Liquid crystal anchoring transitions on aligning substrates processed by plasma beam

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We observe a sequence of the anchoring transitions in nematic liquid crystals (NLC) sandwiched between the hydrophobic polyimide substrates treated with the plasma beam. There is a pronounced continuous transition from homeotropic to low tilted (nearly planar) alignment with the easy axis parallel to the incidence plane of the plasma beam (the zenithal transition) that takes place as the exposure dose increases. In NLC with positive dielectric anisotropy, a further increase in the exposure dose results in in-plane reorientation of the easy axis by 90° (the azimuthal transition). This transition occurs through the two-fold degenerated alignment characteristic for the second order anchoring transitions. In contrast to critical behavior of anchoring, the contact angle of NLC and water on the treated substrates monotonically declines with the exposure dose. It follows that the surface concentration of hydrophobic chains decreases continuously. The anchoring transitions under consideration are qualitatively interpreted by using a simple phenomenological model of competing easy axes which is studied by analyzing anchoring diagrams of the generalized polar and non-polar anchoring models.

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I. INTRODUCTION

Orientational structure of a nematic liquid crystal (NLC) placed in contact with an anisotropic substrate is essentially determined by the properties of the interfacial region where various kinds of surface induced ordering may exist. Among these are smectic layering, biaxiality and orientational alignment (see, e.g., [1, 2, 3] for reviews).

At the macroscopic level, the surface induced orientation of NLC molecules in the interfacial layer manifests itself as the well-known phenomenon of anchoring. In the case of uniaxial anisotropy, anchoring can be roughly described as the tendency of the nematic director \( \mathbf{n} \), to align along the direction of preferential anchoring orientation at the surface. The direction of surface induced alignment is specified by a unit vector \( \mathbf{n}_s \) referred to as the easy axis.

Anchoring is governed by the so-called anchoring energy, \( W_{\text{anch}} \), which is the orientationally dependent (anisotropic) part of the surface tension. In particular, easy axes can be found by minimizing the anchoring potential and, thus, crucially depend on the shape of \( W_{\text{anch}} \).

When the anchoring energy changes, the easy axes may vary in both direction and number. Such variations of the anchoring conditions result in reorientation of the NLC director known as
FIG. 1: (a) Scheme of anode layer source: (1) inner cathode, (2) outer cathode, (3) anode, (4) permanent magnets. (b) Glow discharge and beams of Ar plasma generated by anode layer source. (c) Geometry of plasma beam irradiation: (1) anode layer source, (2) sheet-like plasma flux, (3) moving platform, (4) substrate.

Since the anchoring potential is sensitive to the thermodynamic parameters, the anchoring transitions, similar to the phase transitions, can be driven by temperature, chemical potential and strain. They can also be first and second order depending on whether the anchoring induced reorientation
FIG. 2: Types of NLC alignment observed in our experiments: (a) low tilted (nearly homeotropic) structure (alignment of the 1st type with $75^\circ \leq \theta \leq 90^\circ$ and $\phi = 0^\circ$); (b) high tilted (nearly planar) structure (alignment of the 2nd type with $0^\circ \leq \theta \leq 30^\circ$ and $\phi = 0^\circ$) which is close to planar anchoring and (c) planar anchoring normal to the incidence (the $x$-$z$ plane) (alignment of the 3rd type with $\theta = 0^\circ$ and $\phi = 90^\circ$).

is discontinuous (jump-like) or continuous at the critical point. For planar interfaces, the transitions that occur through out-of-plane, in-plane and mixed director reorientation may be classified as the zenithal, azimuthal and mixed anchoring transitions, respectively.

For example, a discontinuous zenithal transition from planar to homeotropic orientation was found to occur at a flat glass or quartz substrate on cooling toward the smectic-A transition temperature [4] and on the surface of a self-assembled monolayer, which is made sufficiently hydrophobic [5]. By contrast, the temperature-driven zenithal transitions observed at the free NLC surface [6, 7, 8] and at the rubbed polyimide aligning layers [9] turned out to be continuous.

Transitions between different anchorings can be generated by changing either the molecular characteristics of NLC materials or the parameters determining the structure of substrates. The series of the azimuthal anchoring transitions on the cleaved surfaces of some crystals such as gypsum and mica studied in relation to the composition of the atmosphere in water and alcohol vapors above the nematic film [10, 11, 12, 13] represent such transitions.

Of particular interest are the transitions governed by the parameters that characterize the method employed to treat the surface for fabrication of aligning films. A variety of photo-induced
FIG. 3: Pretilt angle, $\theta$, (open squares) and azimuthal angle, $\phi$, (filled circles) measured as a function of the treatment (exposure) time in LC 5CB (a) and LC MJ961180 (b) at plasma-modified PI-F substrates. Treatment conditions are: $\alpha = 75^\circ$, $j=0.4 \, \mu A \, cm^{-2}$, $U=600 \, V$. Zenithal and azimuthal anchoring transitions are marked AT1 and AT2, respectively.

orientational surface transitions that have been observed in [14, 15, 16, 17, 18], are related to the photoalignment technique, in which an aligning layer is irradiated with actinic light (see [19, 20].
FIG. 4: Symmetric antiparallel cells filled with LC 5CB and viewed between a pair of crossed polarizers. The PI-F substrates are treated with the plasma beam over 40 (a), 1000 (b) and 15000 (c) seconds. The cells demonstrate three different types of alignment: (a) high tilted, (b) low tilted and (c) planar, respectively. Treatment conditions are: $\alpha = 75^\circ$, $j=0.4 \, \mu A \, cm^{-2}$, $U=600 \, V$.

Another approach suggested in [21, 22] is to align liquid crystals by obliquely evaporated thin films of silicon oxide SiO$_x$. Anchoring of nematics at the obliquely evaporated SiO$_x$ was studied as a function of the evaporation angle [23] and the film thickness [24]. It was found that an increase in either of these parameters may initiate the sequence of mixed and zenithal continuous surface transitions between three different anchorings: planar monostable, tilted bistable and tilted monostable.

In this paper we deal with anchoring transitions on the substrates treated with ion/plasma beams. Recently this kind of treatment has aroused considerable interest because it offers the greatest promise to replace the traditional rubbing technique in the new generation of liquid crystal displays (LCD) [25, 26, 27]. This processing avoids direct mechanical contact with aligning substrates thus minimizing the surface deterioration. It also provides highly uniform alignment on microscopic and macroscopic scale with a widely controlled pretilt angle and anchoring energy.

We apply this method to treat the films of hydrophobic polyimide and investigate the anchoring transitions at the plasma-modified substrates as a function of the irradiation dose.

The layout of the paper is as follows. Experimental procedure is described in Sec. II. We present our results in Sec. III and, in Sec. IV, discuss how they can be interpreted theoretically using the phenomenological model of two competing easy axes with the anchoring potential taken in the Sen-Sullivan form [28]. Concluding remarks are given in Sec. V.
FIG. 5: The photo of asymmetric cell viewed between parallel polarizer and analyzer. The reference substrate is the rubbed PI film, whereas the tested substrate is the PI-F layer treated with the plasma beam in the static regime ($\alpha = 75^\circ$, $j=7 \, \mu$A cm$^{-2}$, $U=600$ V, $\tau = 5$ min). The directions of rubbing and of the plasma beam are arranged to be parallel. The curve of Gaussian shape, depicted above the cell, schematically represents the distribution of the plasma beam intensity over the tested substrate. In the central part of the tested substrate irradiated at the maximum intensity (part A), NLC alignment corresponds to planar anchoring with the easy axis normal to the incidence plane (alignment of the 3rd type). In periphery part subjected to low irradiation doses (part B), the easy axis of planar anchoring lies in the plane of incidence (alignment of the 2nd type). These parts are separated by planar oriented strips (part C and part C’) of transient two-fold degenerated alignment.
FIG. 6: Contact angle as a function of the exposure time for droplets of LC 5CB (circles), LC MJ961180 (triangles) and distilled water (squares) spread upon plasma treated PI-F substrates. Treatment conditions are: $\alpha = 75^\circ$, $j=0.4 \, \mu\text{A cm}^{-2}$, $U=600 \, \text{V}$.

II. EXPERIMENTAL

A. Setup for plasma beam exposure

The irradiation set up was based on anode layer source (ALS) from the Hall family of sources working in the beam mode [29]. The general construction of this source is presented in Fig. II(a). A glow discharge is initiated in the crossed electric and magnetic fields within the discharge channel formed by inner and outer cathodes and anode. Because of high anode potential, the ions of plasma are pushed out of discharge area. They involve electrons so that the beam of accelerated plasma is formed. In contrast to the Kaufman source widely used for the ion beam alignment processing [25, 30], ALS does not contain any grids and hot elements (such as filaments and other secondary electron sources). The structure is thus simple and allows one to substantially increase reliability.

We used ALS with a race track shaped glow discharge so that the source generates two "sheets" of accelerated plasma (Fig. II(b)). As we have shown previously, this construction suits very well
for the alignment treatment of large-area substrates: in case the substrate is moved across the plasma “sheet”, the only limiting factor for the width of this substrate is the width of the “sheet”. Since ALS can be easily scaled up, this process can be employed in manufacturing of modern LCD fabs (1870 × 2200 mm² in the 7th generation fabs).

The feed gas was argon. The working pressure, \( P \), in our experiments was \( 1.4 \times 10^{-4} \) Torr that corresponded to the current density, \( j \), within the beam 0.4 \( \mu \text{A cm}^{-2} \). The low current was used to vary gradually the exposure dose given by the product of the current density and the exposure (treatment) time, \( \tau_{\text{exp}} \). The anode potential \( U \) determining the maximum energy of plasma \( \text{Ar}^+ \) ions was 600 V.

The geometry of exposure is shown in Fig. 1(c). The substrates were irradiated obliquely and the incidence angle of plasma beam, \( \alpha \), was about 75°. The substrate’s holder was mounted on the PC controlled translator in a vacuum chamber under the discharge channel. The substrates were treated in dynamic and static regime as well. Due to translations, different parts of the sample were passing through the plasma beam many times undergoing alignment treatment repeatedly (the cycling regime of treatment) so that alignment uniformity was substantially improved. The approximate distance between the plasma outlet and the substrate of size of 20 × 30 mm² was 8 cm.

B. Samples and their characterization

We used the fluorinated polyimide (PI-F) containing hydrophobic side chains as a polymer material. The polymer was dissolved in an appropriate solvent and spin coated on the glass plates over indium tin oxide (ITO) electrodes. The substrates were then baked at 180°C over 1.5 h to remove the solvent.

Two types of NLC cells were prepared: (1) identical substrates with the plasma treated PI-F films were assembled to form symmetric NLC cells with antiparallel director orientation; (2) the tested substrate with the plasma-modified PI-F layer and the reference substrate with the rubbed polyimide (PI) layer (9203 from JSR) were arranged so as to form asymmetric NLC cells where the rubbing direction was antiparallel to the direction of plasma irradiation. In both cases the cell thickness was kept at 20 \( \mu \text{m} \).

The symmetric cells were used to measure the pretilt angle of NLC by the crystal rotation method, whereas the asymmetric cells served to determine in-plane direction of the easy axis. The NLCs 5CB and MJ961180 (both from Merk) in an isotropic phase were injected into the cells by capillary action. The LC 5CB with positive dielectric anisotropy \( \Delta \epsilon \) is a well characterized nematic cyanobiphenyl used as a component of industrial TN LC mixtures. The mixture LC MJ961180 with \( \Delta \epsilon < 0 \) is developed for VA LCD. The quality of sample alignment was judged by observation in polarizing microscope and with a naked eye by placing a sample between crossed polarizers.

III. RESULTS

Referring to Fig. 2, orientation of the easy axis induced with the plasma beam processing is specified by the pretilt and azimuthal angles, \( \theta \) and \( \phi \). Fig. 3(a) and Fig. 3(b) show these angles measured as a function of the exposure time in the cells filled with LC 5CB and LC mixture MJ961180, respectively.
For the 5CB cells, the curves indicate a pronounced homeotropic-to-oblique anchoring transition that occurs at low irradiation dose. In this case, the easy axis initially directed along the normal to the substrate (the z axis) inclines continuously in the incidence plane of plasma beam (the x-z plane) towards the plasma beam direction (Fig. 2). When increasing the exposure time $\tau_{exp}$, the pretilt angle first decreases gradually from $90^\circ$ to $75^\circ$. The angle declines steeply to $\theta \approx 25^\circ$ at the critical point. Then it decays to the value about $2^\circ$ which weakly changes with the exposure time.

From dependence of the azimuthal angle on the irradiation time plotted in Fig. 3(a) it can be inferred that the above zenithal transition is followed by the azimuthal transition which takes place in the region of long-time treatment. In this case the result of drastic in-plane reorientation is that the easy axis lying initially in the plane of incidence is rotated through 90 degrees. Thus, we have the transition between two planar anchorings: $n_s = \hat{x}$ and $n_s = \hat{y}$ (see Fig. 2).

So, the results for LC 5CB representing nematic materials of positive dielectric anisotropy clearly indicate two anchoring transitions driven by the irradiation dose: zenithal and azimuthal. The sequence of transitions involves three different anchorings that can be described as three types of LC alignment: (1) high tilted structure (nearly homeotropic) with zero azimuthal angle (alignment of the 1st type) observed in the region of low irradiation doses before the zenithal transition; (2) low tilted structure (nearly planar) with zero azimuthal angle (alignment of the 2nd type) observed between the anchoring transitions; (3) planar anchoring with the easy axis normal to the incidence plane (alignment of the 3rd type) detected above the critical dose of the azimuthal transition. Fig. 4 shows that alignment of the above listed orientational structures is of excellent quality.

The curves presented in Fig. 3(b) were measured in the cells filled with LC mixture MJ961180, which is a nematic material with negative dielectric anisotropy, $\Delta \varepsilon < 0$. It can be seen that, as far as the zenithal transition is concerned, the results for this mixture are quite similar to those obtained for 5CB cells. Quantitatively, as opposed to LC 5CB, the pretilt angle above the critical point remains approximately constant varying in the range between $30^\circ$ and $15^\circ$. The most important difference is that the azimuthal anchoring transition with in-plane reorientation towards the normal of the incidence plane turned out to be suppressed.

The experimental data presented in Fig. 3(a) are insufficient to judge the character of the azimuthal transition unambiguously. In order to clarify behavior of anchoring near the critical point AT2, we used the substrates treated in the static regime of irradiation. Since the beam profile in the transverse direction has the Gaussian shape, the exposure dose appears to be continuously distributed over the substrate area.

In Fig. 5 the sample as viewed between parallel polarizers is presented for a typical asymmetric 5CB cell with the PI-F substrate processed in the static regime. It can be concluded that, in the central part (part A) of the cell exposed to the highest dose with the maximum intensity, anchoring is planar with the director normal to the incidence plane (alignment of the 3rd type). By contrast, periphery part (part B) of the cell is characterized by planar alignment of the 2nd type (the easy axis is parallel to the plane of incidence).

There are two transient strip-like regions between the parts of low and high irradiation doses shown in Fig. 5 as parts C and C’. These regions are divided into narrow domains. Owing to the mirror symmetry, domains oriented symmetrically with respect to the plane of incidence are equiprobable provided that the irradiation dose is fixed.

The “strips” are found to differ in width. The reason is that, for oblique irradiation, plasma fluxes impinging on the upper and lower parts of the substrate are necessarily different in intensity magnitude and distribution shape.
The upper strip is narrow and, as a consequence, the intensity is tightly distributed over the domain with the irradiation dose varying within narrow limits. So, producing a substrate aligned as this strip in the dynamic regime of irradiation can be rather difficult as it requires using a fine tuning procedure for irradiation doses.

IV. DISCUSSION

We can now take a closer look at the properties of the anchoring transitions described in the previous section. Our first remarks concern the character of the transitions.

In our experiments, the irradiation dose driven zenithal transition was found to take place in the plane of incidence for either sign of the NLC dielectric anisotropy. When increasing the dose, it occurs through homeotropic to (nearly) planar reorientation of the easy axis and manifests itself as a steep decline of the pretilt angle in the immediate vicinity of the critical dose (see the curves in Fig. 3). Since reorientation does not show any discontinuities, it may be concluded that the transition is second order. Transitions of this type were previously obtained at films modified with actinic light [15, 16] and cold plasma [31, 32, 33].

Anchoring is monostable planar in 5CB cells treated for so long that irradiation doses are well beyond the critical point of the homeotropic-to-planar transition. As it can be seen from Fig. 3(a), the curve for the azimuthal angle suggests that the zenithal transition, AT1, is followed by the azimuthal one, AT2.

This is the transition between two planar anchorings in which the easy axis is either parallel or normal to the incidence plane (the x-z plane). It is characterized by in-plane reorientation of the director which is rotated abruptly by 90 degrees near the critical point.

But the image of the asymmetric cell with one of the substrates treated in the static regime (see Fig. 5) clearly shows the presence of planar oriented domains where the director is tilted with respect to the plane of incidence. Such strips of transient alignment are typical of second order transitions where fluctuations create domains having close orientations [2, 13]. The transitions of similar character were generated at obliquely evaporated SiO_x films [23, 24] and at photoaligned layers [17].

The changes of anchoring directions are caused by surface modification of the aligning films induced by plasma beam treatment. By analogy with other plasma processes [31, 33], plasma beam may destroy side hydrophobic chains and increase the free energy of the aligning layer.

Gradual reduction of hydrophobic chains on the polymer surface was directly detected by XPS (x-ray photoelectron spectroscopy) method in [31]. We carried out the contact angle measurements that, according to [34], can be used to obtain indirect experimental evidence that the hydrophobic chains concentration diminishes with the exposure dose.

Fig. 6 presents the contact angle as a function of the exposure time measured at room temperature for three kinds of material: LC 5CB, LC MJ961180 and distilled water. It is clear that, for all compounds, the contact angle gradually declines with the exposure dose. It means that surface hydrophobicity monotonically decreases, whereas the surface free energy increases. In contrast to NLC alignment, the contact angles do not reveal any signs of critical behavior at the exposure doses corresponding to AT1 and AT2.

It is reasonable to assume that the critical concentration of hydrophobic chains should be reached to trigger the zenithal anchoring transition. This concentration is associated with the critical value of the surface free energy.

Mechanisms behind the azimuthal anchoring transition in 5CB cells are much less clear. Our assumption is that it is governed by the topography factor. Our previous results [26, 27] suggest
FIG. 7: Anchoring phase diagram in the $w_2$–$w_4$ plane for the non-polar potential (11) with $w_1 = 0$. Solid and dashed lines represent continuous and discontinuous transitions, respectively. The subscript B identifies the regions where the homeotropic and planar structures are separated by the energy barrier.

that the plasma beam may produce anisotropy of the surface relief. In addition, microgrooves generated by plasma beam from ALS were recently detected in [35]. With increasing the exposure dose topographical anisotropy changes direction from the projection of plasma beam on the substrate to the perpendicular direction.

This might explain the azimuthal transition from the 2nd type alignment to the 3rd type alignment for LC 5CB. Such anchoring transition seems to be possible only if the pretilt angle is sufficiently low, whereas the topography factor is of minor importance at high pretilt angles.

Interestingly, our results concerning the materials of different signs of the dielectric anisotropy bear close similarity to those reported in Ref. [36] where orientation of NLC with positive (E8) and negative (MLC 95-465) dielectric anisotropy on obliquely evaporated SiO$_2$ films in relation to the evaporation angle $\alpha$ was studied experimentally. For E8, alignment is planar (and perpendicular to the incidence plane) at sufficiently small evaporation angles ($\alpha < 60$ deg), whereas, for $\alpha > 60$ deg, the alignment is tilted in the incidence plane. By contrast, for $\Delta \varepsilon < 0$, the director remains in the plane of incidence and alignment approaches the homeotropic structure as the evaporation angle decreases. Different alignment behavior of the NLC materials is attributed to the Van der Waals (VdW) interaction and order electricity. The competing effects between the VdW and dipole-to-dipole interactions are considered in [37] to explain why vertical alignment of NLC with
negative dielectric anisotropy on both SiO$_x$ and PI can be improved by doping with a positive dielectric material such as 5CB.

In closing this section we discuss a simple phenomenological model that can be used to describe both the zenithal and azimuthal anchoring transitions qualitatively. Typically, such models are formulated in terms of the phenomenological expressions for the anchoring energy potential. So, the orientational structure in a uniformly aligned NLC cell is determined by the easy axis, which can be computed by minimizing the anchoring energy.

First we consider the most extensively studied case of isotropic flat substrates where the symmetry of the surface is characterized by its normal, $\hat{k} = \hat{z}$. So, the anchoring energy can be written as a function of the pretilt angle, $\theta$, in the following generalized form

$$W_P(c) = w_1 c + \frac{w_2}{2} c^2 + \frac{w_4}{4} c^4,$$

where $c \equiv n_z = \sin \theta$ is the $z$ component of the NLC director $\mathbf{n}$. At $w_1 = w_4 = 0$, the energy (1) simplifies giving the well known Papini-Papoular potential [38, 39].

The first term on the right hand side of Eq. (1) breaks equivalence between $\mathbf{n}$ and $-\mathbf{n}$ due to polar ordering effects in the interfacial layer [40, 41]. The model with this polarity breaking term

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**FIG. 8:** Anchoring phase diagram in the $w_2-w_4$ plane for the potential (1) in the presence of the polar term proportional to $w_1 \neq 0$. There is a metastable state separated from the equilibrium structure by the energy barrier in the regions labeled by subscript B. The special case where the metastable state corresponds to the homeotropic anchoring is marked by prime.
and $w_4 = 0$ (the Parson’s model) was previously employed to describe anchoring transitions on oxidized silane substrates [31, 32] and in freely suspended nematic films [8].

The expression for the anchoring energy with the positive fourth order coefficient $w_4$ coming from the quadrupole-quadrupole interactions and short-range anisotropic repulsive and attractive forces [42, 43, 44] was originally derived by Sen and Sullivan [28]. The non-polar azimuthally degenerated anchoring energy (1) with the quartic term ($w_1 = 0$ and $w_4 \neq 0$) was recently used to analyze temperature-driven transitions between the conical, planar and anticonical anchorings observed on a grafted polymer brush [45].

Anchoring properties of the generalized potential (1) can be conveniently characterized by the anchoring phase diagram in the $w_2$–$w_4$ parameter plane. We present the phase anchoring diagrams for two cases: (a) the non-polar model in the Sen-Sullivan form with $w_1 = 0$ (see Fig. 7) and (b) the generalized polar model with $w_1 \neq 0$ (see Fig. 8).

Referring to Fig. 7 when $w_1 = 0$ and the fourth order (quartic) coefficient $w_4$ is positive, the regions of homeotropic (N), tilted (T), and planar anchorings (P), are separated by two solid lines, $L_2$ and $w_2 = 0$, where the second order transitions take place. More generally, the symbol N (P) mark regions where the easy axis is normal (parallel) to the specified reference plane such as the plane of substrates or the incidence plane.

By contrast, if $w_4$ is negative, the transition between planar and homeotropic structures is discontinuous and does not involve tilted configurations. The structures are of the same energy at the points on the dashed line $L_1$.

In the coexistence regions, $N_B$ and $P_B$, enclosed by the dash-dotted lines, $L'_2$ and $w_2 = 0$, there
FIG. 10: Anchoring parameter $-w_2/w_4 \equiv \sin^2 \theta$ as a function of the treatment time measured in (a) 5CB and (b) MJ961180 cells. Experimental data are fitted using the formula (4) at $\gamma = 1.7 \text{ min}^{-1}$. The curves shown as solid lines are computed with the following dimensionless fitting parameters: (a) $\beta_1 \approx 2.78 \times 10^{-7}$ and $\beta_2 \approx 2.21 \times 10^{-3}$; (b) $\beta_1 \approx 1.52 \times 10^{-5}$ and $\beta_2 \approx 1.1 \times 10^{-4}$.

is an energy barrier between the homeotropic and planar anchorings. According to Ref. [45], the latter can be referred to as the anticonical anchoring. Note that the above results were previously reported for differently parameterized anchoring potentials in [42, 45].

In Fig. 8 we show the anchoring diagram for the less familiar case of the generalized model with non-vanishing polar coefficient $w_1$. The diagram does not depend on the sign of the polar coefficient because the potential (1) is invariant under the symmetry transformation: $c \rightarrow -c$ and $w_1 \rightarrow -w_1$.

For $w_4 > -|w_1|/2$, similar to the non-polar model, the solid line $L_2$ defines the second order transition between the homeotropic and tilted structures. Contrastingly, the second order transition between tilted and planar anchorings is suppressed as there are no regions of planar anchoring at $w_1 \neq 0$. From Fig. 8 this transition appears to be replaced with crossing the boundary curve $L_d$ between the regions $T_B$ and $T$ (the dash-dotted line $L_d$ above the point $O_2$). So, the anchoring in the region $T$ characterized by the tilted equilibrium structure and the absence of metastable states can be regarded as a counterpart of the planar structure (region $P$ in Fig. 7).

In Fig. 8 the line corresponding to the first order transition is depicted as the dashed curve $L_1$. The latter can be derived in the following parameterized form

$$L_1 = \begin{cases} 
  w_2 = |w_1| t^{-1}[1 + 2t^2(1 + t)^{-2}], \\
  w_4 = -2|w_1| t^{-1}(1 + t)^{-2}, 
\end{cases} \quad (2)$$

where the parameter $t$, $0 < t \leq 1$, defines the tilted configuration, $c_{th} = -t w_1/|w_1|$, which is energetically equivalent to the homeotropic structure: $W_p(c_{th}) = W_p(c_{hom})$ at $c_{hom} = -w_1/|w_1|$.

It is clear that both the polar and non-polar models predict the anchoring transitions that can
be either continuous or discontinuous depending on the value of the fourth order coefficient $w_4$. It
turned out that suppressing the planar anchoring is one of the most crucial effects induced by the
polar term proportional to $w_1$. This effect can also be seen from the curves for the pretilt angle
presented in Fig. 9 and computed as a function of the dimensionless parameter $\tilde{w}_2 \equiv w_2/w_4$ at the
fixed ratio $w_1$ and $w_4$.

The model (1) is azimuthally degenerated and thus cannot be applied directly to the transitions
observed in our experiments. The important point is that the incidence plane of irradiation with the
normal directed along the $y$ axis (see Fig. 2) has to be taken into account as an additional element
of the surface geometry.

By the same reasoning as for obliquely evaporated SiO$_x$ [46] we find, on symmetry grounds,
that the anchoring potential may additionally depend on $n^2_y$ and the model (1) can be extended as
follows

$$W = W_z(n_z) + W_y(n_y),$$

$$W_a(n_a) = \frac{w_a^{(z)}}{2} n^2_a + \frac{w_a^{(y)}}{4} n^4_a, \quad a \in \{z, y\}.$$

Note that the polar anchoring terms are neglected in the energy (3), so as not to rule out experi-
mentally observed planar anchoring and the structures tilted in the plane of incidence.

Generally, the $n_y$ dependent terms in the extended model arise from the reduction of symmetry
caused by anisotropy of the substrates. In particular, under certain conditions, the energy (3) can
be derived from the anchoring potential obtained in [47] for azo-dye photoaligned films.

The structure of the expression (3) bears close resemblance to the models formulated in terms of
two competing anchoring directions (easy axes). In the Rapini-Papoular approximation, such dual
axis models were previously employed to describe light-induced anchoring transitions in [16] and
to study competitive effects of photoalignment and microgrooves in [48]. Anchoring properties of
rubbed polyimide alignment layers were also studied by using the model supplemented with the
fourth order term in [9, 49].

For the model (3), the anchoring transitions can be geometrically described in terms of two
points: $w_z \equiv (w_z^{(z)}, w_z^{(y)})$ and $w_y \equiv (w_y^{(y)}, w_y^{(y)})$, so that the plane of reference is the substrate
and the incidence plane for $w_z$ and $w_y$, respectively. These points both lie in the $w_2$-$w_4$ plane and
dependence of the anchoring coefficients, $w_z$ and $w_y$, on the irradiation dose can be depicted as
two trajectories. The trajectories are illustrated in Fig. 7 under the simplifying assumption that the
fourth order coefficients, $w_z^{(y)}$ and $w_y^{(y)}$, are kept constant being independent of the treatment time.

The continuous homeotropic-to-planar transition occurs when the point $w_z$ moves from its
initial position in the region of homeotropic anchoring, $w_z^{(i)} \in \mathbb{N}$, to the final state of planar
anchoring with $w_z^{(f)} \in \mathbb{P}$ through the region of tilted structures, $T$. Reorientation of the director
takes place in the incidence ($x$-$z$) plane provided $w_y$ stay in the region $P$ during the zenithal
transition.

If $w_z$ is in the region $P$, anchoring is planar and the director orientation is determined by
the position of the point $w_y$. The azimuthal transition between planar structures aligned parallel
($n_y = 0$) and normal ($n^2_y = 1$) to the incidence plane can be depicted as the line connecting two
points: $w_y^{(i)} \in \mathbb{P}$ and $w_y^{(f)} \in \mathbb{N}$ (see Fig. 7).

Now we demonstrate that the zenithal anchoring transition can be described quantitatively. For
this purpose we take the assumption of exponential dependence of the anchoring coefficients, $w_z^{(z)}$
and $w_y^{(z)}$, on the exposure time.
On this assumption, the simplest analytical relation for the pretilt angle, $\theta$, can be written in the following form:

$$\sin^2 \theta = -\frac{w_2^{(z)}}{w_4^{(z)}} = \frac{1 + \beta_1 [\exp(\gamma \tau_{\text{exp}}) - 1]}{1 + \beta_2 [\exp(\gamma \tau_{\text{exp}}) - 1]},$$  \hspace{1cm} (4)

where $\tau_{\text{exp}}$ is the exposure (treatment) time. The results of phenomenological models for different photo-oriented films \[50, 51, 52\] and for aligning layers produced by collimated ion beams \[25\] both suggest that the exponential dependence is typical for the corresponding concentrations. So, in our case, it can be regarded as a reasonable approximation for the concentration of hydrophobic chains. Note that, strictly speaking, computing the pretilt angle requires a rather involved theoretical analysis which is beyond the scope of this paper.

The expression (4) can be used to fit the experimental data for 5CB and MJ961180 cells. The results of calculations are presented in Fig. 10. Clearly, they show that the difference between the materials is determined by the two fitting parameters: $\beta_1$ and $\beta_2$. In particular, for 5CB cells, the ratio $\beta_1/\beta_2$ appears to be negligibly small and, as a result, the fourth order coefficient $w_4^{(z)}$ is almost independent of the irradiation dose. But this is not the case for MJ961180 cells.

So, the experimentally observed transitions can be modeled by using the phenomenological anchoring potential (3). Note that, in the strict sense, our experiments do not imply the polar anchoring terms proportional to $w_1^{(z)}$ and $w_1^{(y)}$ are identically absent for all exposure doses. We can only conclude that the coefficient $w_1^{(z)}$ vanishes for 5CB cells at high irradiation doses in the region of planar anchorings, whereas the coefficient $w_1^{(y)}$ is zero during reorientation in the plane of incidence.

Interestingly, the model (3) can also be applied to the temperature induced anchoring transition on a SiO$_x$ surface \[46\]. It can be shown that, when $w_2^{(y)}$ varies from $-w_4^{(y)}$ to zero lying on the line

$$\frac{w_2^{(z)}}{w_4^{(z)}} + \sin^2 \alpha \left[ \frac{w_2^{(y)}}{w_4^{(y)}} + 1 \right] = 0,$$

anchoring changes from planar, $n = (0, 1, 0)$, to tilted, $n = (\cos \alpha, 0, \sin \alpha)$, with the director moving on the plane that forms the angle $\alpha$ with the film. Qualitatively, this reproduces behavior of the NLC director in the course of the mixed anchoring transitions on obliquely evaporated SiO$_x$ films.

V. CONCLUSIONS

We have observed experimentally the second order zenithal anchoring transitions in liquid crystals with positive and negative dielectric anisotropy oriented by hydrophobic substrates obliquely processed with a plasma beam. The transition is characterized by a pronounced decline of the pretilt angle with the exposure dose upon reaching the critical value of surface free energy related to the critical concentration of hydrophobic chains at the surface.

In LC 5CB with $\Delta \epsilon > 0$, the zenithal transition is followed by the azimuthal transition when the exposure dose increases further. It occurs through the in-plane reorientation of the easy axis which is rotated by a right angle. This reorientation is found to involve two-fold degenerated transient structures and, as a consequence, we arrive at the conclusion that the azimuthal transition is second order. This transition can be reasonably explained by experimentally detected change of topographical anisotropy.
We have formulated a simple phenomenological model where two competing anchoring directions appear as a result of additional plasma beam induced anisotropy of the treated substrate. In order to perform qualitative analysis of this model, the anchoring diagrams of the generalized potential were studied for both polar and non-polar cases. The result is that the experimentally observed anchoring transitions can be properly modeled using the non-polar dual axis model supplemented with the fourth order terms.

In conclusion, it should be noted that all types of LC alignment observed in our experiments such as high and low pretilt structures along with planar alignment are of considerable interest for applications. The technology related issues were briefly discussed in our previous publications [26, 27].

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