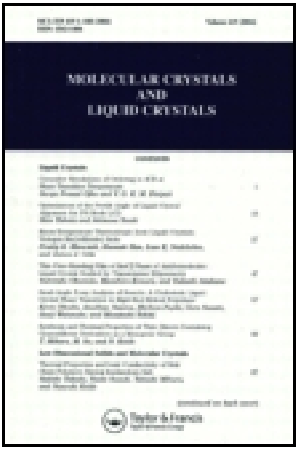

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Anomalous Anchoring Transition in Hybrid Aligned Nematics

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Version of record first published: 24 Sep 2006.

Mol. Cryst. Liq. Cryst., 1996, Vol. 282, pp. 259–268
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ANOMALOUS ANCHORING TRANSITION IN HYBRID ALIGNED NEMATICS

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Abstract The variations in the surface-liquid crystal interactions may cause a substantial change in the alignment of a nematic liquid crystal confined between two solid supports. So far, a number of such anchoring transitions with different nature were reported in the literature. We present an example of anomalous behaviour of temperature-induced anchoring transition in hybrid aligned nematics, where the director tilt at the homeotropic wall (accounted from the normal to the cell plates) first unexpectedly decreases with the temperature and then increases on approaching the nematic-isotropic transition. In the framework of the second order elasticity, a simple model, taking into account in particular the dependence of the elastic constants on the scalar order parameter, is proposed to explain this anomalous behaviour.

INTRODUCTION

In the absence of external fields, the average local alignment of the liquid crystal molecules in a sandwich cell is defined by the surface-liquid crystal interactions. For achievement of homeotropic alignment, for instance, surfactant coatings are commonly used[1]. However, as it has been found recently[2,3], a nematic layer, homeotropically aligned by lecithin coatings (in the form of thin film or monolayer[4]), undergoes on heating a reversible alignment transition from homeotropic to quasi-planar, at a critical temperature below the nematic-isotropic phase transition. This critical temperature can be very near (~0.1°C) to the clearing point or far away (~10°C) from it and the alignment transition might be smooth or very sharp, depending on the liquid crystal and the surface treatment.

Several models were proposed to explain such a temperature-induced surface transition. In /2/, the competition between the homeotropic and the in-plane anchoring strengths was taken into account. A phenomenological model of the phenomenon is presented in /5/ where both nematic-nematic and nematic-substrate interaction were discussed. Barbero et al.[6] dealt with a multilayer model, in the frame of the Kaganov and Omel'yanchuk approach[7] to the Landau-Ginzburg treatment (already discussed by Poniewiersky and Sluckin[8]), pointing out the importance of the existence of a surface in determining the position dependence of the order parameter, thus influencing the phase transition. For describing an anchoring transition in nematics, from homeotropic to planar, in the frame of a Landau-de Gennes approach, the appearance of a smectic subsurface layer was considered[9]. Moreover, Barbero and Durand[10] introduced a surface spontaneous curvature model, in the frame of the second order elastic theory[11], and Alexe-Ionescu et al.[12] described the anchoring transition from homeotropic to planar as a tool for estimating the splay-bend surface-like elastic constant.

As far as we know, the present work is the first observation of anchoring transition performed in a hybrid aligned nematic (HAN) cell. The easy directions at both planar- and homeotropic side were provided by convenient surface treatment of the cell substrates. The resulting anchoring strength is much weaker at the homeotropic wall, whereas at the planar wall, for the sake of simplicity, a strong anchoring is supposed to act. Hence, the tilt angles φ at the boundary, accounted from the cell plate normal, are $\varphi_0 = 90°$ and $\varphi_1 > 0°$ at the planar side and at the homeotropic one, respectively. Thus, starting from a hybrid alignment at room temperature, a continuous transition (without threshold) to a unidirectional planar alignment in the whole layer was expected to take place on heating. Instead, on increasing the temperature, the director tilt at the homeotropic wall was first moving towards 0°, thus becoming more homeotropically aligned, as the homeotropic anchoring strength should become greater, which is an anomalous behaviour. Then, after having reached a minimum, the tilt was quickly increasing towards 90°, as expected.

In this work we present a model explaining in the frame of the second order elasticity such an anomalous behaviour as a competition between bulk elastic, surface-like elastic and anchoring torques, considering their dependencies on the nematic order parameter.

EXPERIMENT

The experimental cell consists of two soda glass plates arranged in a sandwich geometry. The distance between the substrates was kept constant by 4 μm thick Mylar spacer. In order to obtain a hybrid alignment of the molecules in the experimental cell, the inner surface of the glass substrates was covered respectively with lecithin and with polyimide film. The lecithin was deposited onto the glass plate as a thin layer from chloroform solution. The polyimide layer was deposited onto the substrate by spinner and after baking at 180°C was rubbed unidirectionally. The liquid crystal material in the experiment was MBBA (n-(p-methoxy benzylidene)-p-butylaniline) with clearing point at 39 °C. The cell was inserted into a Mettler FP 52 hot stage with temperature control within 0.1°C. The observations on the changes in the alignment of the liquid crystal layer were performed by means of polarizing microscope in both orthoscopic and conoscopic regime. It was found that on heating, the tilt angle of the director at the homeotropic wall with respect to its normal continuously decreased and at certain critical temperature, in our case near the clearing point, the initially hybrid alignment was rapidly transformed to a quasi-planar. This behaviour is opposite to the expected smooth and continuous increase of the tilt with temperature. The anomalous character of the temperature-induced anchoring transition in a nematic hybrid cell could be explained on the basis of the different dependence of the bulk- and surface-like elastic constants on the scalar order parameter, as we shall see later. This anchoring transition was also found to be reversible with temperature, with a small hysteresis of about 0.4°C.

In Figure 1 it is shown an orthoscopic photograph of the anchoring transition in a hybrid cell on cooling from the isotropic phase. In the black spots the material is still in the isotropic phase. First, the reddish areas (labelled in the Figure 1 as *b*) appear on cooling from the isotropic phase and the liquid crystal alignment there is found to be quasi-planar. Lowering the temperature further, the yellow regions appear in the reddish one and start growing rapidly on their expense. The alignment of the liquid crystal layer in these regions is hybrid and holds at lower temperature. However,

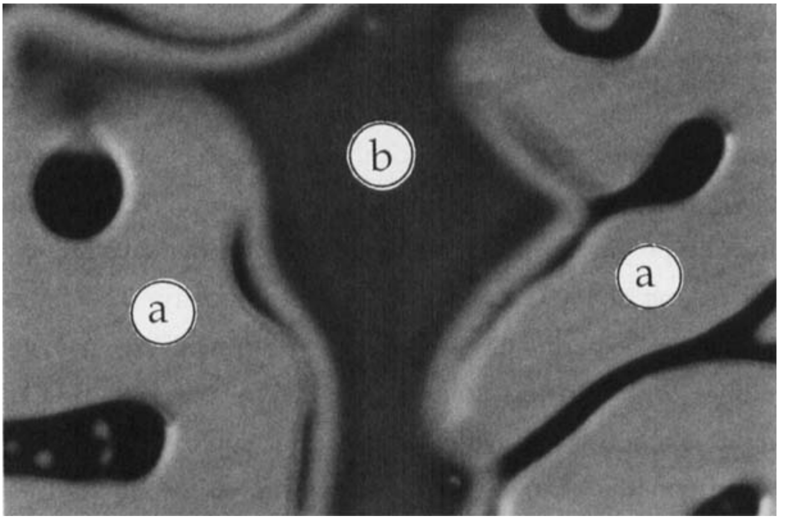

FIGURE 1 Temperature-induced anchoring transition in a HAN cell. The black spots are the isotropic phase. In the transition area between the lower temperature regions (a), with hybrid alignment, and higher temperature regions (b) quasi-planar one, the alignment is hybrid, but with a lower tilt at the homeotropic wall. See Color Plate I.

there is a transition region between the yellow and reddish areas which disappears together with the reddish one at lower temperature. As can be seen from the photograph, the birefringence of the transition region is substantially smaller than the one of the yellow regions. This implies a higher tilt angle of the director at the homeotropic wall in the lower temperature hybrid region than in the transition one which can be reasonably approximated to be close to zero ($\varphi_1 \approx 0°$). Moreover, the conoscopic investigations on the temperature-induced anchoring transition also confirm that the tilt at the homeotropic wall in a nematic cell with a hybrid alignment decreases with increasing temperature before it transforms into a quasi-planar. However, the orthoscopic and conoscopic optical methods can give only a qualitative information of the character of the temperature behaviour of the tilt angle at the homeotropic wall. Now, measurements on the temperature dependence of the value of this tilt angle are in progress and the results will be published elsewhere.

MODEL

Let us consider a hybrid aligned nematic layer of thickness d, with the local tilt angle φ accounted with respect to the normal to the cell walls. The [x,z]-frame of reference is chosen in the layer deformation plane, the z-axis being normal to the cell plates , and the origin O belonging to the lower plate (0), $z_0 = 0$ (see Figure 2), where the easy direction is unidirectional planar (P-) along the x-axis and the anchoring is assumed to be strong (φ_0=90°). At the upper surface (1), z_1=d, the easy direction is homeotropic (H) and the anchoring is assumed to be weak (finite anchoring strength w_1, according to Rapini-Papoular approach[13]). Hence the tilt angle at the upper wall is expected to be φ_1 different from zero. In the framework of the second order elasticity[11, 14-18], the cell free energy reads, in the hypothesis of the bulk elastic isotropy, as:

$$F=\frac{1}{2}K\int_0^d\left(\varphi'^2+\kappa\varphi''^2\right)dz+\frac{1}{2}w_1\sin^2\varphi_1-K_{13}\varphi_1'\sin2\varphi_1 \tag{1}$$

where $K=K_{11}=K_{33}$ is the bulk elastic constant, $\kappa=K^*/K$ is the reduced additional second order elastic modulus, the prime means derivative with respect to z, and the surface terms comprise the anchoring- and the splay-bend contributions, respectively. We would like to point out that the κ term

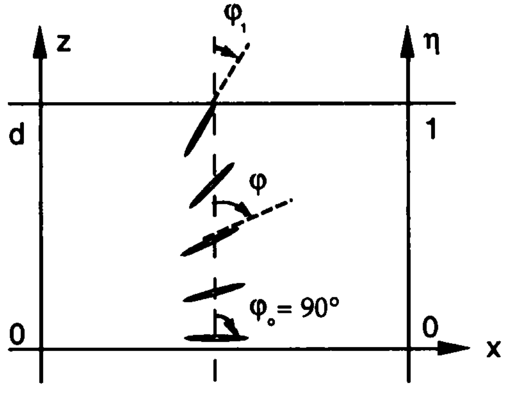

FIGURE 2 The director configuration in the cell and the frames of reference (η= z/d)

allows us to consider well-posed the variational problem[19], and that it is possible to take into account in the bulk one term only, quadratic in the second order derivative, in a rough assumption that the variation of φ can be considered as small. According to the usual procedure, Euler-Lagrange eq. writes:

$$b^2\ddot{\ddot{\varphi}}-\varphi=0 \tag{2}$$

where the dot means derivative with respect to $\eta=z/d$, and $b=\sqrt{\kappa}/d$ is a characteristic penetration length[14], of the order of the molecular interaction (i.e. from 10Å to 100 Å). Putting the solution

$$\varphi = C_1\eta + C_2 + \alpha\sinh(\eta/b) + \beta\cosh(\eta/b) \tag{3}$$

into the boundary conditions

$$\begin{cases} -2\dot{\varphi}_1 + 2b^2\dddot{\varphi}_1 - l_1^{-1}\sin 2\varphi_1 - 2R\dot{\varphi}_1\cos 2\varphi_1 = 0 \\ 2b^2\ddot{\varphi}_1 + R\sin 2\varphi_1 = 0 \\ \varphi_0 = 0 \\ \ddot{\varphi} = 0 \end{cases} \tag{4}$$

where $l_1 \equiv K/w_1 d$ is the reduced extrapolation length[20]

$$(\pi - 2\varphi_1)(1 - R\cos 2\varphi_1) + (R - l_1^{-1})\sin 2\varphi_1 + \frac{1}{2}\frac{R^2}{b}\sin 4\varphi_1 \cong 0 \tag{5}$$

is obtained, since $b^{-1} >> 1$. By expanding to second order in φ_1, eq. (5) transforms into

$$\varphi_1^{\,2} + \frac{2}{\pi}\left[1 - \frac{1 - l_1^{-1}}{2R} + \frac{R}{2b}\right]\varphi_1 + \frac{1}{2}\left(\frac{1}{R} - 1\right) \cong 0 \tag{6}$$

We are interested in the behaviour of φ_1 vs. temperature T since a temperature-induced surface anchoring transition is expected[1-4, 10], moving the HAN configuration towards a P- one. Remembering that [10, 20-23]:

$$\begin{cases} R \equiv \dfrac{K_{13}}{K} \cong \dfrac{a_1 S}{aS^2} = k_1/S \\ b \cong const \\ l_1^{-1} \cong \dfrac{a_2 S}{aS^2} = k_2/S \end{cases} \tag{7}$$

where k_1, k_2 are convenient phenomenological constants, S is the scalar order parameter, which is decreasing with the reduced temperature $\tau =: (1\text{-}T/T_{ni})^{1/2}$ in the nematic range, T_{ni} being the clearing point. Finally φ_1 turns out to be

$$\varphi_1 \cong \frac{\pi}{2} b \frac{\frac{S}{k_1}\left(1-\frac{S}{k_1}\right)}{1-\frac{k_2 b}{k_1^2} S} \tag{8}$$

which exhibits a non-monotonic behaviour of φ_1 as a function of T. For convenient values of the phenomenological parameters contained in (7), a minimum of φ_1 just above room temperature can be reached (see Figure 3), which explain, with a certain approximation of course, the experimental results.

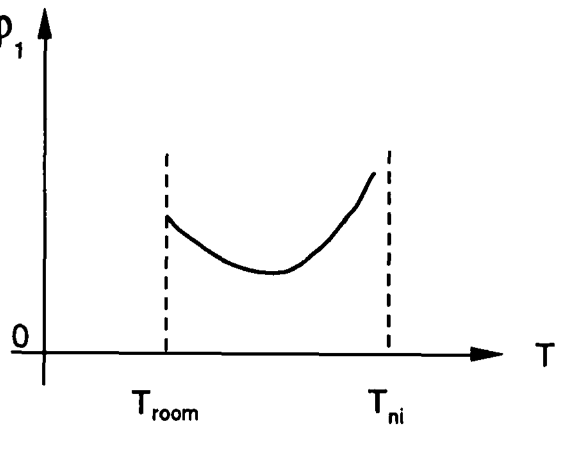

FIGURE 2 Temperature dependence of the tilt at the homeotropic wall φ_1 in HAN cell according to the model for both positive and negative values of K_{13} in the approximation $\varphi_1 << 1\text{rad}$.

CONCLUSION

The alignment of liquid crystals, especially the conditions for achieving a certain type of alignment with appropriate anchoring strength as well as the conditions necessary to change it reversibly or irreversibly, are of fundamental and of application interest. In the last few years, the temperature-induced surface anchoring transition in nematics has attracted a lot of scientific interest but, since the phenomenon is a complex one, it is still far from being well understood. The observed anomalous behaviour of such a transition in a nematic hybrid cell shows the necessity to take into consideration in the description of this phenomenon also the second order elasticity. As the experiment has shown, however, the transition is very sensitive to the experimental conditions. Therefore, it is worthwhile to continue the study on this transition with different liquid crystal materials, for instance, applying at the same time another experimental methods capable to give a quantitative information about the tilt angle near the homeotropic wall. We may learn in the future how to use this anomalous behaviour of the surface anchoring transition in HAN cell for scientific but also for practical purposes.

ACKNOWLEDGEMENTS

This work was supported by the Swedish Research Council for Engineering Sciences under contract TFR 93-440 and it was also partially supported by the Italian National Institute of Matter Physics (INFM) and by the Italian Ministry of the University and the Scientific and Technological Research under contract 94-18260.

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