Temperature Dependence of Anchoring Energy of MBBA on SiO-Evaporated Substrate

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The temperature behaviour of the anchoring energy of nematic liquid crystal MBBA at the substrates with oblique SiO evaporation and director orientation at the interface have been studied by means of magnetic Freédericksz transition technique. The temperature dependence of the coefficients in the phenomenological model of surface anchoring energy has been determined.

Keywords: nematic liquid crystal, anchoring energy, orientational transition

INTRODUCTION

The equilibrium director orientation in a nematic liquid crystal (NLC) layer strongly depends on the anchoring properties of the bounding substrates. In the absence of an external field the confining surfaces impose the orientation in the bulk of nematic layer. If an external field is present the director distribution results from the competition between the surface and bulk torques. Study of the orientational behaviour in an external field provides the information about anchoring properties of NLC at the bounding substrates [1, 2]. Besides, a useful tool for the investigation of interfacial phenomena is the temperature-induced orientational transitions which have been found at some interfaces [3, 4, 5].

Recently the temperature-induced orientational transitions planar → tilted → homeotropic close to the clearing point (nematic - isotropic transition) have been found at the interface between MBBA and a SiO-evaporated substrate [6]. To describe this orientational behaviour the phenomenological model of surface energy similar to [7, 8] taking into account the substrate micro relief has been sug-
In this paper we present the results of experimental investigations of the orientational behaviour of the nematic liquid crystal MBBA in a magnetic field on the same interface as in [6] in the temperature range where the orientational transitions occurred. The director tilt angle at the substrate as a function of temperature has been measured and compared with theoretical predictions. The parameters of the phenomenological model are determined and the temperature dependence of surface energy is found.

**BASIC EQUATIONS**

We consider a nematic liquid crystal layer of thickness \(l\) confined between two identical plates at \(z = 0\) and \(z = l\). Weak anchoring is provided by the substrates with micro relief (grooved surface). The substrate with micro relief is characterised by the grooves axis (along \(x\) axis) and normal vector. Then the phenomenological expression for the surface anchoring energy \(f_s\) for such substrate can be obtained using the expansion in terms of the nematic tensor order parameter \(Q_{ij} = S(T)[n_in_j - 1/3\delta_{ij}]\) up to second order in the scalar order parameter \(S(T)\) (see [6] for details)

\[
f_s = C(S) \cos^2 \theta_0 + D(S) \cos^4 \theta_0 ,
\]

with

\[
C(S) = aS + bS^2, \quad D(S) = dS^2,
\]

where \(\theta_0\) is the angle between the director at the substrate and the \(x\) axis and \(a, b, d\) are the temperature independent model parameters which depend on the micro relief properties and the nematic-substrate interaction. If there is no external field the director distribution in the nematic layer is defined by the surface angle \(\theta_0\), which can be found by minimisation of the surface energy \(f_s\) with respect to \(\theta_0\). Depending on the model parameters \((a, b\) and \(d)\) one could have different scenarios for the temperature behaviour of the surface angle \(\theta_0\). For example, \(a = 0, b < 0, d > 0, b + 2d > 0\) describes a temperature independent pretilt, or, if \(a > 0, b < 0, d > 0, a + b < 0, a + b + 2d > 0\), one has a tilted \(\rightarrow\) homeotropic transition similar to that found in [3]. Here we focus on the case of \(a > 0, b < 0, d > 0, a + b < 0, a + b + 2d < 0\) when the temperature-induced orientational
transition planar $\rightarrow$ tilted $\rightarrow$ homeotropic takes place. Minimisation of surface energy \([1]\) gives the temperature behaviour of surface angle

\[
\cos^2 \theta_0 = \frac{S_p}{S_p - S_h} \left( 1 - \frac{S_h}{S} \right),
\]

with transition points planar $\rightarrow$ tilted ($S_p$) and tilted $\rightarrow$ homeotropic ($S_h$)

\[
S_p = -\frac{a}{b + 2d}, \quad S_h = -\frac{a}{b}.
\]

The temperature dependence of the surface angle $\theta_0$ can be found from Eq. (3) using the experimental data for the scalar order parameter $S(T)$ \([9]\).

In the case when a magnetic field $\mathbf{H}$ is applied along the $z$ axis, the director distribution can be obtained by minimisation of the total free energy (per unit area)

\[
F = \frac{1}{2} \int_0^l \left[ K(\theta) \left( \frac{d\theta}{dz} \right)^2 - \chi a H^2 \sin^2 \theta \right] dz + f_{s1} + f_{s2},
\]

where $K(\theta) = K_1 \cos^2 \theta + K_3 \sin^2 \theta$, $K_1$ and $K_3$ are elastic constants for “splay” and “bend” deformations respectively, $\chi a$ is the diamagnetic anisotropy and $f_{si}$ are the surface energies for the lower ($i = 1$) and upper ($i = 2$) substrates. After the standard procedure one gets the equation for the director profile (first integral of Euler-Lagrange equation)

\[
\frac{d\theta}{dz} = H \sqrt{\frac{\cos^2 \theta - \cos^2 \theta_m}{\chi a K(\theta)}},
\]

and boundary condition (in the case of identical substrates $f_{s1} = f_{s2} = f_s$)

\[
\frac{df_s}{d\theta_0} = H \sqrt{\chi a K(\theta_0)(\cos^2 \theta_0 - \cos^2 \theta_m)},
\]

where $\theta_m$ is the angle in the midplane of the nematic layer and the symmetry of the solution with respect to the midplane has been used ($d\theta/dz = 0$ at $z = l/2$). Integrating (3) from $\theta_0(z = 0)$ to $\theta_m(z = l/2)$ gives the relation between $\theta_m$ and $\theta_0$ by

\[
\frac{\pi H}{2 H_F} = \int_{\theta_0}^{\theta_m} P(\theta) d\theta, \quad P(\theta) = \sqrt{\frac{1 + \eta \cos^2 \theta}{\cos^2 \theta - \cos^2 \theta_m}},
\]
where \( H_F = \sqrt{\frac{\pi}{l}} \sqrt{\frac{K_1}{\chi_a}} \) is the Fréedericksz transition field for strong planar anchoring and \( \eta = \frac{K_3}{K_1} - 1 \).

Using expressions (1), (2), (4) and (7) the temperature behaviour of the surface angle \( \theta_0 \) in the presence of a magnetic field can be derived in the following form

\[
- \sin(2\theta_0)bS\{(S - S_h) - (1 - \frac{S_h}{S_p})S \cos^2 \theta_0\}
= H \sqrt{\chi_a K(\theta_0)(\cos^2 \theta_0 - \cos^2 \theta_m)}.
\]

The values of \( S_p, S_h \) can be easily found from the experimental data on the planar \( \rightarrow \) tilted \( \rightarrow \) homeotropic transition in zero magnetic field. Measuring the temperature dependence of the surface angle \( \theta_0 \) at different values of the magnetic field one can verify the phenomenological model (1), (2) and determine the model coefficients (which should be independent of the magnetic field).

**EXPERIMENTAL**

The experimental cell consists of two glass plates with mylar spacers of thickness \( \sim 35 \mu m \) filled by nematic liquid crystal MBBA. The inner surface of the confining plates was covered by thin layer of SiO, which was vacuum evaporated under the angle 60° with respect to the surface normal. At room temperature one obtains homogeneous planar orientation (along \( x \) axis). The cell was mounted in the hot stage and demonstrated the temperature-induced orientational transition planar \( \rightarrow \) tilted \( \rightarrow \) homeotropic under heating. The accuracy of the temperature measurements was better than 10 mK. To study the orientational behaviour of NLC in a magnetic field the experimental setup consisting of an electromagnet with maximum field 12 kOe and 12 mm gap between the poles has been designed. The stability of the magnetic field was \( \pm 10 \) Oe. The intensity of transmitted light as a function of temperature \( I(T) \) at the fixed values of magnetic field has been measured by a photometer MPM-100 (Zeiss) (light source: He-Ne laser, \( \lambda = 632 \) nm). All measured signals (magnetic field, temperature, and transmitted intensity) were processed by a computer ADC-card.

For the case of cross polars and \( x \) axis at 45° to the polarisers one
has for the transmitted light intensity

\[ I = I_0 \sin^2 \frac{\delta}{2}, \quad \delta = \frac{2\pi}{\lambda} \int R(\theta)dz \]  \hspace{1cm} (10)

with

\[ R(\theta) = \frac{n_o n_e}{\sqrt{n_o^2 \cos^2 \theta + n_e^2 \sin^2 \theta}} - n_o. \]  \hspace{1cm} (11)

Here \( \delta \) is the phase difference; \( \lambda \) is wavelength of light; \( n_o, n_e \) are the ordinary and extraordinary refractive indices. Since \( \delta = \delta(T) \) is monotonically decreasing to zero during planar \( \rightarrow \) tilted \( \rightarrow \) homeotropic transition, it can be easily obtained from the experimental data on the temperature dependence of the transmitted light intensity. Then, taking into account (6), (10) and (11) one obtains the relation between the phase difference and surface angle

\[ \delta = \frac{4l}{\lambda} \frac{H_F}{H} \int_{\theta_m}^{\theta_0} R(\theta)P(\theta)d\theta. \]  \hspace{1cm} (12)

Using the temperature dependence of the material parameters \( K_1, K_3 \) and \( \chi_a \) of MBBA \[9\], expressions (12), (8) allow to calculate the temperature dependence of the surface angle \( \theta_0(T) \) from the experimental data on the phase difference \( \delta(T) \) for the different values of magnetic field.

RESULTS

In Fig. 1 the typical dependence of the transmitted light intensity on the reduced temperature \( \tau = T/T_c \) for zero magnetic field close to the clearing point is shown. The temperature dependence of the surface angle \( \theta_0 \) derived from these experimental data is plotted in Fig. 2 (triangles). The corresponding transition points planar \( \rightarrow \) tilted (\( \tau_p \)) and tilted \( \rightarrow \) homeotropic (\( \tau_h \)) are shown at Fig. 1 by arrows. The dependence \( \theta_0(\tau) \) for zero magnetic field has been fitted by Eq.(3) and the transition points have been determined: \( \tau_p = 0.9961 \) and \( \tau_h = 0.9984 \).

In the presence of a magnetic field the surface angle deviates from the initial value \( \theta_0 = 0 \) and then monotonically increases up to \( \theta_0 = \pi/2 \) with increasing temperature (Fig. 2). Note, that the temperature of the tilted \( \rightarrow \) homeotropic transition is decreased with increasing magnetic field. The solid lines in Fig. 2 show the behaviour of the
Figure 1: Typical temperature dependence of the transmitted light intensity in the range of the orientational transition (thickness \( l = 36.9 \, \mu m \)).

Figure 2: Experimental (symbols) and theoretical (solid lines) temperature dependence of the surface angle \( \theta_0 \) in a MBBA layer (thickness \( l = 36.9 \, \mu m \)).
surface angle calculated from the theoretical model for corresponding magnetic fields. Using in Eq. (9) the values of $\tau_p$ and $\tau_h$ found for zero magnetic field, one obtains $b = -0.055$ erg/cm$^2$ by fitting to the experimental data for $\theta_0(\tau)$ for different values of magnetic field. In a wide range of magnetic field in the experiments the coefficient $b$ was found to be independent of $H$.

Finally, in Fig. 3 the temperature dependence of the coefficients $C(\tau)$, $D(\tau)$ and $C(\tau) + 2D(\tau)$ are presented together with the surface energy $f_s$ [Eq. (1)]. One sees that $C(\tau)$ changes sign at the tilted $\rightarrow$ homeotropic transition point ($\tau_h$) and $C(\tau) + 2D(\tau)$ at the planar $\rightarrow$ tilted transition point. The surface energy $f_s$ is quite small and decreases to zero at the clearing point. At temperature $T = 26 ^\circ C$ one gets for the surface energy $8 \cdot 10^{-3}$ erg/cm$^2$.

It should be noted, that MBBA is a rather unstable substance, which can have an influence on the determination of model coefficients. For estimation of possible errors the coefficients $C$, $D$ were calculated taking into account the uncertainties in the experimental data and material parameters. Varying the material parameters in the range of $\pm 10\%$ results in $\sim 20\%$ uncertainty in the anchoring energy. The influence of inaccuracies in the measured quantities (magnetic field, temperature, thickness etc.) was essentially smaller ($\sim 3 \div 5\%$).
Thus, the temperature-induced orientational transitions planar → tilted → homeotropic at the MBBA - SiO-evaporated substrate has been investigated. From the experimental data on the transmitted light intensity in the presence of a magnetic field the temperature dependence of the surface angle has been found and the parameters of the phenomenological model of surface energy have been determined. The results demonstrate a good quantitative agreement between the experimental data and the suggested surface energy model.

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