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Nematic anchoring transitions on bistable SiO films driven by temperature and impurities

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The influence of temperature and impurities on the surface orientation of nematic 5CB on obliquely SiO evaporated glass plates has been studied. We observe on cooling a continuous anchoring transition from the planar alignment to the tilted one. The experimental data have been interpreted by using elastic models developed by Durand and coworkers in which the surface order parameter can vary in space, close to the surface.

1. Introduction

SiO coating of substrates is a well known method to obtain planar or tilted liquid crystal surface orientations [1]. Depending on the deposition conditions, the anchoring can be monostable or bistable [2, 3]. Similar monostable anchoring can be obtained by means of other surface treatments more interesting at present for industrial applications [4–6]. This is the case for rubbed polymers, photopolymers [7], etc. On the other hand, SiO coating is, up to now, the simplest way to obtain surface anchoring bistability in nematics.

The SiO deposition can be controlled by several parameters that influence the final film morphology and hence the nematic anchoring. Among these parameters, the better understood are the deposition angle and the film thickness [2]. Recently, several other parameters have been studied, such as the deposition rate, the distance between the SiO source and the substrate, and the starting substrate roughness [8]. All these parameters define irreversibly the final SiO film structure. Other parameters which do not change the structure of the SiO layer, but which influence the nematic–solid interaction, are also important in defining and controlling the actual surface state of the nematic [8]. These parameters can induce real anchoring transitions in the sense that they can change reversibly the easy axis orientation.

In this paper, we study the influence of temperature and impurities on the surface state of nematic 5CB on SiO film and we report and discuss memory effects related to the observed anchoring transitions.

2. Experimental set-up

For our experiments, we work with technological parameters for the SiO deposition chosen to obtain at room temperature the three main anchoring surface states simply by changing the thickness δ of the SiO layer. δ is measured on a quartz balance perpendicular to the SiO beam.

- (1) $\delta < 150 \text{ \AA}$: monostable unidirectional planar alignment (P) perpendicular to the oblique SiO deposition beam. The easy axis is defined by $\phi = 0^\circ$ and $\theta = 90^\circ$, where ϕ is the azimuthal angle and θ is the zenithal angle (figure 1).

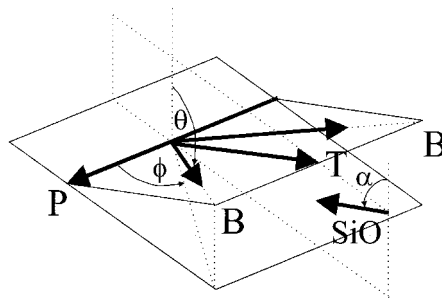


Figure 1. Director orientations of the P, B and T plates with respect to the SiO beam; ϕ and θ are the azimuthal and zenithal angles, respectively.

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- (2) $150 \text{ \AA} < \delta < 250 \text{ \AA}$: bistable tilted alignment (B), symmetric with respect to the plane of incidence of the SiO beam ($0 < |\phi| < 90^\circ$, $\phi = \pm |\phi|$, $0 < \theta < 90^\circ$).
- (3) $\delta > 250 \text{ \AA}$: monostable tilted alignment (T) in the plane of incidence of the SiO beam ($\phi = 90^\circ$, $0 < \theta < 90^\circ$).

The deposition angle, measured with respect to the surface normal, is fixed at 75° and the deposition rate is about 5 \AA s^{-1} . The substrates where the SiO is deposited are standard conductive ($4 \Omega/\square$) ITO covered glass plates by Balzers. The symbol \square means that the electrical resistance of the conductive film, measured by putting electrodes along two opposite sides of a square, is always 4Ω and it depends only on the film thickness.

Here, we are interested only in the anchoring geometry and not on the associated anchoring strength. For this purpose, we prepared thick cells with one of the plates studied and a counter-plate with standard treatment for homeotropic or planar alignment. Due to the large thickness ($20\text{--}50 \mu\text{m}$), the torque exerted by the counter plate on the SiO coated surface can be considered negligible.

The zenithal angle is measured by means of standard birefringence observations made using a polarizing microscope. The azimuthal angle is measured using the wave guide property of the distorted texture in the sample, with a suitable twist of the analyser and polarizer of the optical microscope (Mauguin regime for the transmitted light in thick cells). As the zenithal angle measurements are less accurate than the azimuthal ones, they have been used only to confirm the known dependence between ϕ and θ , according to the model in ref. [2]. The influence of the ϕ - θ coupling on the anchoring energy has been investigated by Nobili and Durand [9]. In practice, surface anchoring transitions can be described only by means of the ϕ -variation. Moreover the measurement of the azimuthal angle is very fast and this facilitates the interpretation of the observed memory effects. Samples were placed in an oven to control the temperature in the range $20\text{--}60^\circ\text{C}$, i.e. from the nematic phase (at room temperature for 5CB) up to sufficiently far into the isotropic phase.

3. Temperature dependence

To minimize the complications related to memory effects, we fill our cells with the nematic in the isotropic phase at 50°C and then cool the sample slowly to the nematic phase. This slow passage through the I-N transition results in very uniform and reproducible alignment of the nematic material. All samples with the SiO film thickness in the range $100\text{--}300 \text{ \AA}$ show a monostable unidirectional planar alignment ($\phi = 0^\circ$, $\theta = 90^\circ$) just

below the clearing point T_c (figure 2). This alignment does not change as long as the temperature does not vary: it is a real state of equilibrium for the surface and it is not due to memory effects. Now we decrease the temperature. Each experimental point is taken in about two minutes, just the time necessary for temperature equilibration of the cell before the measurement.

For the P anchoring plates, we find that the easy axis does not change on decreasing the temperature to 20°C and no anchoring transition is observed. For the T anchoring plates (known to give a monostable oblique alignment at room temperature), the temperature range close to T_c , where the initial unidirectional planar alignment is observed, is very narrow (always less than 1°C). A further decrease of the temperature induces an anchoring transition with a time constant of almost 2°C : now we observe random domains with left or right ϕ -rotation of the easy axis. During this anchoring transition, the alignment is in fact bistable. The temperature dependence of ϕ , for the T plates is quite fast: ϕ goes from 0° to about 90° in $3\text{--}4^\circ\text{C}$. At lower temperature, we always observe the expected tilted monostable alignment in the plane of the SiO beam. In the case of B plates, the behaviour is qualitatively similar to that of the previously described T plates. However, the planar regime, close to T_c , is now larger, the anchoring transition spreads over a wider temperature range and, at room temperature, ϕ almost saturates at values lower than 90° (see curve B in figure 2). Similar anchoring transitions have been reported recently by Komitov *et al.* for several nematic materials [10].

The typical plots presented are reproducible when we coat the plates with rigorous control under the same experimental conditions. Moreover, when temperature variations are small and relatively fast, each experimental point of these curves is reasonably well reproduced. When temperature variations are larger or the sample remains for too long (hours) at a fixed low temperature,

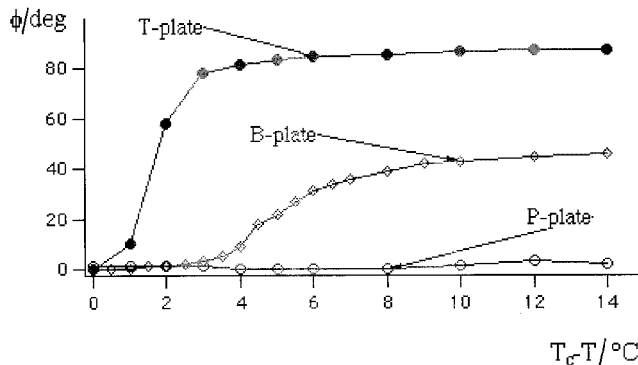


Figure 2. Experimental values of the azimuthal anchoring direction ϕ versus the temperature for the P, B and T plates.

the curves are no longer reproducible. Typical examples are the curves presented in figure 3, measured at increasing temperature for the same plates of figure 2 and after 1 h at room temperature. Qualitatively the behaviour is reversible: the ϕ angle for T and B plates diminishes, but it does not attain the 0° value corresponding to the initial planar alignment. We recall that the planar alignment condition is achieved only for $\phi = 0^\circ$ and surface alignments with $\phi \neq 0^\circ$ are tilted. The B plates can return very close to the planar easy axis but never exactly. The temperature of the anchoring transition to the planar state seems now to be shifted into the isotropic phase.

4. Memory effects

In figure 4 we present the ϕ temperature dependencies measured at decreasing and at increasing temperature for the same B plate. As explained before, the two curves are not the same: the picture looks like a typical hysteresis loop. In fact, this is not the case: our 'hysteresis loop' depends on the speed of acquisition of the experimental points. If the acquisition rate is infinitely slow

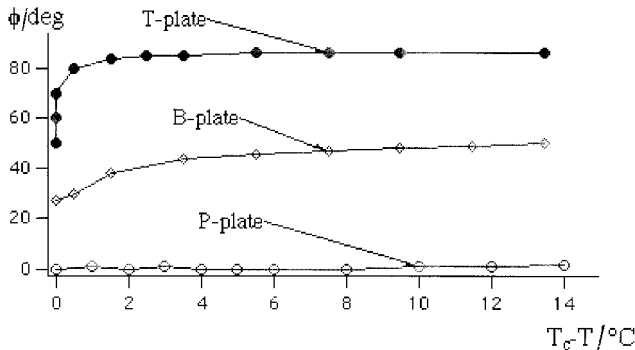


Figure 3. Temperature dependence of ϕ on the same plates of figure 2, measured after one hour at room temperature; the anchoring transition to the planar state is shifted into the isotropic phase.

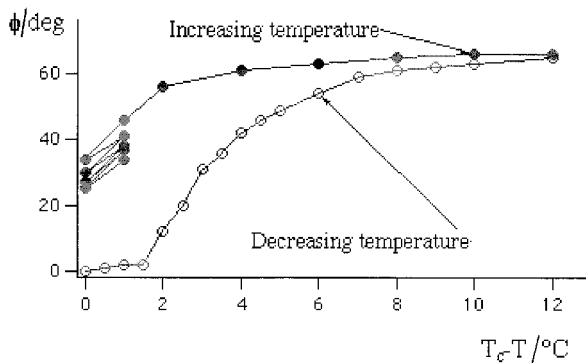


Figure 4. Temperature dependence of ϕ measured at decreasing and increasing temperature for the same B plate; the apparent hysteresis loop depends on the speed of acquisition of the experimental point.

(several weeks) the loop collapses towards a single intermediate curve.

The temporal ϕ -relaxation seems to be a very complicated process with several intrinsic time constants ranging from a few minutes to several weeks. To illustrate this phenomenon, we present in figure 4 several points, close to T_c , taken on varying the temperature alternately and repeatedly. One sees that ϕ -variations always show the same slope, ϕ values become closer and closer to the planar state, but this approach becomes slower and slower.

Usually all the nematic properties depend strongly on the temperature, and the time scale for temperature relaxations is very fast, limited by the thermal diffusion 10^{-6} – 10^{-3} s. On the contrary, we observe that the nematic surface alignment follows the temperature variations very slowly. To our knowledge, this is one of the first reports on the extremely slow spontaneous relaxation of anchoring transitions [11].

5. Influence of impurity

We observe also that these transitions are strongly influenced by impurity adsorption on the SiO layer. This phenomenon is easily demonstrated by observing regions close to impurity particles accidentally deposited on the plate during the SiO coating or during the sample preparation.

In figures 5 and 6, we present a T plate with two dust particles, which are sources of unknown impurity diffusion on the surface. Close to T_c , the orientation on all the plates is planar and the regions where the impurities have diffused, cannot be distinguished. At $T_c - T \simeq 2^\circ\text{C}$, the anchoring on the clean part of the plate has become bistable with $\phi = \pm 17^\circ$. At the same temperature, in the two elliptical regions around the dust particles, the anchoring remains monostable planar: the impurity diffusion has changed the surface alignment properties (figure 5). When we further decrease the temperature, at $T_c - T \simeq 4^\circ\text{C}$, we find that the elliptical regions also undergo the anchoring transition (figure 6).

In figure 7 we report ϕ versus temperature plots measured inside and outside the impurity regions. We see clearly that the anchoring transition is shifted towards lower temperatures for the surface regions where impurities have diffused. These regions present a bistable anchoring at room temperature, transforming the T-plate into a B. Therefore, in principle, it is possible to control the surface anchoring given by a SiO coated plate, just by deposition of small quantities of suitable impurities.

Usually, the most common 'impurity' adsorbed on the SiO layer is water vapour from the ambient atmosphere. In fact, we observed a strong influence of humidity on the anchoring transition reported here. Plots of ϕ versus

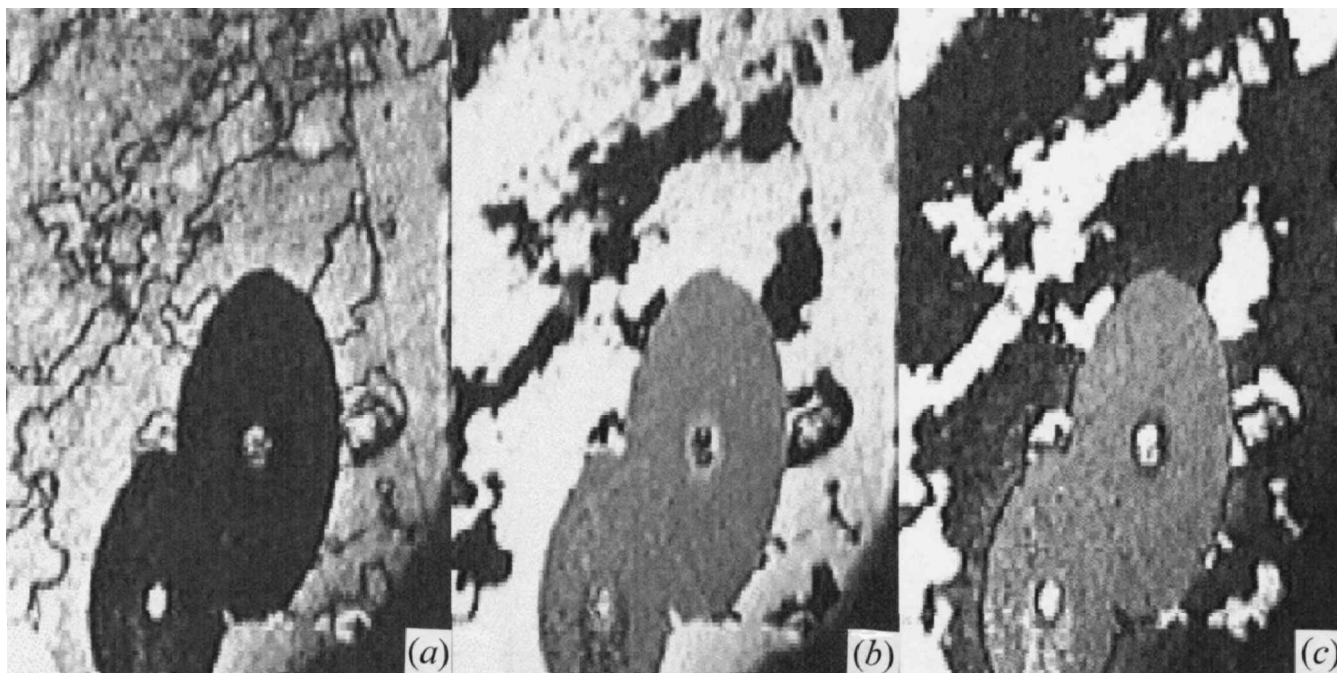


Figure 5. A region of a T plate with two dust particles observed between crossed polarizers. (a) Monostable planar orientation close to the dust particles at $T_c - T \simeq 2^\circ\text{C}$; (b), (c) bistable orientation with $\phi = \pm 17^\circ$ at the same temperature in the clean region of the plate.

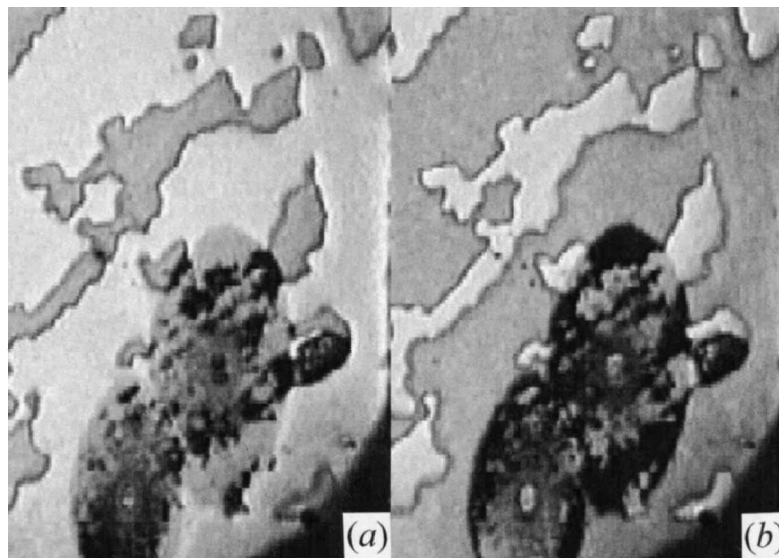


Figure 6. The same plate as figure 5 at $T_c - T \simeq 4^\circ\text{C}$: the elliptical regions in which the impurities have diffused undergo the bistable transition with $\phi \simeq \pm 25^\circ$.

δ are reported in figure 8 for T-plates with the same SiO coatings, but in two different situations: curve 1, showing a continuous transition from the unidirectional planar anchoring to the oblique one, is the result of observations made on a fresh plate, just after the SiO deposition and with a very short time of exposure to air; curve 2, showing a constant planar state, corresponds to measurements made on a plate after 80 h of exposure to air at room temperature and with about 100% humidity.

The SiO layer is expected to act as a trap for gas and vapour molecules; due to its porosity and high polarity, water molecules adsorb easily on the layer. When the plate has been exposed to humidity for a long time (several hours) we observed, by means of Atomic Force Microscopy, the formation of a continuous water layer that wets the AFM tip and attracts it by capillary forces. The continuous water film disappears if the plate is exposed to dry air for a few hours.

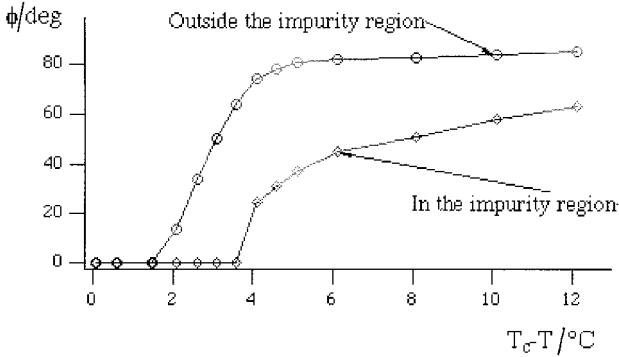


Figure 7. Temperature dependence of ϕ measured inside and outside the impurity regions.

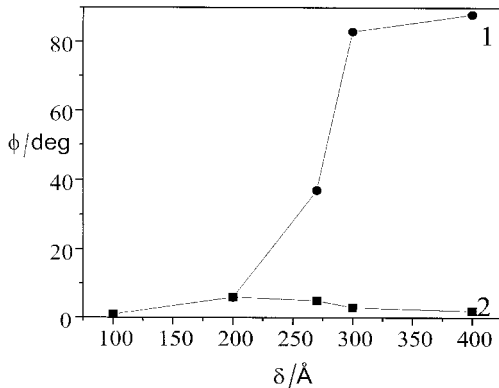


Figure 8. Plot of ϕ versus the SiO thickness δ for T plates in two different situations: curve 1 is the result of observations made on a plate just after the SiO deposition, while curve 2 corresponds to measurements made on a plate after 80 h of exposure to air at room temperature and with 100% humidity.

Figure 9 shows the temperature dependence of ϕ obtained for three plates with exactly the same SiO coating, but with different exposures to humidity. Firstly, all three plates have been exposed for a few days to air saturated with water vapour at room temperature. Then the temperature dependence of ϕ is measured for the

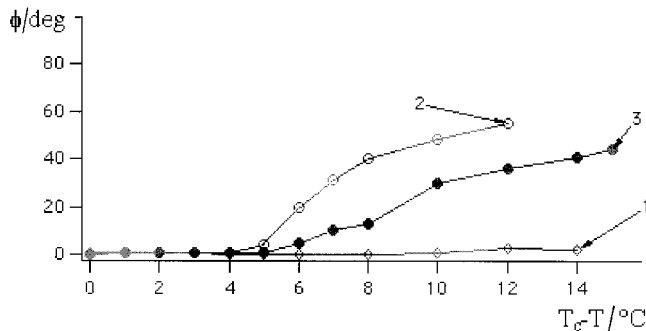


Figure 9. Temperature dependence of ϕ for three plates with the same SiO coating, but different exposure times to humidity.

first plate (curve 1): the surface anchoring is monostable planar, without temperature dependence. The other two plates are now dried at 250°C for 90 min and the second plate is immediately studied (curve 2). In this case, we find a pronounced anchoring transition from monostable planar to bistable anchoring. Finally the third plate is exposed again to humidity for 40 h and we observe that again the anchoring transition is present, but smoothed and shifted towards lower temperatures. Hence, it is evident that the humidity has a strong influence on the anchoring transition and its effects are reversible.

6. Discussion

The nematic anchoring on SiO layers is quite a complicated phenomenon: the SiO layer is a highly porous and polar medium with a complex morphology characterized by high anisotropic roughness [12, 13]; the nematic material close to the boundary plate is strongly perturbed both in its orientation and its order parameter. Moreover, the spatial order variation in the nematic is quite rapid with strong gradients, unusual for bulk properties [14]. A complete description of such a complicated system does not exist at present and it is beyond the aim of this paper.

It is well known that azimuthal anchoring is related to the surface topography: if the nematic molecules prefer to be parallel to the local boundary surface and the surface z undulates with wave vector \mathbf{q} ,

$$z(\mathbf{r}) = A_q \sin(\mathbf{q} \cdot \mathbf{r})$$

then the minimum of the elastic energy is obtained when the nematic director is perpendicular to \mathbf{q} [15] and the surface energy is given by

$$F_q(\phi) = \frac{k}{4} A_q^2 q^3 \cos^2 \phi$$

where ϕ is the azimuthal angle between \mathbf{q} and the director \mathbf{n} . The SiO surface that we study is very rough: there exists a continuum of undulation wave vectors over all the azimuthal directions and with wavelengths ranging from the atomic to the microns scale; the corresponding amplitudes compare with the wavelengths [12].

The total surface energy is

$$F_{\text{tot}}(\phi) = \sum_{q_{\min}}^{q_{\max}} F_q(\phi)$$

where q_{\min} is related to the sample size and q_{\max} depends on the coherence length ξ of the nematic–isotropic transition, $q_{\max} = 2\pi/\xi$.

The aligning effects of the different undulations are in competition and the resulting alignment is given by a delicate balance between them. For this reason, a small change in the SiO layer structure induces large rotations

of the easy axis. However, from this point of view, it is difficult to understand the temperature induced anchoring transitions: the surface structure and hence the \mathbf{q} distribution is independent of the temperature.

To describe the temperature variations of the alignment we need to go beyond elastic models and to consider the order variation close to the surface. This means simply that we take into account the temperature dependence of the correlation length ξ and hence of the elastic cutoff q_{\max} . As the \mathbf{q} distribution is strongly anisotropic, any q_{\max} variation with temperature changes the balance of the surface energy for the different possible orientations and it can induce anchoring transitions. Recent experimental observations show that the amplitude of the surface modes with wavelength comparable to ξ is not negligible [12] especially if one takes into account that close to the surface ξ is much larger than in the bulk, due to the surface induced melting of the nematic order [16]. Therefore ξ acts as an anisotropic temperature dependent ‘filter’ of the elastic modes responsible for the alignment. The roughness at a scale comparable to ξ or smaller cannot be relaxed by elastic distortion, but it contributes to the surface nematic melting. The bulk nematic is then oriented on an effective surface smoother than the SiO layer.

From this point of view, one expects that this kind of temperature dependent anchoring transition should be typical of all surfaces with very high and anisotropic roughness, especially if the dominant wavelength of surface undulation is comparable with the coherence length at room temperature.

One of the most striking features of the system we studied is the observed memory effect and the very slow relaxation times involved. The bulk nematic is a very fluid system and its reactions to external order perturbations are very fast, on a sub-microsecond time scale. On the contrary, the SiO layer is a rigid system and its relaxations under external perturbations are infinitely slow. The observed slow, but finite, times for the anchoring transition relaxation lead us to seek a physical mechanism that involves both the liquid system and the rigid one. The best candidate is the absorption of the nematic molecules on the SiO layer.

The highly porous SiO film traps the nematic molecules in contact with the solid surface. The nematic surface layer created in this way memorizes the nematic order existing during its formation. Once built, the anisotropic surface layer remains very stable: each molecule sticks on its adsorption site and, at room temperature, the probability of its getting free is negligible. If now one varies the temperature, both the order and the orientation of the nematic surface layer remain ‘frozen’ for a very long time, though the system is out of equilibrium.

The relaxation times of this first layer are very long for three reasons. The first is that, even for a single molecule, the reorientation rate is very slow, due to the high energy barrier of the adsorption. The second is that the reorientation of the layer is a collective process. When, by accident, a molecule gets free, it can reorient and readsorb or it can be replaced by another molecule, but, during the readsorption, it is submitted to the anisotropic orientational field of close neighbours and hence, on average, its final orientation will be not far from the initial orientation. The third reason is the steric hindrance effect: when a molecule releases an adsorption site, the shape of this hole is very close to the molecular shape. Hence the close packing on the surface forces the molecule to readsorb in almost the same orientation. This means that the first nematic layer has a large orientational ‘inertia’. Then adsorption can explain the slow response time of the anchoring transition observed in our system.

We note that similar memory phenomena can be expected in other systems, for instance at the interface nematic-polymer alignment layer. The lack of experimental evidence for other systems can be explained by the mismatch of the time scales of the memory effects with those of the measurements; we paid special attention to the aging of our samples, and deliberately studied a large temporal range (from minutes to weeks).

The influence of the impurities can be easily understood in the frame of the above discussion. The impurities are concentrated on the nematic-SiO interface (or at the surface of the SiO before filling the cell with nematic). Now, they are adsorbed on the SiO surface, occupying all or a significant part of the vacant adsorption sites. The presence of impurities affects both the alignment and the order of the first nematic layer. For instance, isotropic impurities can strongly increase the nematic coherence length ξ close to the surface. They can even completely melt the nematic order close to the SiO. This explains the influence of the impurities on the anchoring transitions reported in this paper.

Obviously, impurities can also affect the relaxation times for surface alignment reorientation. On one hand, impurities can have adsorption activation energies different from the nematic, thus changing directly the relaxation times. On the other hand, the collective slowing down of the relaxation times is very sensitive to the local nematic order, which is itself influenced by impurities. The surfaces investigated are particularly sensible to adsorption, but we expect that other alignment layers too should be affected by impurities.

7. Conclusions

In conclusion, we studied the temperature driven anchoring transitions of nematic 5CB and SiO layers,

vacuum deposited at oblique incidence. We observed on cooling anchoring transitions from planar alignment, whose easy axis is perpendicular to the SiO beam, to tilted alignments in the plane of incidence, crossing the region with bistable tilted anchoring. The transition from the planar to the tilted alignment is continuous (second order). The temperature controlled reorientation of the easy axis is reversible, but strong memory effects are observed, with relaxation times ranging from a few minutes to some weeks. These anchoring transitions are also affected by impurities, in particular by humidity. The experimental observations are qualitatively explained by invoking the anisotropic surface roughness of SiO and strong adsorption of nematic and impurity molecules on it.

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