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Alignment memory of a nematic liquid crystal and thermal isotropization of the surface adsorbed layer

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Abstract – We use a digital image analysis of the schlieren textures to study the effect of memory of the surface anisotropy in a nematic-liquid-crystal cell and establish its relation to the surface adsorbed molecular layer. The anisotropy is induced on an isotropic glass surface by a flow of the nematic liquid. The proposed technique allows us to quantify the alignment and its changes under the effect of temperature. The temperature at which the memory of the alignment texture is lost is interpreted as the temperature of the full isotropization of the initial anisotropic surface layer adsorbed during the flow: the molecules oriented along the flow are thermally desorbed whereas newly adsorbed bulk molecules have isotropic distribution. The measured temperature dependence of the director alignment texture is used to estimate the adsorption energy of the liquid-crystal molecule onto the surface.

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Introduction. – A layer of liquid-crystal (LC) molecules adsorbed on a substrate is directly connected to the director alignment in a LC cell and therefore is a key element for the development of LC devices which essentially rely on a delicate control of the aligning surface [1–4]. The preferred direction imposed by the surface to the adsorbed LC molecules is transmitted into the bulk because of long-range orientational order in liquid crystals, therefore determining the bulk director alignment in the surface plane [5,6]. The initial anisotropy occurs because at the initial moment the surface was in contact with an orientationally anisotropic medium and thus the distribution function of the axes of the adsorbed molecules was anisotropic. For instance, such an anisotropy on cell surfaces can be induced by a flow of the nematic liquid during filling the cell. Manifestation of this initial surface anisotropy in the subsequent behavior of the LC cell is associated with the surface memory [7]. The fundamental question therefore is how to create and erase an anisotropy in the surface adsorbed layer. Recent studies have shown that the desorption plays a very important role in both of these processes.

Alike adsorption, the desorption of molecules from the surface can be of two different types, i.e., selective (or anisotropic) and isotropic. The photo-alignment effect gives an example showing how the LC orientation can be explained by a selective adsorption and desorption of dye molecules [8,9]. Moreover, there has been a strong evidence that the anisotropy of a surface layer, even consisting of very complex molecules, can be connected just to a subnanoscale layer’s roughness produced by an anisotropic light-induced desorption [10,11]. It was demonstrated [10] that a similar reason is behind the UV-light–induced anisotropy in adsorbed layers consisting of essentially different molecules.

Thermal desorption is of isotropic type and, therefore, can result only in erasing the initial anisotropy of adsorbed layers. In spite of the different angular characteristics, thermal desorption has the same physical origin and is described by the same adsorption energy as anisotropic desorption. At the same time, a thermal desorption from a surface in contact with a liquid phase is necessarily accompanied by an adsorption, and the observed effect

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is due to the balance between these two processes rather than to the desorption alone. The advantage of studying thermal desorption is that it is simpler than the selective one since the surface relief is not involved.

High interest to the physical phenomena at the interface of a LC and a bounding medium [12] has resulted in a variety of experimental techniques developed to study surface adsorbed monolayers. Such techniques are thermal-desorption spectroscopy [13], second harmonic generation [14–16], scanning tunneling microscopy [17]. The recently proposed image processing techniques [18–21] are also of great potential in studying material properties of liquid crystals. These techniques have been successfully used for the investigation of phase transitions both in thermotropic [18,19] and lyotropic LCs [20,21].

In this paper we propose a digital image processing of the schlieren textures to study the effect of thermal desorption on the orientational memory of a LC cell. The proposed approach allows us to quantify the alignment and connect the surface memory effect to the thermal desorption via the duration and temperature of the thermal treatment. We show that the process of temperature-induced erasing of the surface memory is related to a thermal isotropization of the adsorbed layer: the orientational memory diminishes when molecules of the initial flow-oriented adsorbed layer desorb since the newly adsorbed molecules have the isotropic bulk distribution. It is shown that under a very basic qualitative assumption about the adsorption process, this model reduces to a complicated optical setup as in the second harmonic generation technique [14–16]. Second, as the desorption process is separated from the adsorption, there is no need in a high-vacuum apparatus as in the thermal-desorption spectroscopy [13]. And, last but not the least, we deal with a situation extremely close to the real application of LCs: the desorption is studied in standard cells which consist of two glass slides separated by a gap of a few micrometers and filled with the LC material.

Experimental method. –

Cell preparation. Liquid-crystal cells were assembled using two thoroughly cleaned glass plates without any coating. Uniformly distributed 6.5 µm glass fiber spacers were used to control the cell gap. In our experiments we used 5CB LC material obtained from EM Chemicals. The initial anisotropy in the glass substrates was created using the flow alignment technique in cells of a special design. We used the Asymtek XY Dispenser for the UV glue deposition to create a cell with inner volume of a T-like shape, fig. 1. After a UV curing we placed the cell into the vacuum filling stage and pumped off air to achieve a pressure of about 3 millibar. Then, a sufficiently large drop of the LC material (sufficient to fill the whole T-like cell’s volume) was placed at the filling hole and the air valve was opened.

This filling technique gives a good homogeneous liquid-crystal alignment in the cell’s channel, see fig. 3(a), whereas in the additional chamber the orientation is rather nonuniform. The role of this chamber is to provide a sufficiently large volume to maintain the pressure difference between the channel’s ends (i.e., between the outer atmospheric air and the chamber) for longer time thus inducing stronger orientational anisotropy in the adsorbed LC layer and produce a larger area with uniform alignment. In the experiments we used only the central part of the straight channel, fig. 1, where the orientation of the LC material was practically perfect.

After the filling, all thus obtained cells were kept at the room temperature for 24 hours to ensure that the LC material is in equilibrium with the bounding surfaces. As a heating element in our setup we used the microscope hot stage HS-1 (Instec Inc.) with an attached liquid circulating bath (VWR Scientific Products) serving as a cooler. We filled the liquid circulating bath with water maintained at 10 °C for the fastest possible cooling rate. Time counting and control over the hot stage and circulating bath, as well as image acquisition and data processing, were performed by a custom-designed software running under the MatLab environment.

Each LC cell with a uniform initial director alignment was used in a single thermal cycle consisting of the following stages: a) preheating to some specific temperature \( T_{cold} = 25 \)°C; b) keeping the cell at \( T_{cold} \) for 100 s to achieve the thermal equilibrium in the system; c) heating to some specific temperature \( T_h \) and keeping the cell at this temperature for 5 min; d) cooling back to \( T_{cold} \) and waiting for the director to equilibrate. Figure 2 shows the temperature regime as a function of time for three different heating cycles: \( T_h = 50 \)°C, 100° C, and 150° C (other thermal cycles are similar). At the end of the first stage right before heating to \( T_h \), and at the end of the last stage when the cell is in the equilibrium at \( T_{cold} \), we take microscopic images of the LC texture in the cell in crossed polarizers, fig. 3. In the course of our experiment, each cell undergoes a single thermal cycle characterized by the temperature \( T_h \). Then, for a given cell, by comparing the initial texture with the texture obtained after the heating
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![Temperature as a function of time for the cycles with heating temperatures $T_h = 50 \, ^\circ\text{C}$, $100 \, ^\circ\text{C}$, and $150 \, ^\circ\text{C}$. In all cases $T_{\text{cold}} = 25 \, ^\circ\text{C}$. The arrows indicate the time when microscopic images of the LC texture were taken.](image)

Fig. 2: Temperature as a function of time for the cycles with heating temperatures $T_h = 50 \, ^\circ\text{C}$, $100 \, ^\circ\text{C}$, and $150 \, ^\circ\text{C}$. In all cases $T_{\text{cold}} = 25 \, ^\circ\text{C}$. The arrows indicate the time when microscopic images of the LC texture were taken.

cycle, we estimate a number of liquid-crystal molecules that were desorbed during the cycle with given $T_h$. The underlying idea and procedure of image quantifying are described below.

**Image processing and quantifying the director alignment.** Our method is based on quantifying the alignment in a LC cell by a digital image processing of its schlieren texture. Microscopic images of a LC texture in crossed polarizers usually contain a noise. Mostly it comes from thermal angular fluctuations of the LC molecules, so-called “flickering”. To exclude the noise when making microscope pictures we collected a series of 13 frames with a time interval of approximately 0.04 s and averaged them to obtain a single microscopic picture of the LC texture. And in order to rescale the intensity of the texture image to exactly $[0, 1]$ interval, we collected not just a single image of the cell’s schlieren texture, but a series of images, simultaneously rotating the crossed polarizer and analyzer. Initially, the polarizer and analyzer axes were, respectively, horizontal and vertical with respect to the director orientation set by the LC flow. Then they were rotated by $90^\circ$ and the picture was taken every $10^\circ$ of rotation. From this series of ten pictures, for each pixel we extracted the intensity profile $I(\alpha)$ as a function of the polarizer angle $\alpha$. Then, by fitting this intensity profile with the ansatz $I_0 \sin[2(\alpha + \alpha_0)]^2$, where $\alpha_0$ is the fitting parameter standing for the angle between the optical axis (LC director) and the direction of the LC flow, we could find the refined orientation of the LC director. Further processing consists of the calculation of the normalized transmission intensity as $I_{\text{norm}} = \sin(2\alpha_0)^2$ for each pixel of our images. Therefore we finally obtained the schlieren texture image where the light intensity changes from true zero, when LC director is parallel to one of the crossed polarizers, to unity when the LC director is at $45^\circ$ to the polarizers. Hereafter we refer to the new texture as refined schlieren texture.

Thus, the refined schlieren texture intensity is calculated by processing ten images taken in the course of the simultaneous $90^\circ$ rotation of the crossed polarizers. For a given cell and, therefore, for each of its pixels, the refined schlieren texture image is obtained twice: for the first time, right before the cell was heated to the temperature $T_h$, and, for the second time, after the cell was cooled back to $T_{\text{cold}}$ and the director had equilibrated. In addition to the averaging over 13 frames for each image, described above, the refining procedure also contributes to noise removal since the final intensity value for each pixel is calculated by fitting the intensities of ten such averaged images of the same spot.

In fig. 3 are shown the microscopic images of the initial director textures and those after the cycles with the heating temperature $T = 50 \, ^\circ\text{C}$, $90 \, ^\circ\text{C}$, $120 \, ^\circ\text{C}$, $140 \, ^\circ\text{C}$, and $160 \, ^\circ\text{C}$. We see that heating to temperatures below $90 \, ^\circ\text{C}$ (which is almost three times the clearing point $\sim 35.6 \, ^\circ\text{C}$ of 5CB) causes practically no texture changes while heating to higher temperatures produces a noticeable effect, and that the higher the heating temperature $T_h$ the more significantly the final texture, figs. 3(d,e,f), differs from the initial uniform alignment, fig. 3(a).

Performing a pixel-by-pixel comparison of the intensity in the initial and the final refined schlieren texture we
count how many pixels $\tilde{N}_{pix}$ out of the total number $N_{pix}$ have changed their intensity by a value larger than the threshold value $\Delta I$ which was set at 3\% in all our experiments. As the intensity of a pixel is related to the alignment of the director with respect to the direction of the initial homogeneous alignment, the number $N_{pix} - \tilde{N}_{pix}$ of unchanged pixels can be considered as a quantitative measure of the alignment memory of the surface adsorbed molecular layer. Based on the simple model described below, we assume that $\tilde{N}_{pix}$ is proportional to the number of LC molecules that were detached from the cell surface during the heating cycle with a given $T_h$ which allows us to connect the desorption process to the alignment measure $\tilde{N}_{pix}$. To this end we introduce the digital image coverage

$$
\theta_{im} = 1 - \tilde{N}_{pix}/N_{pix},
$$

which serves as a measure of the digitally quantified image of the alignment texture. The experimental image coverage $\theta_{im}$ as a function of the heating temperature $T_h$ is shown in fig. 4 by circles.

**Thermal desorption and erasing the surface anisotropy (thermal isotropization).** When studying the adsorption-related phenomena, the standard experimental situation is that the only accessible quantity is the surface coverage $\theta$ and its temporal changing rate $d\theta/dt$ [22]. The surface coverage changing rate $d\theta/dt$ is the result of the balance between adsorption rate $d\theta_{ads}/dt$, which is the rate of arrival of molecules at the surface, and the desorption rate $d\theta_{des}/dt$, which is the rate of departure of molecules from the surface:

$$
d\theta/dt = d\theta_{ads}/dt - d\theta_{des}/dt.
$$

At the same time, separating the adsorption from desorption and studying their rates individually is a complicated problem. This problem is easiest when the adsorbing surface is in contact with a low-pressure gas, as in this case the adsorption rate can be negligible compared with the desorption rate which thus becomes fully responsible for the total coverage and can be measured by itself (thermal-desorption spectroscopy [13]). When, however, the surface is in contact with a liquid phase, which is exactly the case we deal with, the problem of studying an adsorption or desorption individually is severest by virtue of a liquid’s very high density. Nonetheless, in our particular case, the anisotropy of the adsorbed layer helps to estimate the desorption rate and thereby the desorption energy.

Initially, i.e., after the filling and stages a) and b) of the thermal cycle, the angular distribution of adsorbed molecules is anisotropic: some $N_{anis}$ surface vacancies (out of total $N_{vac}$) are occupied by the molecules adsorbed with certain average orientation along the flow direction; the initial surface coverage is $\theta(0) = \theta_{anis}(0) = N_{anis}/N_{vac}$. It is these $N_{anis}$ molecules that determine the surface anisotropy which gives rise to the good homogeneous initial alignment in the newly filled cells. Further, we saw from fig. 3 that substantial changes in the director alignment occur after the cycles with the heating temperature $T > 90^\circ$C at which 5CB material is in a deep isotropic phase. At such temperatures, therefore, the cell’s surface is in contact with the isotropic liquid whose molecules have an isotropic angular distribution. As we mentioned above, the thermal reorientation of the adsorbed 5CB molecules is negligible, hence the changes of alignment can be induced only by the desorption of some of those $N_{anis}$ molecules constituting the initial anisotropic surface adsorbed layer. When some $N_{des}$ such molecules desorb from the layer, they either collide with the bulk molecules and get read sorbed or diffuse farther from the surface. In the first case, after the collisions the memory of the orientation in the initial adsorbed layer is lost and the molecules are read sorbed with the isotropic angular distribution. In the second case, the vacancy left after desorption will be either filled by adsorbed bulk molecules with isotropic angular distribution or remain vacant. In all of these cases the orientational anisotropy of the layer will be determined only by those $N_{anis} - N_{des}$ molecules that have never left the surface layer and preserved their initial orientation; the surface coverage by these initially adsorbed molecules becomes $\theta_{anis} = \theta_{anis}(0) - \theta_{des}$, where $\theta_{des} = N_{des}/N_{vac}$. Thus, a desorption of the initially surface adsorbed molecules irretrievably erases the alignment memory of the surface via isotropization of the angular distribution of the surface adsorbed molecules. It is then natural to make the simplest assumption that the number of pixels $N_{pix} - \tilde{N}_{pix}$ with the unchanged intensity is proportional to the number $N_{anis} - N_{des}$ of molecules which have not yet left the initially adsorbed surface layer, i.e.,

$$
N_{pix} - \tilde{N}_{pix} \propto N_{anis} - N_{des}. \tag{3}
$$

We emphasize that this thermal isotropization is determined by the desorption alone and is irrespective of the the total coverage that may remain practically unchanged. Moreover, owing to the liquid’s high density, in the course of the experiment the total number of adsorbed molecules has to be very close to its maximum value $N_{vac}$; all vacancies are occupied by adsorbed molecules and
the only difference is in their orientation. Therefore, one can set \( N_{anis} \approx N_{vac} \) and \( \theta_{anis}(0) \approx 1 \). Using the above definition (1) of \( \theta_{im} \) and dividing (3) by the constant \( N_{pix} \), one obtains \( \theta_{im} \propto 1 - \theta_{des} \). As initially \( \theta_{im} = 1 \) and \( \theta_{des} = 0 \), this relation becomes the equation

\[
\theta_{im} = 1 - \theta_{des}. \tag{4}
\]

By connecting the digitally quantified image of the texture with the desorption of the aligned molecules from the surface, this equation describes erasing the alignment memory in the process of the surface isotropization.

We arrive at the following picture of the physical processes in a LC cell during the heating cycle. At \( T_{cold} \approx 25^\circ C \) the desorption is negligible and almost all surface vacancies are occupied by the initially adsorbed molecules which preserve their orientation. Then at \( T_h \) some of these molecules desorb from the surface layer; the opened vacancies get filled immediately, but the newly adsorbed molecules, being distributed isotropically, do not change the anisotropy; the memory of the initial orientation is thus partially erased and the alignment becomes worse. After the cell has been cooled back to \( T_{cold} \) the desorption practically ceases, and the image reflects the changes which can be attributed to the desorption at \( T_h \).

**Fitting the experimental digital image data.** – We used the first-order Arrhenius equation for the desorption rate \( d\theta_{des}/dt \) [16,22], i.e.,

\[
d\theta_{des}/dt = \nu (1 - \theta_{des}) \exp \left(-\frac{E_{des}}{k_B T(t)}\right), \tag{5}
\]

where \( \nu \) is the so-called pre-exponential factor, \( E_{des} \) is the desorption energy, \( k_B \) is Boltzmann’s constant, \( t \) and \( T(t) \) are the time and temperature, respectively. An uncertain point in using eq. (5) is the choice of the pre-exponential factor \( \nu \). Usually, for a gas adsorption on a metal surface \( \nu \sim 10^{13} s^{-1} \) [22,23], but for larger molecules [24–26] or interacting adsorbed molecules [27] it can be orders of magnitude higher. In [25] \( \nu \) is found to be in the range \( \sim 10^{18} - 10^{19} s^{-1} \) for \( C_n \) \( H_{2n} \) \((n = 3–12)\) on different surfaces; \( \nu \sim 10^{14} - 10^{15} s^{-1} \) for desorption of polyaromatic hydrocarbons from a graphite surface [28]; in [29] \( \nu \sim 10^{19\pm0.5} s^{-1} \) was found for a set of straight chain alkanes (\( H(CH_2)_n H \) with \( n \) from 5 to 60) on the surface of a single-crystalline graphite. It is also accepted that for adsorbed molecules that cannot move freely across the surface, the magnitude of the pre-exponential factor is \( \sim 10^{16} s^{-1} \) [16,30]. These experimental results were obtained for desorption from a solid substrate to a high vacuum or gaseous phase rather than to a liquid phase and hence cannot unambiguously prompt the magnitude of the pre-exponential factor for desorption to the liquid phase. We found that \( \nu = 10^{16} s^{-1} \) provides a good theoretical fit to our experimental data. At the same time, this value of the pre-exponential factor is consistent with the experimental data obtained for desorption of 8CB material in [16,30].

Equation (5) with \( \nu = 10^{16} s^{-1} \) was solved numerically for \( \theta_{des} \) vs. time, \( \theta_{des}(t) \), using the experimental discrete time dependence of the temperature for the cycle with heating temperature \( T_h \), fig. 2, and imposing the initial condition \( \theta_{des}(t = 0) = 0 \). The experimental point \( \theta_{im}(T_h) \) corresponds to the difference \( 1 - \theta_{des}(T_h) \) calculated for the time \( t_{T_h} \) when, in the given cycle, the cell was cooled from \( T_h \) to \( T_{cold} \). Then, by using the least-square fitting to the experimental data with these theoretical values of \( 1 - \theta_{des}(T_h) \), we found \( E_{des} \approx 1.48 eV \). The best fit with this \( E_{des} \) is shown by the solid line in fig. 4.

Note that the found value \( E_{des} \approx 1.48 eV \) for desorption of 5CB molecules from a clean glass surface agrees well with \( E_{des} \approx 1.38 eV \) obtained for 8CB on a clean glass in ref. [16].

**Conclusion.** – We presented an efficient and easy-to-implement method for studying the thermal desorption and surface alignment memory of LC materials. The method is based on quantifying the alignment by digital processing of the image of the director texture and relating the thus obtained digital image coverage (1) with the desorption effect on the surface anisotropy, eq. (4). This relation has become possible because erasing of the anisotropy of a surface adsorbed layer is determined solely by the desorption. Our results demonstrate that the surface adsorption and desorption-driven isotropization are indeed responsible for the surface memory effect. The experimental technique has the advantage that it works with the LC cells similar to those used in the application of LCs and does not require complicated and expensive setups. The method gives the way to measure desorption characteristics of LC materials directly in a highly dense liquid phase. In particular, we found the desorption energy for molecules of 5CB and established temperature dependence of the orientational memory in a cell filled with 5CB material. These data are of fundamental importance for elucidating the surface alignment of LCs, and, particularly, the dynamics of surface gliding and orientational memory effects in LCs.

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