE 1 Schematic drawing of NLC configuration in measuring chamber NLC director, z axis and external magnetic field $\vec{H}$ are in the same plane. In such situation, any integral physical quantity depends on z (unidimensional case).

Equilibrium orientation of the director $\vec{n}(z)$, given by the $\theta(z)$ distribution, is determined by minimizing the functional (1). The $\theta(z)$ function gives an extreme of the functional (1) $\Leftrightarrow$ $\delta\Im = 0$. This extreme is a minimum if $\delta^2\Im = 0$. From these conditions we obtain the well-known Euler-Lagrange equation with boundary conditions[3,4,5]. The Euler-Lagrange equation will be referred to as the director equation (2) and equations (3a) and (3b) as boundary conditions imposed by the limiting surfaces.

$$-\frac{d}{2} < z < \frac{d}{2} \qquad \frac{\partial F}{\partial \theta} - \frac{d}{dz}\frac{\partial F}{\partial \theta_{,z}} = 0 \tag{2}$$

$$z = +\frac{d}{2} \qquad \left(\frac{\partial F}{\partial \theta_{,z}}\right)_{\frac{d}{2}} + \frac{dF_{s1}}{d\theta_1} = 0 \tag{3a}$$

$$z = -\frac{d}{2} \qquad -\left(\frac{\partial F}{\partial \theta_{,z}}\right)_{-\frac{d}{2}} + \frac{dF_{s2}}{d\theta_2} = 0 \tag{3b}$$

Subscripts "1" and "2" refer to boundary angles on both surfaces and to relevant surface energies.

Two important facts must be noted:

(i) First term in the equations (3a) and (3b) corresponds to the contribution of bulk energy into surface one.

(ii) The NLC-surface interaction energy depends only on an angle and does not depend on z-derivative of the angle: $F_{s1} = F_{s1}(\theta_1)$, $F_{s2} = F_{s2}(\theta_2)$.

Obviously, in order to solve this set of equations, angular dependence of interaction energies F_{s1} and F_{s2} must be known in analytical forms[3,6,7,12,].

Now take into account that bulk free energy density $F = F_K + F_E + F_M$ may consist of three terms:

F_K - the term that describes elastic energy,

F_E - the term that describes influence of an electric field on the nematic and

F_M - the term that describes influence of the magnetic field on the nematic.

The situation may thus now be summed up as follows. We do not know analytical forms of the nematic-substrate interaction potentials F_{s1} and F_{s2},,,and moreover, we are not able to measure tilt angle during an experiment. We are only able to measure tilt angle before an experiment, in an undistorted sample. In such situation we must assume a symmetry of interactions with limiting surfaces. This means that tilt angles on both cell walls are equal. Consequently, the distribution function is symmetrical with respect to the middle of the sample.

THEORY

It is well known that properties of a liquid crystal cell depend on the director field pattern $\vec{n}(r)$. In our case (an unidimensional one) it is enough to know the $\theta = \theta(z)$ function. The idea of the self-consistent director field method[15,16] may be briefly summed up as follows. We choose a physical quantity W that depends on the director field distribution $\theta(z)$. We must be able to measure and calculate this quantity. Measured value of this quantity is denoted by W_M and calculated value by W_L. Next, W_L and W_M values are compared and made equal: $W_L = W_M$. This may be accomplished e.g. by modifying the elastic constant K_{ii} value in the expression for W_L. The $W_L = W_M$ equality holds for a given director distribution $\theta(z)$. The director field distribution determined in this way may be referred to as the self-consistent one, as it is obtained through the procedure that has the features of self-consistent field method (SCF) known from quantum mechanics.

Obviously, the chosen physical quantity W is an integral one and must satisfy the following conditions:

(i) it depends on director field distribution, i.e. on the $\theta(z)$ function,

(ii) it depends on the K_{ii} elastic constants,

(iii) it depends (among others) on initial angle θ_B.

The W quantities most useful for our purposes are: dielectric constant ε and phase shift δ between extraordinary and ordinary rays, resulting from light transmission through the liquid crystal cell. Depending on whether $W= \varepsilon$ or $W= \delta$, we may distinguish dielectric and optical methods of director field distribution $\theta(z)$ determination.

From what has been said of the SCF method it follows that it has been conceived for determining the $\theta(z)$ function. Fig.2 shows director distribution functions for the cell shown in Fig.1.

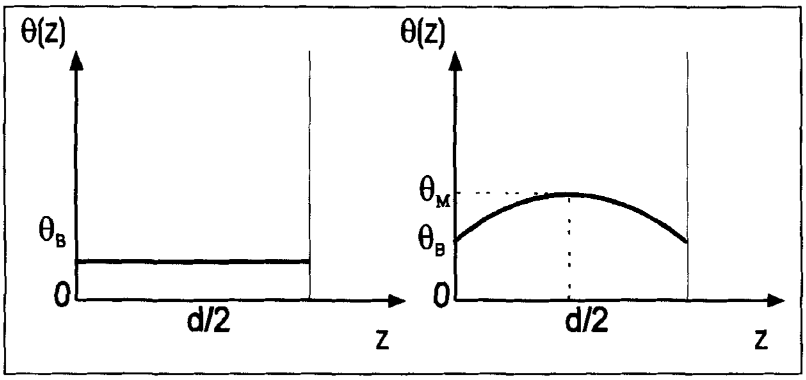

FIGURE 2 Schematic plots of $\theta(z)$ distribution for the cell shown in Fig.1 (a) $\vec{B} = 0$ and $\vec{E} = 0$, $\theta(z) = \theta_B$; (b) $\vec{B} \neq 0$ and $\vec{E} \neq 0$, $\theta(z) = f(z)$.

Treatment presented in the paper[15] results in the basic set of equations (4-8) that describe physical properties of considered cell filled with a NLC.

$$[K_{11}\cos^2\theta(z) + K_{33}\sin^2\theta(z)]\frac{d^2\theta(z)}{dz^2} =$$
$$= \Delta\varepsilon\varepsilon_0 E^2(z)\sin\theta(z)\cos\theta(z) + \Delta\chi\mu_0 H^2 \sin[\theta(z)+\Psi]\cos[\theta(z)+\Psi] \tag{4}$$

Integration with the fact that for $z = d/2$, $\theta(d/2) = \theta_M$ and $\theta,(-d/2) = 0$, taken into account, gives

$$\frac{d\theta(z)}{dz}=\left\{2\left[\int_{\theta_m}^{\theta}\frac{\Delta\varepsilon\varepsilon_0 E^2(z)\sin\theta'\cos\theta'}{K_{11}\cos^2\theta'+K_{33}\sin^2\theta'}d\theta'+\int_{\Theta_m}^{\Theta}\frac{\Delta\chi\mu_0 H^2\sin^2(\theta'+\Psi)\cos^2(\theta'+\Psi)}{K_{11}\cos^2\theta'+K_{33}\sin^2\theta'}d\theta'\right]\right\}^{\frac{1}{2}} \tag{5}$$

$$\vec{D}(z)=\varepsilon(z)\varepsilon_0\vec{E}(z) \tag{6}$$

$$\varepsilon(z)=\varepsilon_\perp+\Delta\varepsilon\cdot\sin^2\theta(z) \tag{7}$$

$$\mathrm{div}\vec{D}=0 \tag{8}$$

Note that equation (8) implies constant z-component of the $\vec{D}$ vector.

In this moment, the monitoring quantity W is introduced into our treatment. Suppose that the considered cell is filled with the NLC characterized by given material constants. Voltage U is applied to electrodes of this cell, as shown in Fig.3.

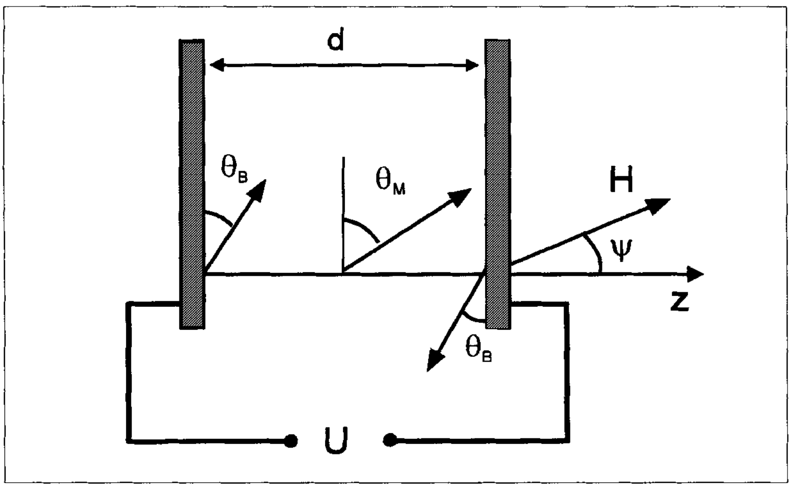

FIGURE 3 Measuring cell filled with the LC material characterized by material constants K_{11}, K_{33}, $\Delta\varepsilon$, $\varepsilon_\perp$ and $\Delta\chi$. Initial equilibrium of the director $\vec{n}$ in the layer of thickness d and boundary angle θ_B was attained by applying magnetic field described by $\vec{B}$ and ψ

Measuring voltage U, which simultaneously plays the role of distorting voltage, is applied to the cell shown in Fig.3. We measure the W_M quantity ($W_M = \varepsilon^\psi$ or δ^ψ) given by (9) and (10).

$$\varepsilon^{\Psi}(U,d,H,\theta_B)=\frac{d}{\int_{\theta_B}^{\theta_m}\left[\varepsilon_\perp+\Delta\varepsilon\sin^2\theta(z)\right]^{-1}\left[\frac{d\theta(z)}{dz}\right]^{-1}d\theta} \tag{9}$$

$$\delta^{\Psi}(U,d,H,\theta_B)=\frac{2\pi}{\lambda}\left[\int_0^d\frac{n_o n_e\left[\frac{d\theta(z)}{dz}\right]^{-1}d\theta}{\sqrt{n_o^2\cos^2\theta(z)+n_e^2\sin^2\theta(z)}}-n_o\cdot d\right] \tag{10}$$

Equation (8) may thus be rewritten in the form of (11).

$$\varepsilon^{\Psi}(U,d,H,\theta_B)\frac{U}{d}=\left\{\varepsilon_\perp+\Delta\varepsilon\sin^2\theta(z)\right\}E(z) \tag{11}$$

Note that $\left(\frac{d\theta(z)}{dz}\right)^{-1}=dz$ and may be expressed by equation (5). Equation (5) involves an unknown function E(z), which may now be determined semi-empirically form equation (11).

Equations (9) or (10) supplemented with (11) may be solved only numerically[15,16].

Now return to equations (2), (3a) and (3b). Note that first terms in boundary conditions (3a) and (3b) correspond to the bulk contribution into surface energy. Equations (2), (3a) and (3b) may be interpreted as[4,5]:

(2) - τ - bulk torque density,

(3a) - τ_1 - surface torque density,

(3b) - τ_2 - surface torque density.

It is clear that the following statements are true:

(i) Equation (2) (the Euler-Lagrange equation) implies that in equilibrium state bulk torque density is zero.

(ii) Equation (2) (the Euler-Lagrange equation) is equivalent to the condition of equilibrium of elastic torques and torques due to external fields.

(iii) Restoring torque resulting from surface anchoring energy

$$\tau_s = -\frac{dF_s}{d\theta_s} \tag{12}$$

is balanced by torque transmitted from bulk onto surface

$$\tau = -\frac{\partial F}{\partial \theta_{,z}} \tag{13}$$

Returning to equation (4), we may write that it follows from equation (2) that

$$\frac{\partial F}{\partial \theta} = \Delta\varepsilon \cdot \varepsilon_0 E^2(z)\sin\theta(z)\cos\theta(z) + \Delta\chi\mu_0 H^2 \sin[\theta(z)+\Psi]\cos[\theta(z)+\Psi] \tag{14}$$

$$\frac{d}{dz}\frac{\partial F}{\partial \theta_{,z}} = \left[K_{11}\cos^2\theta(z) + K_{33}\sin^2\theta(z)\right]\frac{d^2\theta(z)}{dz^2} \tag{15}$$

Considering equations (12), (13), (14) and (15) we conclude that elastic torque transmitted from bulk onto surface is described by the relation:

$$M_g = \frac{\partial F}{\partial \theta_{,z}} = \frac{dF_s}{d\theta_s} = \int_0^d \{\Delta\varepsilon \cdot \varepsilon_0 E^2(z)\sin\theta(z)\cos\theta(z) + \\ + \Delta\chi\mu_0 H^2 \sin[\theta(z)+\Psi]\cos[\theta(z)+\Psi]\} dz \tag{16}$$

Equations (16) are very important.

Employing the SCF method we may determine $\theta_{,z}$. Next, from (16) we may semi-empirically (i.e. experimentally) determine the boundary angle derivative of the interaction potential.

Possibility of experimental determination of the M_g potential is very important, as we do not know the particular form of the F_s potential that describes NLC-substrate interactions. All we know about it is that it depends on $\theta_{,z}$. Of course, in order to solve the problem of the NLC-substrate interaction on the basis of equations (2), (3a) and (3b) only, the knowledge of angular functions $F_{s1}(\theta)$ and $F_{s2}(\theta)$ in their explicit forms is necessary.

RESULTS

In order to determine $dF_s/d\theta_s$ semi-empirically, we have employed results of measurements performed for 6CHBT, taken from[15] . K_{11} and K_{33} constants are determined by the SCF method in two-constants approximation. Results of numerical calculations are shown in Fig.4.

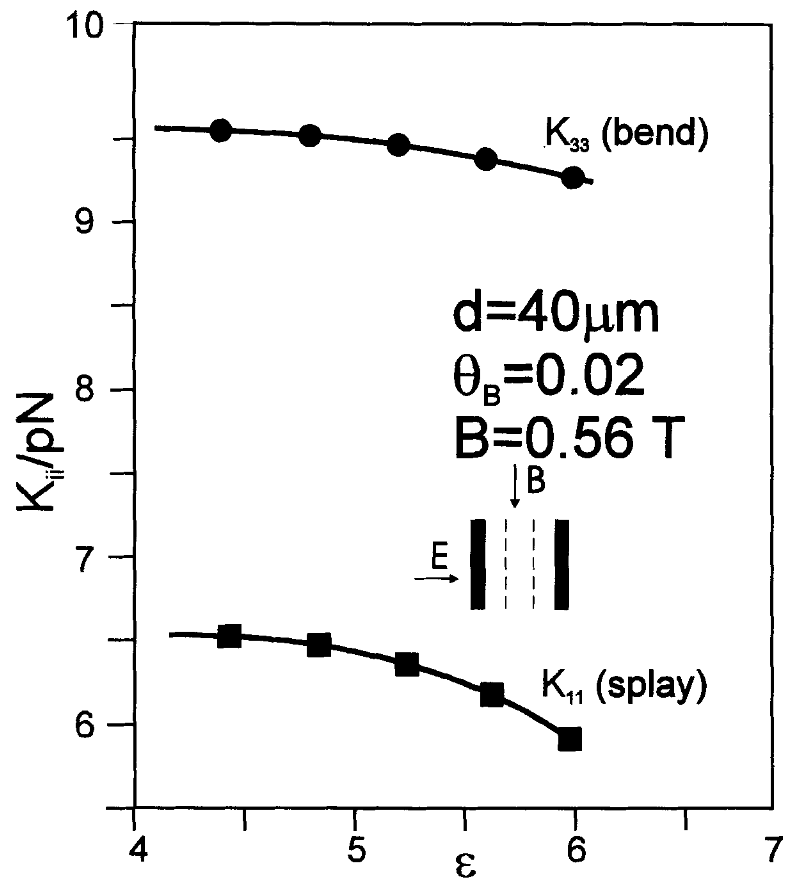

FIGURE 4 Calculated elastic constants K_{11} and K_{33} as functions of deformation, with dielectric constant ε employed as its measure. Results for 6CHBT, temperature t = 298 K

The only factor responsible for decrease of effective elastic constants is finite value of the NLC-substrate interaction energy. In order to estimate the NLC-substrate interaction potential, we perform the following computer experiment.

We calculate, in two-constants approximation ($K_{11} \neq K_{33}$), dielectric constants ε_L with strong anchoring assumed ($E_{anch} = \infty$) for various θ_B angles. Results of calculations are shown in Fig.5.

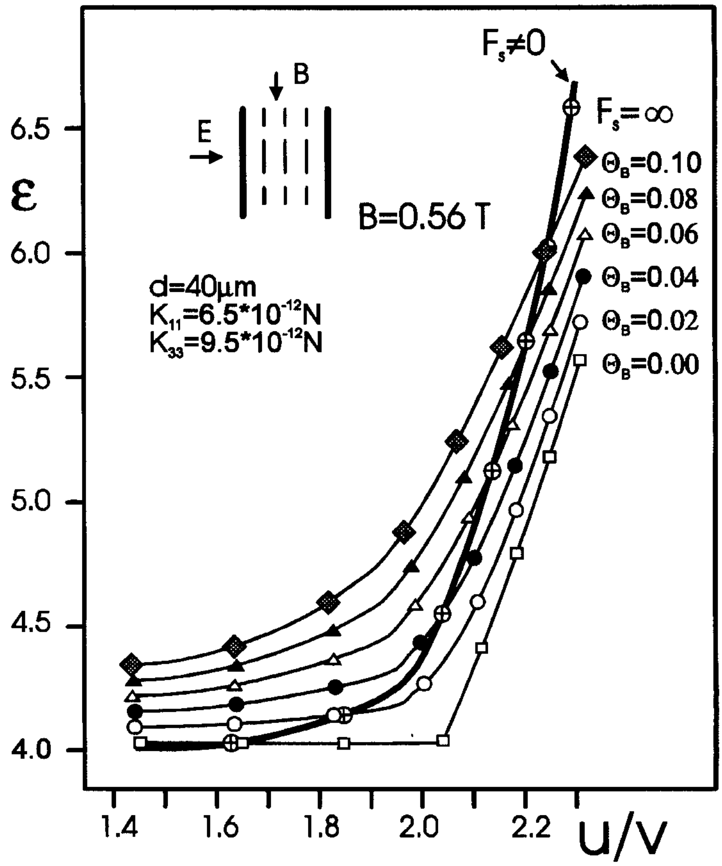

FIGURE 5 The ε_M^{Ψ} (measured) value versus distorting voltage (E_{anch}- finite, $\theta_B \neq$ const during deformation) and the ε_L^{Ψ} (calculated) value for $E_{anch} = \infty$ and $\theta_B =$ const.

In Fig.5 experimental curve is superimposed on theoretical curves (Fig.5 taken from[15]). Theoretical ε_L^{Ψ} curves are determined by points in which we calculate the elastic torque M_g transmitted from bulk onto surface.

Points of intersection of experimental characteristic curve (with changing θ_B and finite anchoring energy) and theoretical curves (determined for $E_{anch} = \infty$ and $\theta_B =$ const) are those points where Euler-Lagrange equations, together with boundary conditions, are satisfied. These points are marked with ⊕ characters in Fig.5.

These points, versus θ_B, are shown in Figs.6 and 7.

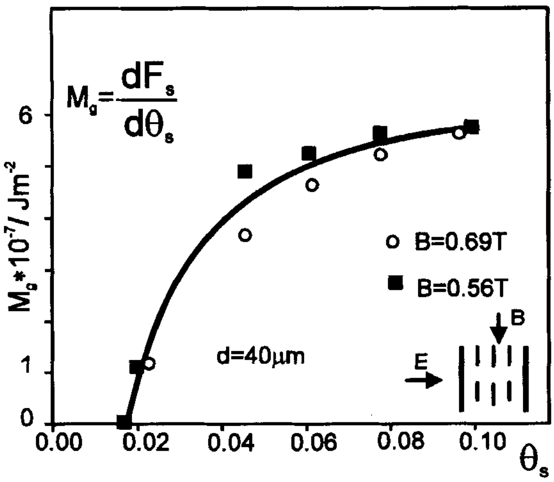

FIGURE 6 The $M_g := dF_s/d\theta_s = f(\theta_s)$ dependence for a planar cell with limiting surfaces coated with a typical polyimide.

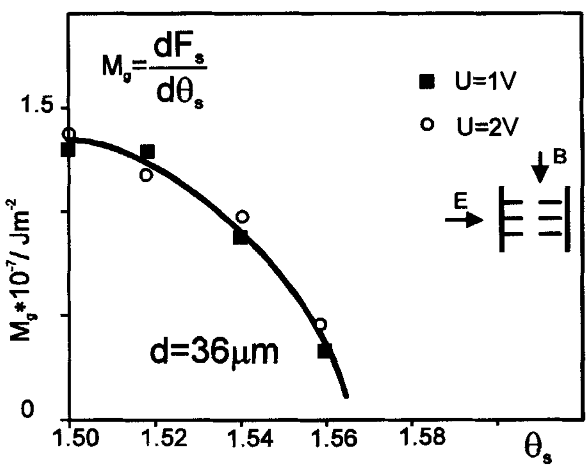

FIGURE 7 The $M_g := dF_s/d\theta_s = f(\theta_s)$ dependence for a homeotropic cell with limiting surfaces coated with lecithin.

As we know $dF_s/d\theta_s$ as a function of θ_s (experimental determination of this function is shown in Figs.6 and 7), we are able to determine the coefficient of polar anchoring energy E_{anch}, which, for small deformations, is given by[11]

$$E_{anch} = \frac{\Delta M_g}{\Delta\theta_s} = \frac{d}{d\theta_s}\left[M_g\right] = \frac{d}{d\theta_s}\left(\frac{dF_s}{d\theta_s}\right) = \left.\frac{d^2F_s}{d\theta_s^2}\right|_{\theta_s=\theta_B} \qquad (17)$$

CONCLUSIONS

From our experiments we obtained, for 6CHBT at 298 K:

(i) for planar cells with various kinds of polyimide coatings, anchoring energy $E_{anch} = 10^{-5}$ J/m^{-2},

(ii) for a homeotropic cell with lecithin coating, $E_{anch} = 10^{-7}$ J/m^{-2}.

The procedure that we propose allows for semi-empirical determination of functional dependence of the NLC-substrate interaction potential, without any prior knowledge of interaction potential profile.

According to our estimations, the coefficient of polar anchoring energy for NLC-lecithin interface is two orders of magnitude lower than for NLC-polyimide interface. These coefficients have been determined from characteristic curves shown in Figs.6 and 7 for angles close to $\pi/2$ and 0.

The error of this estimation is below 0.5 order of magnitude.

REFERENCES

1. B.Jerome, Rep.Prog.Phys., 54, 391 (1991)*.
2. T.Marusij, J.Reznikov, V.Reshetnyak, V.Chigrinov , Poverhnost, 7, 5 (1990)*.
3. L.M.Blinov, E.Kac, A.A.Sonin, Usp.Fiz.Nauk, 152, 449 (1987).
4. F.Simoni, R.Bartolino, G.Barbero, P.Aiello, B.Valenti, Mol.Cryst.Liq.Cryst. 13 , .303, (1984).
5. F.Simoni, Physics of Liquid Crystalline Materials, edited by I. Khoo and F. Simoni (1991).
6. S.Naemura, J.Appl. Phys. 51, 6149, (1980).
7. G.Barbero, N.V.Madhusudana, G.Durand, Z.Naturforsch, 39a, 1066 (1984).
8. L.Blinov, A.Kabayenkov, A. A.Sonin, Liq. Cryst,. 5, 645 (1989).
9. J.Gleeson, P.Palffy-Muhoray, Liq. Cryst., 5, 663 (1989).
10. S.Faetti, V.Palleshi , Liq. Cryst., 2, 261 (1987).
11. S.Faetti, Physics of Liquid Crystalline Materials, edited by I. Khoo and F. Simoni (1991).
12. G.Barbero, A.Strigazzi, Il Nuovo Cimento, 64B, (1981).
13. M.Warenghem, N.Isaert, J.Opt. 16, 37 (1985).
14. A.A.Sonin, Doctoral Thesis , Moscow (1988).
15. Z.Raszewski, J.Kędzierski, J.Rutkowska, J.Zieliński, J.Żmija, R.Dąbrowski, T.Opara, Liq.Cryst., 14, 1659 (1993).
16. J.Kędzierski,, Z.Raszewski, J.Rutkowska,T.Opara, J.Zieliński, J.Żmija, R.Dąbrowski, press in Mol.Cryst.Liq.Cryst.

* This paper recalls very comprehensive bibliography. For this reason we have listed only several selected items. In case of interest we kindly suggest to refer to the above-mentioned paper.