# **Light-induced gliding of the easy orientation axis of a dye-doped nematic liquid crystal**

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We studied the effect of light-induced gliding of the easy axis of dye-doped nematic liquid crystal on an aligning polymer surface. The observed drift of the easy axis is over tens of degrees and is caused by light-induced anisotropic adsorption and/or desorption of dye molecules on or from the aligning layer in the presence of light-induced bulk torque. We present a theoretical model that explains the experimental data in terms of the light-induced changes of the adsorbed dye molecules angular distribution due to their exchange with the dye molecules from the liquid crystal bulk.

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## **I. INTRODUCTION**

The traditional description of reorientation of the liquid crystal (LC) director in an electric or magnetic field suggests a fixed position of an easy orientation axis  $\vec{e}$  on aligning surfaces of a cell  $\lceil 1 \rceil$  $\lceil 1 \rceil$  $\lceil 1 \rceil$ . Field-induced deviation of the director from the direction  $\vec{e}$ , e.g., due to finite surface anchoring, may result in a gradual drift of the easy axis away from its initial position (so-called *gliding effect*) [[2–](#page-8-1)[10](#page-8-2)]. Adsorption and/or desorption of elongated LC molecules on or from the aligning surface and cooperative reorientation of polymer fragments and LC molecules are considered as possible mechanisms of the gliding. The adsorption and/or desorption mechanism was proposed by Vetter *et al.* [[2](#page-8-1)] for a description of the gliding effect on the polyvinyl-alcohol surface (to our knowledge, it was the first observation of the easy axis drift). According to Vetter, the drift of the easy axis is caused by the rotation of the symmetry axis of the distribution function of the long axes of adsorbed LC molecules under the influence of a reorientation torque. Since the first adsorbed molecules tend to align along the initial direction of the easy axis  $\vec{e}$ , mismatching between director and easy axis due to finite anchoring leads to adsorption of molecules along a new direction of the director,  $\vec{n}$ . As a consequence, the symmetry axis of the angular distribution function of the long axes of adsorbed molecules reorients, i.e., the easy axis changes its orientation. If the reorientation torque keeps acting, the drift of the easy axis continues until the torque disappears.

Later on, the gliding effect caused by adsorption and/or desorption processes was studied experimentally and theoretically in  $\lceil 4-8 \rceil$  $\lceil 4-8 \rceil$  $\lceil 4-8 \rceil$ . Recently, it was shown that the gliding due to adsorption and/or desorption processes might be accompanied by the cooperative reorientation of director and polymer fragments of the aligning layer  $[8,10]$  $[8,10]$  $[8,10]$  $[8,10]$ . Due to weak anchoring, the electric field reorients the director on the polymer surface, which, in turn, drags the flexible polymer fragments. As a result, the electric field reorients both LC molecules and flexible fragments resulting in a drift of an easy axis.

Until now the gliding effect was observed under the action of an electric or magnetic field, and spontaneous desorption and/or adsorption of LC molecules governed the easy axis drift. At the same time, as it was first shown in  $[11]$  $[11]$  $[11]$  and further in  $[12-18]$  $[12-18]$  $[12-18]$ , the light-induced anisotropic adsorption and/or desorption of elongated dye molecules of methyl red (MR) dye on a polymer surface produces an easy orientation axis on this surface. Therefore, one can suggest that the electromagnetic field of the light, on par with electric and magnetic fields of lower frequencies, also causes gliding of the easy axis.

To observe an efficient gliding effect, one needs to have the following.

*Layer of adsorbed anisotropic molecules on an aligning surface*. Existence of a layer of adsorbed MR molecules on a polymer aligning surface of fluorinated polyvinylcinnamate (PVCN-F) was suggested in  $[14]$  $[14]$  $[14]$  and was directly observed with x-ray measurements by Francescangeli *et al.* in [[17](#page-8-9)]. This layer is forming during tens of minutes after the cell filling. Its stationary thickness is about  $5 \text{ nm}$  (at dye concentration 0.5 wt  $\%$ ) that corresponds to 3–5 layers of MR molecules.

*Molecular exchange between an aligning surface and LC bulk due to adsorption and/or desorption.* Characteristics of spontaneous exchange by MR molecules between LC bulk and the surface are not known, although such an exchange should exist because of general physical reasons. Regarding molecular exchange between the bulk and the surface, it exists for sure due to the light-induced adsorption and/or desorption of dye molecules. This exchange determines the sta-tionary characteristics of light-induced anchoring [[14](#page-8-8)[–16](#page-8-10)]. As it was shown by Komitov *et al.* [[19](#page-8-11)], irradiation of MRdoped LC results in light-induced desorption of trans isomers of MR molecules and in light-induced adsorption of cis isomers of MR molecules from the LC bulk. The competition of these processes determines the angular distribution of the long axes of adsorbed MR molecules on the surface and final direction of the light-induced easy axis.

\*Corresponding author; fedoren@iop.kiev.ua *Finite (preferably weak) anchoring*. Finite anchoring pro-

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vides mismatching between  $\vec{n}$  and  $\vec{e}$ , which increases with a decrease of the anchoring energy. As measured in Ref.  $[15]$  $[15]$  $[15]$ , the value of the anchoring of the dark adsorbed layer is in fact weak, and a low value of the anchoring energy remains of the same order of magnitude after the light irradiation  $\text{(anchoring energy } W \sim 0.1 - 1 \ \mu\text{J/m}^2\text{)}.$ 

*A bulk torque that deviates the director away from the easy axis.* It is well known that doping of the nematic LC with a small concentration of dye may result in a colossal enhancement of the light-induced reorientation torque applied to the LC bulk  $\lceil 20,21 \rceil$  $\lceil 20,21 \rceil$  $\lceil 20,21 \rceil$  $\lceil 20,21 \rceil$ . As it was shown in  $\lceil 22,23 \rceil$  $\lceil 22,23 \rceil$  $\lceil 22,23 \rceil$  $\lceil 22,23 \rceil$ , the addition of MR to the nematic LC pentyl-cianobiphenyl (5CB) results in the sliding of the director on the tested polymer surface, and light-induced torque causes a deviation from the easy axis by several degrees. This value is typical for observation of the gliding effect in the magnetic field  $\left[7,8\right]$  $\left[7,8\right]$  $\left[7,8\right]$  $\left[7,8\right]$ 

Thus, all necessary conditions for the easy axis drift are valid in the case of light irradiation. This paper reports the observations and study of light-induced gliding of an easy axis of dye-doped nematic liquid crystal on an aligning polymer surface. It should be noted that easy axis gliding is accompanied by the reorientation of the director on an aligning surface and the last effect has been already reported in [ $12,15,24$  $12,15,24$  $12,15,24$ ]. At the same time, the light-induced director reorientation was explained in terms of the production of two mutually perpendicular easy axes in those papers. It was suggested that the first easy axis was perpendicular to the light polarization and was caused by polarization-dependent lightinduced desorption of dye molecules. The second easy axis was parallel to the light polarization and was due to lightinduced adsorption of dye molecules. Both easy axes were supposed to be fixed in that model. In the present paper we show that irradiation of the cell in the nematic phase causes continuous light-induced drift of the only one easy axis. The observed drift of the easy axis is over ten degrees and is caused by the light-induced anisotropic adsorption and/or desorption of dye molecules on or from the aligning layer in the presence of the light-induced bulk torque. We present a theoretical model that explains the experimental results in the terms of the light-induced changes of the angular distribution of the adsorbed dye molecules due to their exchange with the dye molecules from the liquid crystal bulk.

## **II. EXPERIMENTAL DETAILS AND RESULTS**

The light-induced drift of the easy orientation axis was studied in nematic LC pentyl-cyanobiphenyl 5CB from EMD Chemicals Inc. doped with the azo-dye MR from Aldrich. To decrease interaction between MR molecules, a low weight concentration of MR *c*= 0.5*%* was chosen. At room temperature most MR molecules are in a trans form and absorb light in the blue-green region of spectra  $[25]$  $[25]$  $[25]$ . Light absorption results in effective trans-cis isomerization of MR molecules  $[25,26]$  $[25,26]$  $[25,26]$  $[25,26]$  which, in turn, leads to the light-induced adsorption of cis isomers on a polymer surface  $\lceil 17-19 \rceil$  $\lceil 17-19 \rceil$  $\lceil 17-19 \rceil$ .

We used a combined LC cell consisting of reference and tested substrates. Cell gap was determined by 30  $\mu$ m polymer spacers. The reference substrate was covered with a

<span id="page-1-0"></span>

FIG. 1. Experimental setup. 1: Diode-pump solid state laser; 2: polarizer set 45° angle with the rubbing direction of the LC cell reference substrate; 3: lens  $(f_1=0.7 \text{ m})$ ; 4: LC cell; 5: lens  $(f_2)$  $(2-0.05)$  m); 6: polarizer parallel to the rubbing direction; 7: He-Ne laser; 8: image transferring lens; 9: analyzer: 10: CCD matrix; and 11: computer.

rubbed polyimide layer that provided strong unidirectional planar alignment of the LC director with a small pretilt  $(\sim 1.5^{\circ})$ . The tested substrate was covered with a layer of PVCN-F that provided degenerated planar alignment of 5CB. To prevent dissolution of the polymer by LC, PVCN-F film was irradiated during 40 s with a nonpolarized UV beam  $(intensity I<sub>UV</sub> \approx 5 mW/cm<sup>2</sup>)$  using a Hg lamp. The cell was filled with LC at a temperature above the clearing point and slowly cooled down to the room temperature. During the cooling, the cell was put on a metal brick, so that the reference substrate was at the bottom. As a result, the cell was cooled to the nematic phase starting from a reference substrate. This procedure resulted in a satisfactory uniform planar alignment of LC over the cell parallel to the rubbing direction of the reference surface  $\vec{e}_{\text{ref}}$ .

The basic experimental setup is presented in Fig. [1.](#page-1-0) The combined cells were irradiated from the side of the tested surface by a linearly polarized pump beam from the diodepumped solid state laser  $(\lambda = 0.473 \mu m, P_{pump} \le 5 mW)$ . The pump beam was focused with the lens, and its half-width in the plane of the LC was  $d \approx 0.4$  mm. The polarization direction of the pump beam  $E_{\text{pump}}$  was at the angle  $\vartheta_0 = 45^\circ$ ⇁ to the initial direction of the director  $\vec{n}_0 || \vec{n}_{\text{ref}} || \vec{n}_{\text{test}}$  in the cell. The linearly polarized probe beam from the He-Ne laser  $(\lambda)$  $= 0.632 \mu m$ ,  $P_{\text{probe}} \le 1 \text{ mW}$  tested the irradiated spot from the side of the reference surface. The diameter of the probe beam at the plane of the LC was much larger than the diameter of the irradiated spot, and the probe intensity was assumed constant over the irradiated spot. The polarization of the probe beam,  $\vec{E}_{\text{test}}$ , was parallel to  $\vec{n}_{\text{ref}}$ .

It is well known  $[11,12,15]$  $[11,12,15]$  $[11,12,15]$  $[11,12,15]$  $[11,12,15]$  that in the geometry considered, light-induced adsorption and/or desorption of MR molecules results in the formation of an easy orientation axis  $\vec{e}_{\text{test}}$ , which is not parallel to the initial direction  $\vec{n}_0 || \vec{n}_{\text{ref}}$ . This results in the twist deformation in the cell. This deformation is smooth, and the Mauguin regime for the propagation of the probe is certainly realized in the cell  $[11,14]$  $[11,14]$  $[11,14]$  $[11,14]$ . Therefore, the polarization  $\vec{E}_{\text{probe}}$  followed the director over the cell, and on the tested surface  $\vec{E}_{\text{probe}}$  is parallel to the director  $\vec{n}_{\text{test}}$ . Thus, by recording the changes of the intensity of the probe beam behind the analyzer one can follow the changes of the position of the director on the tested surface. To do that, the enlarged image of irradiated area was registered by the charge coupled device (CCD) matrix and analyzed with a computer. The sign of the director rotation was determined by the analyzer rotation until the dark state, at which the transmission axis of the analyzer was perpendicular to  $\vec{n}_{test}$  at the tested surface.

Cooling the cells from the isotropic phase to the room temperature leads to the formation of an anisotropic layer of adsorbed LC and MR molecules. These "dark" adsorbed molecules serve as an aligning layer for the LC bulk  $[7,15]$  $[7,15]$  $[7,15]$  $[7,15]$ . Our preparation procedure ensures the starting of the nematic phase formation from the reference substrate. The front of the nematic phase propagates toward the tested surface, and the MR and LC molecules are preferably oriented along the rubbing direction on the isotropic-nematic interface. Therefore, the maximum of the angular distribution of the dark adsorbed molecules on the tested surface and easy axis  $\vec{e}^{\text{dark}}_{\text{test}}$ emerges parallel to the rubbing direction on the reference surface.

To estimate the anchoring energy of the LC on the adsorbed layer we slowly rotated the tested substrate in the azimuthal plane by the angle  $\psi_0$ =45° that corresponded to the turn of the easy axis  $\vec{e}_{\text{test}}^{\text{dark}}$  by the same angle. The rotation time was about 1 min which was much shorter than the characteristic time of possible gliding of the easy axis due to the elastic torque (tens of hours and days)  $[27]$  $[27]$  $[27]$ . Observation in a polarizing microscope showed the formation of the twist structure in the cell with the twist angle  $\varphi_{\text{test}} = \angle \vec{n}_{\text{test}} \vec{e}_{\text{ref}}$  that varied from cell to cell in the range of 25°−35°. The torque balance on the tested substrate is as in  $\lceil 11 \rceil$  $\lceil 11 \rceil$  $\lceil 11 \rceil$ .

$$
\frac{\sin 2(\phi_{\text{test}} - \varphi_{\text{test}})}{\varphi_{\text{test}}} = \frac{2K_{22}}{W_{\text{test},0}L}.
$$
 (1)

<span id="page-2-0"></span>Here  $\phi_{\text{test}} = \angle (\vec{e}_{\text{test}}, \vec{e}_{\text{ref}})$  is the angle of the easy axis direction (in our case  $\phi_{\text{test}} = \psi_0 = 45^\circ$ ),  $K_{22}$  is a Frank constant for twist deformation,  $W_{\text{test},0}$  is an anchoring energy of the LC in the Rapini-Papoular approximation, and  $W_{\text{test}}$  $=\frac{1}{2}W_{\text{test},0} \cos^2(\varphi_{\text{test}}-\varphi_{\text{test}})$  is the surface potential. For our parameters  $L = 30$   $\mu$ m and  $K_{22} = 3.6 \times 10^{-12}$  N, the expression ([1](#page-2-0)) gives the value of  $W_{\text{test}}^{\text{dark}} \approx 0.3 - 0.8$   $\mu$ J/m<sup>2</sup>. This value is close to the one obtained earlier in  $\lceil 15 \rceil$  $\lceil 15 \rceil$  $\lceil 15 \rceil$  and is considered as intermediate anchoring (anchoring parameter  $K_{22} / W_{\text{test}}L$  $\approx$  1). In this case deviation of the director on the tested surface and drift of the easy axis in the external field may be essential  $\left[7,8\right]$  $\left[7,8\right]$  $\left[7,8\right]$  $\left[7,8\right]$ .

Irradiation of the cell with the pump beam resulted in the reorientation of the LC director on the tested surface from its initial position parallel to  $\vec{n}_{ref}$ . The typical dynamics of the reorientation angle  $\varphi_{\text{test}}^{h\nu}$  is presented in Fig. [2.](#page-2-1) If the pump beam was repeatedly interrupted during the light exposure, the director relaxed to a stationary angle  $\varphi_{\text{test}}$ , which increased with time (Fig.  $3$ ). One can see that the director reorients away from the polarization vector  $\vec{E}_{\text{pump}}$  first ( $\varphi_{\text{test}}^{hv}$  $(0.06)$  and toward  $\vec{E}_{\text{pump}}$  ( $\varphi_{\text{test}}^{h\nu}$  > 0) later with exposure time *t*exp. The important point is that the switching off of the pump beam after achieving the quasistationary reorientation angle

<span id="page-2-1"></span>

FIG. 2. Dependence of the twist angle  $\varphi_{\text{test}}^{h\nu}$  on exposure time  $t_{\text{exp}}$ . Light intensity  $I_{\text{pump}} = 1.6 \ \text{W/cm}^2$ . The arrows mark light irradiation switching on and off moments.

 $\varphi_{\text{test}}^{hv} \approx 29^{\circ}$  did not lead to the recovery of the initial planar alignment; the director relaxed to the angle  $\varphi_{\text{test}} \approx 32^{\circ}$  (see Fig. [2](#page-2-1)). This value did not change with time (at least for a year) and with temperature (at least up to  $70^{\circ}$ C). The final deviation of the director from its initial position increases both with the light intensity and the irradiation dose.

This residual twist deformation in the irradiated area clearly manifests that easy axis changes its direction. Easy axis might reach its final position in two different ways:

(1) by continuous light-induced drift of the easy axis from its initial position  $\vec{e}_{\text{test}}^{\text{dark}}$ ;

(2) by the formation of a new light-induced easy axis in the direction of the final position and a gradual increase of the anchoring energy associated with this axis.

To determine which scenario is realized, we carried out the experiment that allowed a determination of the actual dependence of the light-induced easy axis on time. We irradiated several spots in the combined cell with different exposure times *t*exp. Then the tested surface was rotated by the angle  $\psi$  in the azimuthal plane between crossed polarizers until the light extinction was achieved. At this position of the substrates the easy axis  $\vec{e}_{\text{test}}$  was parallel to  $\vec{e}_{\text{ref}}$ ; i.e., the angle  $\psi$  coincided with the orientation of the easy axis on the tested surface  $\phi_{\text{test}}$ . The obtained exposure dependence of the easy axis position on time,  $\phi_{\text{test}}(t_{\text{exp}})$ , is presented in Fig. [4.](#page-3-0) This

<span id="page-2-2"></span>

FIG. 3. Dynamics of the director reorientation at multiple interruptions of the pump. The dashed curve corresponds to the director position when the pump is off; solid curve: director position when the pump is on. Light intensity  $I_{\text{pump}} = 1.6 \text{ W/cm}^2$ ,  $t_{\text{exp}}$ : exposure time.

<span id="page-3-0"></span>

FIG. 4. (Color online) Exposure time  $(t_{exp})$  dependence of theoretical (lines) and experimental (scattered curves) data of (a) the light-induced easy axis  $\phi_{\text{test}}$  measured by the rotation of the tested substrate; (b) the director  $\varphi_{\text{test}}$  while the pump is off; and (c) the director  $\varphi_{\text{test}}^{h\nu}$  under light action. *I*<sub>pump</sub>= 1.6 W/cm<sup>2</sup>.

dependence evidently demonstrates the light-induced gliding of the easy axis with time. The dependencies of director orientations  $\varphi_{\text{test}}(t_{\text{exp}})$  and  $\varphi_{\text{test}}^{h\nu}(t_{\text{exp}})$  on exposure time derived from Fig. [3](#page-2-2) are also presented in Fig. [4.](#page-3-0)

The difference between the angles of the easy axis  $\phi_{\text{test}}$ and the director  $\varphi_{\text{test}}$  (see Fig. [4](#page-3-0)) allowed for the estimation of exposure dependence of the anchoring energy of LC  $W_{\text{test}}$ on the tested surface, using Eq.  $(1)$  $(1)$  $(1)$  (Fig. [5](#page-3-1)). The measured values of the anchoring energy are of the order 0.1  $\mu$ J/m<sup>2</sup> and correspond to a weak anchoring of the LC on the aligning surface. One can see that irradiation results in a slow increase of the anchoring energy with the exposure time. One may also assume a slow decrease of  $W_{\text{test},0}$  at the beginning of exposure, but a large experimental error does not allow one to be sure.

The dependences of the easy axis direction  $\phi_{\text{test}}(t_{\text{exp}})$  and the quasistationary position of the director  $\varphi_{\text{test}}(t_{\text{exp}})$  are qualitatively different from the dynamics of the director re-orientation under irradiation (Fig. [4](#page-3-0)). A visible drift of the easy axis starts only after certain exposure time, and the easy axis always reorients toward the polarization vector  $E_{\text{pump}}$ . → The dependence  $\varphi_{\text{test}}(t_{\text{exp}})$  of the quasistationary position of the director is qualitatively the same and the angle  $\varphi_{\text{test}}$  is always less than  $\phi_{\text{test}}$ . By contrast, the director starts reorienting immediately after the light switching on and the sign of the director turn changes with an increase of the exposure.

<span id="page-3-1"></span>

FIG. 5. Experimental dependence (scattered curve) of the anchoring energy  $W_{\text{test},0}$  on the exposure time  $t_{\text{exp}}$  and the theoretical approximation (solid line).  $I_{\text{pump}} = 1.6 \text{ W/cm}^2$ .

Exposure time, at which the sign of the director turn is changed decreases with a light intensity increase. The value  $\varphi_{\text{test}}^{hv}$  always differs from the value  $\varphi_{\text{test}}$  which points at the presence of a light-induced torque in the system.

The presence of the light-induced torque is clearly seen from Fig. [3.](#page-2-2) The switching of the light on, initiates the fast director turn outward  $E_{\text{pump}}$  (characteristic time,  $\tau_{\text{fast}}$ ⇁  $\sim 10^{-3}$  s) that does not cause any drift of the easy axis; the director relaxes after switching off the pump with the same characteristic time. Such a fast director reorientation on the tested surface away from  $\vec{E}_{\text{pump}}$  due to the light-induced *bulk torque* in the dye-doped LC was previously observed in [[22](#page-8-15)], and it was associated with sliding of the director over the surface with weak anchoring. Another cause of the fast director reorientation might be light-induced *surface torque* due to some quick changes of the anchoring on the tested surface, e.g., due to surface-induced nonlinear effect (SINE) [[28](#page-8-22)]. To clarify the source of the reversible fast reorientation, we compared the response of the director to the pump irradiation in two combined cells. One of them was filled with LC doped with MR, i.e., this cell contained both MR molecules in the bulk and in the "dark-adsorbed" MR layer on the tested surface. The second cell was initially filled with MR-doped LC and refilled with clear LC in several hours, i.e., after the dark-adsorbed layer was formed. Unlike the first cell, in the second one we did not observe any fast director reorientation, but only an appearance of nonreversible director reorientation away from  $E_{\text{pump}}$  at long expo-⇁ sures. As it was shown in  $[16,30]$  $[16,30]$  $[16,30]$  $[16,30]$ , this type of light-induced reorientation is caused by the light-induced desorption of MR molecules from the dark-adsorbed layer. Thus, one can conclude that the fast component of the director reorientation away from  $E_{\text{pump}}$  originates from the light-induced bulk → torque. This torque and the fast component of the director reorientation retained during all the gliding process and its contribution to the director reorientation is proportional to the light intensity.

Repeated interruption of the pump beam during the light exposure showed that besides the fast component of the director reorientation, a slow component appears with time. It points out the presence of active light-induced surface processes during the director reorientation. The slow component of the director reorientation  $(\tau_{slow} \sim 10^{-1} - 1 \text{ s})$  appears already at the early exposures when the director goes away from  $E_{\text{pump}}$ . For the exposure times, at which the director → starts turning toward  $E_{\text{pump}}$  the characteristic times of the → slow reorientation component strongly increase  $(\tau_{\text{slow}} \sim 10^2$  $-10^3$  s). Since the slow component of the director reorientation is much longer than the characteristic times of the director reorientation in the bulk, one can unambiguously conclude that the slow component is caused by light-induced surface processes.

Thus, the described experiments clearly show that irradiation of the azo-doped liquid crystal in a combined cell with polarized light causes effective drift of the easy axis on the aligning tested surface in the presence of the light-induced bulk torque. The initial anchoring energy of the LC on the tested surface is weak and it slowly increases with the exposure time.

<span id="page-4-0"></span>

FIG. 6. Geometry of the experiment for theoretical calculations.

## **III. THEORETICAL MODEL**

In this chapter we consider the effect of light-induced gliding and describe experimental data leaning upon the results of gliding effect studies in electric and magnetic fields  $[4–8]$  $[4–8]$  $[4–8]$  $[4–8]$  and our previous investigations of a light-induced anchoring  $[14–16]$  $[14–16]$  $[14–16]$  $[14–16]$ . As it was shown in the Introduction, the drift of the easy orientation axis can be described by modification of the angular distribution function of the long axes of adsorbed MR molecules due to their light-induced adsorption and/or desorption on or from the aligning layer in the presence of the light-induced bulk director torque. To describe the light-induced gliding theoretically, we first consider the formation of the "dark" easy axis on the aligning surface due to spontaneous adsorption of MR molecules. Second, we derive the expression for the light-induced bulk torque that deviates the director from its initial position. Third, we consider rotation and modification of the angular distribution function of the adsorbed MR molecules imposed by this torque via light-induced adsorption and/or desorption. Finally, we connect the light-induced changes of the angular distribution function with the direction of the easy axis and the value of the anchoring energy and compare the theoretical prediction with the experimental results. Referring to Fig. [6,](#page-4-0) we regard a cell filled with liquid crystal, where the axis *Oz* is normal to the substrates and the axis *Oy* is parallel to *E* . We consider a planar alignment of LC. In our case the → light-induced torque causes reorientation of the director in the plane of the substrates. Therefore, the director  $\vec{n}$  and the angle  $\varphi$  only depend on the *z* coordinate:  $\vec{n} = \vec{n}(z, t)$ ,  $\varphi$  $=\varphi(z,t)$ , and  $\varphi_{\text{test}}(t) = \varphi(0,t)$ .

#### **A. Formation of the "dark" easy axis**

The dark easy orientation axis on the tested surface  $\vec{e}^{\text{dark}}_{\text{test}}$ appears due to the spontaneous adsorption of trans isomers of MR molecules from the LC bulk. The order parameter of the long axes of the MR molecules in LC is close to the order parameter of the LC molecules,  $S$  [[15](#page-8-12)]. Therefore, the angular distribution function of the MR molecules is close to the distribution function of the LC molecules, which is described in the Maier-Saupe theory as  $[1]$  $[1]$  $[1]$ 

$$
\Phi_V(\Omega_V, \varphi_{\text{test}}) = \frac{1}{N_{\text{norm}}} \exp[\beta S P_2(\vec{n}(\Omega_V), \vec{d})],\tag{2}
$$

<span id="page-4-1"></span>where  $\Omega_V = \Omega_V(\theta_V, \varphi_V)$  is a spatial angle in the spherical reference frame,  $\theta_V$  is a polar angle between a long axis of a molecule and the normal to the substrate,  $\varphi_V$  is an azimuthal angle between molecules and  $Ox$ ,  $N_{\text{norm}}$  is a normalization factor,  $P_2$  is the Legendre polynomial,  $\beta = \alpha / k_B T$ , and  $\alpha$  is a constant. Here and later all distribution functions are normalized.

After cooling of the cell, the director nearby the tested surface is parallel to the director on the reference surface  $\vec{n}_{\text{ref}}$ . Therefore, the maximum of the angular distribution of the long axes of adsorbed trans-MR molecules  $\Phi_{\text{test}}(\varphi_{\text{test}}^{\text{mol}})$  is parallel to  $\vec{n}_{ref}$ . In our case the pretilt angle of the LC on the adsorbed layer of MR molecules is nearly zero. Therefore, similarly to  $[5,6]$  $[5,6]$  $[5,6]$  $[5,6]$ , we presume that adsorbed MR molecules lie in the surface plane and the probability of adsorption of a molecule at the angle  $\varphi_{\text{test}}^{\text{surf}}$  is proportional to the number of MR molecules oriented in LC at different angles  $\theta_V$  with the same angle  $\varphi_{\text{test}}^{\text{surf}}$ .

$$
\Phi_{\text{test}}(\varphi_{\text{test}}^{\text{mol}}) = \Phi_{V\perp}(\varphi_{\text{test}}^{\text{mol}}) = \int_0^\pi \Phi_V(\Omega_V, \varphi_{\text{test}}) \sin \theta_V d\theta_V,
$$
\n(3)

where  $\varphi_{\text{test}}^{\text{mol}} = \varphi_V$ .

The interaction potential between a LC molecule in a bulk nearby of the surface and a MR molecule on the surface can be written as  $w_{1,2} \sim (\vec{e}_1, \vec{e}_2)^2$ , where  $\vec{e}_1$  and  $\vec{e}_2$  are the long axes of the adsorbed MR molecule and the LC molecule correspondingly.

$$
w_{1,2}(\Omega_V, \varphi_{\text{test}}^{\text{mol}}) = \frac{1}{2} w_0 \cos^2(\varphi_V - \varphi_{\text{test}}^{\text{mol}}) \sin^2 \theta_V.
$$

Here  $w_0$  is a molecular anchoring coefficient that corresponds to the amplitude of the interaction potential between the LC molecule and the adsorbed MR molecule.

LC molecules in the bulk are not oriented exactly along one direction [as seen from Eq.  $(2)$  $(2)$  $(2)$ ]. Therefore, to obtain the expression for the interaction of the adsorbed MR molecule with an ensemble of LC molecules  $w_{1,\text{LC}}$  we should multiply the energy  $w_{1,2}$  by the distribution function of the long axes of the LC molecules  $\Phi_V(\Omega_V, \varphi_{\text{test}})$  and integrate it over  $\Omega_V$ 

$$
w_{1,\text{LC}}(\varphi_{\text{test}}, \varphi_{\text{test}}^{\text{mol}}) = \frac{1}{2} w_{\text{test}} \int_{-\pi/2}^{\pi/2} d\varphi_V \cos^2(\varphi_V - \varphi_{\text{test}}^{\text{mol}})
$$

$$
\times \int_0^{\pi} \Phi_V(\theta_V, \varphi_V, \varphi_{\text{test}}) \sin^3 \theta_V d\theta_V.
$$

Here  $w_{\text{test}}$  is a molecular anchoring coefficient that corresponds to the amplitude of interaction potential between an ensemble of LC molecules near the surface and the adsorbed MR molecule.

Finally, to get an expression for the macroscopic anchoring energy of the LC with a layer of adsorbed MR molecules,  $W_{\text{test}}$ , we should multiply the value  $w_{1,\text{LC}}$  by the distribution function of the long axes of adsorbed MR molecules  $\Phi_{\text{test}}(\varphi_{\text{test}}^{\text{mol}})$  and integrate it over  $\varphi_{\text{test}}^{\text{mol}}$ 

<span id="page-5-0"></span>
$$
W_{\text{test}} = \frac{1}{2} w_{\text{test}} N_{\text{test}} \int_{-\pi/2}^{\pi/2} d\varphi_V \int_{-\pi/2}^{\pi/2} d\varphi_{\text{test}}^{\text{mol}} \Phi_{\text{test}}(\varphi_{\text{test}}^{\text{mol}})
$$

$$
\times \cos^2(\varphi_V - \varphi_{\text{test}}^{\text{mol}}) \int_0^{\pi} \Phi_V(\theta_V, \varphi_V, \varphi_{\text{test}}) \sin^3 \theta_V d\theta_V.
$$
(4)

Here  $N_{\text{test}}$  is the surface concentration of the dye molecules.

The angular distribution function of the MR molecules in the dark adsorbed layer is symmetrical, e.g.,  $\Phi_{\text{test}}(\varphi)$  $=\Phi_{\text{test}}(-\varphi)$ , where  $\varphi$  is counted from the direction of the easy axis. In this case the anchoring potential  $(4)$  $(4)$  $(4)$  reduces to the classical expression for the Rapini-Popular potential  $\lceil 1 \rceil$  $\lceil 1 \rceil$  $\lceil 1 \rceil$  as follows:

$$
W_{\text{test}} = \frac{1}{2} W_{\text{test},0} \cos^2 \varphi_{\text{test}},
$$
 (5)

<span id="page-5-4"></span>where the anchoring energy

$$
W_{\text{test},0} = w_{\text{test}} N_{\text{test}} \xi,\tag{6}
$$

and

$$
\xi = \int_{-\pi/2}^{\pi/2} \cos(2\varphi_V) d\varphi_V \int_0^{\pi} \Phi_V(\Omega_V) \sin^3 \theta_V d\theta_V
$$

$$
\times \int_{-\pi/2}^{\pi/2} \Phi_{\text{test}}(\varphi_S) \cos(2\varphi_S) d\varphi_S. \tag{7}
$$

The parameter  $\xi$  characterizes the anisotropy of the symmetrical angular distribution function of adsorbed molecules. Since the bulk distribution function  $\Phi_V(\Omega_V)$  is determined by the parameter  $S$  [see Eq.  $(2)$  $(2)$  $(2)$ ], there is a one to one correspondence between the parameters  $\xi$  and *S*. For instance, for the value of  $S = 0.32$  at room temperature,  $\xi \approx 0.15$  |[29](#page-8-26)|.

#### **B. Light-induced deviation of the director near the surface**

Light-induced bulk torque causes the initial deviation of the director from the easy axis and induces its consequent gliding. To derive the expression for the light-induced bulk torque, we will follow Janossy's model of interaction of light with the dye-doped LC  $[20,31]$  $[20,31]$  $[20,31]$  $[20,31]$  and use the results of theoretical studies of propagation of polarized light through the dye-doped LC of Andrienko et al. [[29](#page-8-26)]. According to Janossy, energy of interaction  $f^{h\nu}$  between the MR molecules and the polarized light field  $\vec{E}_{\text{pump}}$  is proportional to  $(\vec{n}, \vec{E})^2$ . The pump beam being linearly polarized at the entrance to the LC becomes elliptically polarized after propagating through the cell. Its ellipticity  $\varepsilon$  is a periodical function with the pitch of  $\lambda / (n_e - n_o)$ . As a result, the energy  $f^{h\nu}$  is proportional to  $I_{\parallel} \cos^2 \theta + I_{\perp} \sin^2 \theta$ , where  $I_{\parallel} = I_{\text{pump}} \cos^2 \varepsilon$  and  $I_{\perp}$  $=I_{\text{pump}} \sin^2 \varepsilon$ , and  $I_{\parallel}$  and  $I_{\perp}$  are intensities of components  $\vec{E}_{\parallel}$ and  $\vec{E}_{\perp}$  along and perpendicular to the polarization ellipse axes.  $\vartheta(z)$  is the angle between  $\vec{n}(z)$  and the long principal axis of the light polarization ellipse.

The surface density of the LC in a field of the pump beam takes the form

$$
F^{hv} = \int_0^L k \left[ \frac{\cos^2 \vartheta(z) \cos^2 \varepsilon(z)}{+\sin^2 \vartheta(z) \sin^2 \varepsilon(z)} \right] I_{\text{pump}}(z) dz, \tag{8}
$$

<span id="page-5-1"></span>where *k* is a constant. The values  $\varepsilon = \varepsilon(z)$  and  $\vartheta = \vartheta(z)$ change periodically along the *z* axis  $[29]$  $[29]$  $[29]$ , and the intensity *I*pump exponentially decreases while the pump beam propagates through the cell containing the absorbing dye. In this case the influence of the optical field on the director in the whole cell can be replaced by the effective impact just in a thin layer near the input surface  $l_{\text{eff}} \ll L$  [[29](#page-8-26)]. In this layer both director and intensity of the pump beam can be assumed constant and Eq.  $(8)$  $(8)$  $(8)$  is reduced to simple form as follows:

$$
F^{hv} = k \cos^2 \theta H_{\text{eff}}.
$$
 (9)

Total surface density of the free energy of the LC in the cell reads

<span id="page-5-2"></span>
$$
z \in [0, L - l_{\text{eff}}]:
$$
  
\n
$$
F_1(t) = \frac{1}{2} \int_0^{L - l_{\text{eff}}} dz \left\{ K_{22} \left[ \frac{\partial \varphi(z, t)}{\partial z} \right]^2 \right\} - W_{\text{test}},
$$
  
\n
$$
z \in [L - l_{\text{eff}}, L]: \quad F_2(t) = F^{hv} - W_{\text{ref}}, \quad (10)
$$

where  $K_{22}$  is the Frank's elastic constant. In the strong anchoring approximation on the reference surface minimization of the functional  $(10)$  $(10)$  $(10)$  leads to the following director distribution in the cell  $\vec{n}(z)$ :

$$
z \in [0, L - l_{\text{eff}}]: \quad \varphi(z) = \frac{\varphi_{\text{test}}}{L - l_{\text{eff}}} z \approx \frac{\varphi_{\text{test}}}{L} z,
$$

$$
z \in [L - l_{\text{eff}}, L]: \quad \varphi(z) = \varphi_{\text{test}}.
$$
 (11)

The twist of the director on the tested surface  $\varphi_{\text{test}}(L)$  is determined by the equilibrium between the elastic torque  $M_v = -K_{22}[\varphi(L)/L]$ , the light-induced bulk torque  $M^{hv}$  $=dF^{hv}/d\vartheta$ , and the surface anchoring torque  $M_{\text{test}}$  $=dW_{\text{test}}(\varphi)/d\varphi(L)$  as follows:

$$
-K_{22}\frac{\varphi(L)}{L} + \frac{dW_{\text{test}}(\varphi)}{d\varphi(L)} + k\sin(2\vartheta)I_{\text{eff}} = 0.
$$
 (12)

<span id="page-5-3"></span>Equation ([12](#page-5-3)) describes the dependence of the LC director near the surface on the light intensity and on the anchoring energy, which is determined by the angular distribution function of the adsorbed molecules  $(4)$  $(4)$  $(4)$ .

## **C. Light-induced changes of the angular distribution function of the adsorbed MR molecules**

According to  $[17]$  $[17]$  $[17]$ , the dark adsorbed MR layer consists of trans isomers of dye molecules. The thickness of this layer is

<span id="page-6-0"></span>

FIG. 7. Schematic structure of the adsorbed MR molecules layers, and their change due to the adsorption and/or desorption processes: (1) the structure of the top level at the moment  $t$ , where  $N_{\text{test}}^{\text{trans}}$  and  $N_{\text{test}}^{\text{cis}}$  are the concentrations of trans-MR and cis-MR molecules in the top layer; (2) the structure at the moment  $t + \Delta t$  after the adsorption of cis-MR molecules  $dC_{\text{test}}^{\text{cis}}$ , and the desorption of trans-MR molecules  $dC_{\text{test}}^{\text{trans}}$ ; and (3) the structure of the top level at the moment  $t + \Delta t$  if the surface morphology is not taken into account. The concentration of cis molecules increases on the value  $dN_{\text{test}}^{\text{cis}}$  and the concentration of trans molecules decreases on the same value  $dN_{\text{test}}^{\text{cis}}$ .

about 5 nm, which is much thicker than the monolayer of the MR molecules. Contribution of the adsorbed MR molecules to the anchoring decreases quickly with the distance from the top of the layer. Therefore, we suppose that only molecules of the top layer contribute to the anchoring. In this case the values  $W_{\text{test}}$  and  $N_{\text{test}}$  in Eq. ([4](#page-5-0)) are determined by the top layer of adsorbed molecules.

The top layer consists of two types of MR molecules: dark-adsorbed trans isomers and light-adsorbed cis isomers (see Fig. [7](#page-6-0)). Let  $N_{\text{test}}^{\text{trans}}$  and  $\Phi_{\text{test}}^{\text{trans}}$  denote the concentration and the distribution function of trans isomers in the top layer.  $w_{\text{test}}^{\text{trans}}$  denotes the anchoring coefficient of the adsorbed trans isomer with the ensemble of LC molecules near the surface. We also denote the concentration, the distribution function, and the anchoring coefficient of the light-adsorbed cis

isomers by  $N_{\text{test}}^{\text{cis}}, \Phi_{\text{test}}^{\text{cis}},$  and  $w_{\text{test}}^{\text{cis}}$ . The total number of adsorbed MR molecules is fixed as follows:

$$
N_{\text{test}} = N_{\text{test}}^{\text{trans}} + N_{\text{test}}^{\text{cis}}.\tag{13}
$$

Supposing an additive contribution of cis and trans isomers to the anchoring, the expression for the anchoring energy Eq.  $(4)$  $(4)$  $(4)$  reads

<span id="page-6-2"></span>
$$
W_{\text{test}} = \frac{1}{2} \int_{-\pi/2}^{\pi/2} d\varphi_V \int_{-\pi/2}^{\pi/2} d\varphi_{\text{test}}^{\text{mol}} \left[ \begin{array}{l} w_{\text{test}}^{\text{trans}} N_{\text{test}}^{\text{trans}} \Phi_{\text{test}}^{\text{trans}}(\varphi_{\text{test}}^{\text{mol}}) \\ + w_{\text{test}}^{\text{cis}} N_{\text{test}}^{\text{cis}} \Phi_{\text{test}}^{\text{cis}}(\varphi_{\text{test}}^{\text{mol}}) \end{array} \right] \times \cos^2(\varphi_V - \varphi_{\text{test}}^{\text{mol}}) \int_0^{\pi} \Phi_V(\theta_V, \varphi_V, \varphi_{\text{test}}) \sin^3 \theta_V d\theta_V.
$$
\n(14)

In this expression, concentrations  $N_{\text{test}}^{\text{trans}}$  and  $N_{\text{test}}^{\text{cis}}$  of MR molecules on the surface, and their angular distributions  $\Phi_{\text{test}}^{\text{trans}}$ and  $\Phi_{\text{test}}^{\text{cis}}$  are determined by light-induced exchange by trans and cis isomers between the adsorbed layer and the MR molecules in LC. To describe this process, we need to derive the rate equations for trans and cis isomers taking into account their orientation with respect to the director and polarization of light.

#### *1. Rate equation for cis isomers*

Absorption of trans isomers in LC near the surface may cause their transformation to cis form and the consequent adsorption of cis isomers by the surface  $[19]$  $[19]$  $[19]$ . We can assume that highly dichroic MR molecules absorb light only along their long axes  $\vec{l}_{MR}$ . In this case the probability of the adsorption of cis isomers is proportional to  $(l_{MR}, E)^2 \Phi_V(\theta_V, \varphi_V, \varphi_{test})$ . In a polar reference frame, → →

<span id="page-6-1"></span>
$$
P_{\text{ad}}(\varphi_V) = A_+ I \int_0^\pi \Phi_V(\theta_V, \varphi_V, \varphi_{\text{test}}) \sin^2 \varphi_V \sin^3 \theta_V d\theta_V,
$$
\n(15)

where  $A_{+}$  is a coefficient of light-induced adsorption. Integration  $P_{\text{ad}}(\varphi_V)$  over  $\varphi_V$  yields a rate equation that describes the evolution of the *total* number of the light-adsorbed cis isomers  $C_{\text{test}}^{\text{cis}}$  as follows:

$$
\frac{dC_{\text{test}}^{\text{cis}}}{dt} = N_V d_{\text{MR}} \int d\varphi_V \left[ A_+ I \int_0^{\pi} \Phi_V(\theta_V, \varphi_V, \varphi_{\text{test}}) \sin^2 \varphi_V \sin^3 \theta_V d\theta_V \right],\tag{16}
$$

where  $N_V$  is a concentration of the MR molecules in the LC bulk;  $d_{MR}$  is an average distance between dye molecules.

It should be pointed out that not all adsorbed cis isomers take an equivalent part in the anchoring since some of them overlay cis isomers that were adsorbed before. Thus, adsorption of  $dC_{\text{test}}^{\text{cis}}$  cis isomers leads to an increase of concentration of these isomers in a top layer, which contributes to the anchoring only by changing the value  $dN_{\text{test}}^{\text{cis}}$  (see Fig. [7](#page-6-0)) as follows:

$$
\frac{dN_{\text{test}}^{cis}(t)}{dt} = \frac{dC_{\text{test}}^{cis}}{dt} \left(1 - \frac{N_{\text{test}}^{cis}(t)}{N_{\text{test}}}\right). \tag{17}
$$

<span id="page-7-0"></span>Taking into account Eqs.  $(15)$  $(15)$  $(15)$ – $(17)$  $(17)$  $(17)$ , the rate equation for the number of adsorbed cis isomers  $\Phi_{\text{test}}^{\text{cis}}(\varphi_{\text{test}}^{\text{mol}},t)N_{\text{test}}^{\text{cis}}$  oriented at the angle  $\varphi_{\text{test}}^{\text{mol}}$  in the top layer is

<span id="page-7-3"></span>
$$
\frac{d[\Phi_{\text{test}}^{\text{cis}}(\phi_{\text{test}}^{\text{mol}},t)N_{\text{test}}^{\text{cis}}]}{dt} = N_V l_{\text{MR}} P_{\text{ad}}(\phi_{\text{test}}^{\text{mol}})
$$

$$
-\frac{dC_{\text{test}}^{\text{cis}}N_{\text{test}}^{\text{cis}}\Phi_{\text{test}}^{\text{cis}}(\phi_{\text{test}}^{\text{mol}},t). (18)
$$

Here the first term in the right part describes the total number of adsorbed cis isomers, and the second term describes a number of adsorbed MR cis isomers that overlay previously adsorbed MR cis isomers.

#### *2. Rate equation for trans isomers*

Probability of desorption of trans isomers is proportional to the orientation of the long axes of trans isomers with respect to the light polarization  $(\vec{l}_{MR}, \vec{E})^2$  and their angular distribution function  $\Phi_{\text{test}}^{\text{trans}}(\varphi_{\text{test}}^{\text{mol}})$  as follows:

$$
P_{\text{des}}(\varphi_{\text{test}}^{\text{mol}}) = A \_I_{\text{pump}} \Phi_{\text{test}}^{\text{trans}}(\varphi_{\text{test}}^{\text{mol}}) \cos^2(\varphi_{\text{test}}^{\text{mol}}). \tag{19}
$$

<span id="page-7-1"></span>Here *A*<sup>−</sup> is the coefficient of light-induced desorption of trans isomers. The rate equation that describes the desorption of trans isomers is obtained by the integration of Eq.  $(19)$  $(19)$  $(19)$  over  $\varphi_{\text{test}}^{\text{mol}}$  as follows:

$$
\frac{dC_{\text{test}}^{\text{trans}}}{dt} = N_{\text{test}}^{\text{dark}} \int_{-\pi/2}^{\pi/2} P_{\text{des}}(\varphi_{\text{test}}^{\text{mol}}) d\varphi_{\text{test}}^{\text{mol}}.
$$
 (20)

Here *C* is the *total* number of the light-desorbed trans isomers  $C_{\text{test}}^{\text{trans}}$ . The rate equation that describes the number of trans isomers oriented at the angle  $\varphi_{\text{test}}^{\text{mol}}$  in the top layer reads

<span id="page-7-2"></span>
$$
\frac{d[\Phi_{\text{test}}^{\text{trans}}(\varphi_{\text{test}}^{\text{mol}},t)N_{\text{test}}^{\text{trans}}]}{dt} = -\frac{dC_{\text{test}}^{\text{is}}N_{\text{test}}^{\text{trans}}}{dt} \Phi_{\text{test}}^{\text{trans}}(\varphi_{\text{test}}^{\text{mol}},t) - N_{\text{test}}^{\text{trans}} P_{\text{des}}(\varphi_{\text{test}}^{\text{mol}})} + \frac{dC_{\text{test}}^{\text{trans}}N_{\text{test}}^{\text{trans}}}{dt} \Phi(\varphi_{\text{test}}^{\text{mol}},0). (21)
$$

The first term in the right part of Eq.  $(21)$  $(21)$  $(21)$  describes the decrease of the amount of trans isomers in the top layer due to their overlaying by light-adsorbed cis isomers. The second term depicts the loss of trans isomers due to light-induced desorption (see Fig. [7](#page-6-0)). When trans isomers desorb from the top layer, other trans isomers from the inner molecular layer start playing a role in the anchoring by contributing to the angular distribution  $\Phi_{\text{test}}^{\text{trans}}(\varphi_{\text{test}}^{\text{mol}})$  and to the anchoring energy. This effect is described by the third term of Eq.  $(21)$  $(21)$  $(21)$ .

Thus, Eqs.  $(18)$  $(18)$  $(18)$  and  $(21)$  $(21)$  $(21)$ , together with the expression for the anchoring energy  $(14)$  $(14)$  $(14)$  and Eq.  $(12)$  $(12)$  $(12)$  for the director near the surface, describe light-induced changes of the angular distribution of the top layer of the adsorbed MR molecules that determine the gliding effect. Reorientation of the director in the cell  $(\sim 0.1 - 1 \text{ s})$  is much faster than the character-

<span id="page-7-4"></span>

FIG. 8. (Color online) Effective normalized angular distribution function of the adsorbed MR molecules layer  $\Phi_{\text{test}}^{\text{eff}}$  $= w_{\text{test}} \Phi_{\text{test}}(\varphi_{\text{test}}^{\text{mol}})$  at the moments *t*=0; 60; 120; 240, and 800 s.

istic times of the gliding of the easy axis  $(\sim 10-100 \text{ min})$ . Therefore, we divide the exposure time to the discrete sequence of equal time intervals *dt*, which are much longer than the times of the bulk director reorientations and much shorter than the times of desorption and/or adsorption. At a given iteration we solved the static problem for the director distribution  $n(z)$  and its position on the surface  $\varphi_{\text{test}}(t_{\text{exp}})$ [Eqs.  $(12)$  $(12)$  $(12)$  and  $(14)$  $(14)$  $(14)$ ] with the fixed distribution of the adsorbed molecules  $(18)$  $(18)$  $(18)$  and  $(21)$  $(21)$  $(21)$ . Then we calculated the new distribution function of the adsorbed molecules by solving the systems ([18](#page-7-3)) and ([21](#page-7-2)) at  $\varphi_{\text{test}}(t_{\text{exp}})$ . We used this direction of  $\varphi_{\text{test}}(t_{\text{exp}})$  in the next iteration to calculate the next director position  $\varphi_{\text{test}}(t_{\text{exp}}+dt)$ . As a result, we obtained the evolution of the position of the director. Also, we obtained the dependence of the effective molecular distribution function  $\Phi_{\text{test}}^{\text{eff}}$  in the top layer on exposure time as follows:

$$
\Phi_{\text{test}}^{\text{eff}}(\varphi_{\text{test}}^{\text{mol}}) = \frac{N_{\text{test}}^{\text{cis}} \psi_{\text{test}}^{\text{cis}} \Phi_{\text{test}}^{\text{cis}}(\varphi_{\text{test}}^{\text{mol}}) + N_{\text{test}}^{\text{trans}} \psi_{\text{test}}^{\text{trans}} \Phi_{\text{test}}^{\text{trans}}(\varphi_{\text{test}}^{\text{mol}})}{w_{\text{test}}^{\text{eff}} N_{\text{test}}},
$$
\n(22)

where  $w_{\text{test}}^{\text{eff}} = (N_{\text{test}}^{\text{cis}} w_{\text{test}}^{\text{cis}} + N_{\text{test}}^{\text{trans}} w_{\text{test}}^{\text{trans}})/N_{\text{test}}$ .

This function describes the evolution of the easy axis and the anchoring energy during the light exposure. We used the following values of the experimental parameters in the calculations: *L*=30  $\mu$ m,  $K_{22} = 3.6 \times 10^{-12}$  N,  $\psi = 45^{\circ}$ ,  $I_{pump}$  $= 1.6 \text{ W/cm}^2$ ;  $\varphi_{\text{test}}(0) = -5^\circ$ ,  $W_{\text{test}}(0) = W_{\text{test}}^{\text{trans}} = 0.25 \mu \text{J/m}^2$ . The fitting parameters were  $w_{\text{test}}^{\text{cis}}N_{\text{test}}^{\text{cis}}/w_{\text{test}}^{\text{trans}}N_{\text{test}}^{\text{trans}} = 1.1$  and  $A_{+} = A_{-} = 2.5 \times 10^{-2}$  s<sup>-1</sup>. The results of the calculations of the normalized function  $\Phi_{\text{test}}^{\text{eff}}(t_{\text{exp}})$  are presented in Fig. [8.](#page-7-4) One can note two remarkable features of the distribution function  $\Phi_{\text{test}}^{\text{eff}}(t_{\text{exp}})$  changing with time. First, the maximum of  $\Phi_{\text{test}}^{\text{eff}}(t_{\text{exp}})$  gradually shifts toward the polarization  $\vec{E}_{\text{pump}}$ , which corresponds to the light-induced drift of the axis of easy orientation. The calculated dependencies of the easy axis and director on exposure time are presented in Fig. [4.](#page-3-0) One can see good correspondence of the calculated curves and the experimental data. Second, both the shape of the function  $\Phi_{\text{test}}^{\text{eff}}$  and its integral over the azimuthal angle  $\varphi_{\text{test}}^{\text{mol}}$ are changed during the drift of the easy axis. It points to the change of the surface potential  $W_{\text{test}}$  and its amplitude  $w_{\text{test}}N_{\text{test}}$  during irradiation [see Eq. ([4](#page-5-0))]. The results of the numerical calculations of  $W_{\text{test},0}(t)$  are presented in Fig. [5](#page-3-1) by

the solid line and qualitatively coincide with the experimental data. The experimental data are also depicted in the figure and they do not reveal a pronounced decrease of the anchoring energy predicted by the calculations. It is no surprise since the function  $\Phi_{\text{test}}^{\text{eff}}$  is not a symmetrical one, especially at small exposures and the surface potential  $W_{\text{test}}(4)$  $W_{\text{test}}(4)$  $W_{\text{test}}(4)$  cannot be reduced to the Rapini-Popular form [see Eq.  $(5)$  $(5)$  $(5)$ ]. At the same time, our experimental data for the anchoring energy  $W_{\text{test 0}}$  were obtained in the approximation of the Rapini-Popular potential.

## **IV. CONCLUSION**

We have found that the light-induced dye molecule exchange between the polymer surface and the LC bulk may cause efficient drift of the easy axis on the aligning surface. The observed drift of the easy axis is over tens of degrees and is caused by light-induced anisotropic adsorption and/or desorption of dye molecules on or from the aligning layer in the presence of the light-induced bulk torque. We have proposed the theoretical model that explains the experimental data in terms of the light-induced changes of the angular distribution of the adsorbed dye molecules due to their exchange with the dye molecules from the liquid crystal bulk.

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According to the model, dye molecule exchange results in a shift of the maximum of the angular distribution function of adsorbed dye molecules that leads to the drift of the easy axis. Simultaneous deformation of the shape of the distribution function causes observed dependence of the anchoring energy on the exposure time.

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