Influence of the flow on the anchoring of nematic liquid crystals on a Langmuir-Blodgett monolayer studied by optical second-harmonic generation

Valentina S. U. Fazio\textsuperscript{1,2,*}, Lachezar Komitov\textsuperscript{1}  
Christian Rad"uge\textsuperscript{2}, Sven T. Lagerwall\textsuperscript{1},  
Hubert Motschmann\textsuperscript{2}

\textsuperscript{1} Department of Microelectronics and Nanoscience, Liquid Crystal Physics,  
Chalmers University of Technology & G"oteborg University,  
SE-41296 G"oteborg, Sweden  
\textsuperscript{2} Max-Plank-Institute of Colloids and Interfaces  
D-14476 Golm/Potsdam, Germany

Abstract

The influence of capillary flow on the alignment of the nematic liquid crystal MBBA on fatty acid Langmuir-Blodgett monolayers was studied by optical second-harmonic generation. The surface dipole sensitivity of the technique allows probing the orientation of the first liquid crystal monolayer in the presence of the liquid crystal bulk. It was found that capillary flow causes the first monolayer of liquid crystal molecules in contact with the fatty acid monolayer to be oriented in the flow direction with a large pretilt (78 degrees), resulting in a quasi-planar alignment with splay-bend deformation of the nematic director in the bulk. The large pretilt angle also suggests that the Langmuir-Blodgett film itself is affected by the flow. The quasi-planar flow-induced alignment was found to be metastable. Once the flow ceases, circular domains of homeotropic orientation nucleate in the sample and expand until the whole sample becomes homeotropic. This relaxation process from flow-induced quasi-planar to surface-induced homeotropic alignment was also monitored by SHG. It was found that in the homeotropic state the first nematic layer presents a pretilt of 38 degrees almost isotropically distributed in the plane of the cell, with a slight preference for the direction of the previous flow.

\*e-mail: fazio@fy.chalmers.se
1 Introduction

Substrate-induced alignment of liquid crystals (LCs) is of crucial significance for LC display devices. Liquid crystal molecular ordering at an interface can be significantly different from that in the bulk [1, 2]. This problem is not only of fundamental interest, but also of practical importance. In the past decade numerous studies have been dedicated to the phenomenon of anchoring of liquid crystals on solid substrates [3], but the mechanisms by which a surface imposes a certain orientation to a liquid crystal is far from being well understood. Most of the research in this field has been done with nematic liquid crystals (NLCs) which are the simplest liquid crystalline phase formed by elongated molecules that, in average, are oriented parallel to each other [4]. Depending on the treatment, a solid surface may orient the LC in a certain direction, called anchoring direction, which is not necessarily parallel to that of the first few molecular layers in contact with the surface [5].

In the bulk of a nematic liquid crystal the molecules are aligned along a preferred direction called director, \( \mathbf{n} \), in a nonpolar manner [4], i.e.

\[
\mathbf{n} \leftrightarrow -\mathbf{n}.
\]  

(1)

This leads to a macroscopic structure which is centrosymmetric, where second-harmonic generation (SHG) is forbidden (in the dipole approximation). The second-harmonic (SH) nonlinear polarization is proportional to the SH nonlinear susceptibility \( \chi^{(2)} \) which, under the dipole approximation, vanishes for a medium with inversion symmetry [6]. At an interface, however, the inversion symmetry is broken and \( \chi^{(2)} \neq 0 \) [7]. This makes SHG a surface-sensitive technique which can be used for instance to determine the orientational distribution of a surface monolayer of LC molecules in absence or in presence of the LC bulk.

Generally, capillary flow influences the orientation induced by a solid substrate on a nematic liquid crystal [8], in particular when the anchoring in weak, as in the case of homeotropic alignment by surfactants. In the case of aligning Langmuir-Blodgett (LB) monolayers of fatty acids it is found [9] that during capillary flow in the nematic phase the liquid crystal (MBBA) is quasi-planarly oriented along the flow direction with a bulk splay-bend deformation (see Figure 1). As soon as the flow ceases, circular homeotropic domains (orientation along the substrate normal) nucleate in the sample and expand until the whole sample becomes homeotropic. The speed of expansion of the homeotropic domains is found to be very sensitive to the fatty acid monolayer [10]: it decreases with increasing the length of the fatty acid alkyl chain and changes substantially for small variations in the chain, like the addition of two \( \text{CH}_3 \) groups. This fact suggests that the LB film
Figure 1: During filling (left) the NLC adopts a quasi-planar alignment with splay-bend deformation and preferred orientation along the filling direction (left). Once the flow stops, domains of homeotropic orientation nucleate and expand in the sample (right).

plays a role in the process of relaxation from the flow-induced quasi-planar to the surface-induced homeotropic alignment. The achieved homeotropic alignment is generally very good [11] but the surface preserves a memory of the flow which can be revealed after that electric-field–induced breaking of the homeotropic anchoring takes place in the sample [12].

In this work we used optical SHG to study the alignment of a nematic liquid crystal (5CB) on a LB monolayer of stearic acid (C18) during and after capillary flow. The technique allows us to evaluate the orientational distribution of the nematic molecules of the first monolayer in contact with the aligning LB film [13] and thus to study indirectly the effect of the capillary flow on the LB monolayer itself.

2 Theory

In SHG the second-harmonic signal is generated by the nonlinear polarization

\[ P^{(2)}(2\omega) = \chi^{(2)} : E(\omega) E(\omega), \]

where \( E(\omega) \) is the excitation field at the fundamental frequency \( \omega \), and \( \chi^{(2)} \) is the second-order nonlinear susceptibility tensor. In the case of surface SHG \( P^{(2)}(2\omega) \) and \( \chi^{(2)} \) are the surface second-order nonlinear polarization and susceptibility tensor, respectively. The intensity \( I(2\omega) \) of the generated second-harmonic light is given by [14]:

\[ I(2\omega) \propto \left| e_{2\omega} \chi^{(2)} : e_\omega e_\omega \right|^2 I^2(\omega), \]

\[ (3) \]
where $I(\omega)$ is the fundamental light intensity and $e_{2\omega}$ and $e_\omega$ represent the polarization of the SH and of the fundamental light, respectively.

If LC molecules are adsorbed on a surface, they generally form a polar layer as the surface imposes a preferred molecular alignment. In this case, the nonlinear susceptibility of the substrate is negligible with respect to that of the LC monolayer. Moreover, if the LC possesses a dominant hyperpolarizability $\beta^2_{\xi\xi\xi}$ along the long molecular axis $\xi$, the second-order nonlinear optical susceptibility coefficients can be written in the simple form [15]:

$$d_{xyz} = \frac{1}{2} \chi^{(2)}_{xyz} = \frac{1}{2} N_s \langle (\mathbf{x} \cdot \xi)(\mathbf{y} \cdot \xi)(\mathbf{z} \cdot \xi) \rangle \beta^{(2)}_{\xi\xi\xi},$$

(4)

where $N_s$ is the surface density of the molecules, $\mathbf{x}$, $\mathbf{y}$ and $\mathbf{z}$ are the substrate coordinates as shown in Figure 4, and $\langle \rangle$ denotes the average over the molecular orientational distribution function, $f_{\theta\phi}$, where $\theta$ and $\phi$ are the polar and azimuthal angles of $\xi$ with respect to the substrate coordinate system (see Figure 4).

For an isotropic distribution of molecules in a monolayer there are only two independent non-vanishing components of $\bar{d}$ [15], namely $d_{zzz}$ and $d_{izz}$, where $i = x, y$:

$$d_{zzz} = \frac{1}{2} N_s \langle \cos^3 \theta \rangle \beta^{(2)}_{\xi\xi\xi},$$

(5)

$$d_{izz} = \frac{1}{4} N_s \langle \sin^2 \theta \cos \theta \rangle \beta^{(2)}_{\xi\xi\xi},$$

(6)

where $\theta$ is the angle between $\xi$ and $\mathbf{z}$ (polar angle in Figure 4). For molecules having a preferred alignment along $\mathbf{x}$ (as, for instance, a flow-induced orientation, with the flow in the $\mathbf{x}$ direction) the independent components of the $\bar{d}$-tensor are six [15]:

$$d_{zzz} = \frac{1}{2} N_s \langle \cos^3 \theta \rangle \beta^{(2)}_{\xi\xi\xi},$$

$$d_{xxx} = \frac{1}{2} N_s \langle \sin^3 \theta \rangle \langle \cos^3 \phi \rangle \beta^{(2)}_{\xi\xi\xi},$$

$$d_{zxy} = d_{yzy} = d_{yyz} = \frac{1}{2} N_s \langle \cos \theta - \cos^3 \theta \rangle \langle 1 - \cos^2 \phi \rangle \beta^{(2)}_{\xi\xi\xi},$$

$$d_{zxx} = d_{zxx} = d_{xxz} = \frac{1}{2} N_s \langle \cos \theta - \cos^3 \theta \rangle \langle \cos^2 \phi \rangle \beta^{(2)}_{\xi\xi\xi},$$

$$d_{xxz} = d_{xxz} = d_{zzz} = \frac{1}{2} N_s \langle \sin \theta - \sin^3 \theta \rangle \langle \cos \phi \rangle \beta^{(2)}_{\xi\xi\xi},$$

$$d_{xyy} = d_{yxy} = d_{yyx} = \frac{1}{2} N_s \langle \sin^3 \theta \rangle \langle \cos \phi - \cos^3 \phi \rangle \beta^{(2)}_{\xi\xi\xi}. $$

(6)
where $\phi$ is the molecular azimuthal angle, the angle that the projection of the long molecular axis makes with the $x$ axis, as defined in Figure 4. In Equation 6 the distribution functions for $\theta$ and $\phi$, $f_\theta$ and $g_\phi$, are assumed to be independent [15] (this is however not always the case [16]), i.e., $f_\theta \phi = f_\theta \cdot g_\phi$.

The distribution functions for the polar angle $\theta$ (polar distribution functions) generally used are $\delta$- and Gaussian functions:

$$f_\theta = F \delta(\theta - \theta_0), \quad f_\theta = F e^{-\frac{(\theta - \theta_0)^2}{2\sigma^2}},$$

where $\theta_0$ and $\sigma$ are the average molecular tilt and its variance. Combining the $d$-coefficients in Equation 6 leads to

$$\langle \sin^3 \theta \rangle_{f_\theta} = \frac{d_{xxx} + d_{xyy}}{d_{xxx} + d_{xyy} + d_{xzz}},$$

$$\langle \cos^3 \theta \rangle_{f_\theta} = \frac{d_{zzz}}{d_{zzz} + d_{xxx} + d_{zyy}},$$

where $\langle \rangle_{f_\theta}$ is the average over the polar distribution function. Thus, by measuring the $d$-coefficients with a SHG experiment $\theta_0$ and $\sigma$ can be calculated.

The azimuthal distribution function $g_\phi$ can be built up from a Fourier series [15]:

$$g_\phi = \sum_n a_n \cos n\phi.$$ 

From the remaining independent combinations of the $d$-coefficients in Equation 6 the Fourier coefficients $a_n$ can be determined up to the third order.

Finally, from the azimuthal distribution function $g_\phi$ a surface in-plane order parameter, $S_s$, can be calculated. Assuming independent distributions for $\theta$ and $\phi$, $S_s$ can be written as [17, 18]:

$$S_s = \langle \cos 2\phi \rangle_{g_\phi} = \frac{1}{2} a_2 = \frac{d_{xxx} - d_{zyy}}{d_{xxx} + d_{zyy}},$$

where the average is done over the area illuminated by the laser beam. In case of perfect order in the liquid crystal monolayer $S_s = 1$, while for a completely isotropic azimuthal distribution of molecules in the monolayer $S_s = 0$.

### 3 Experiment

LB monolayers of stearic acid (C18) were deposited onto ITO coated glass plates that were assembled in sandwich cells 10 $\mu$m thick. The isotherm of
Figure 2: Isotherm of stearic acid (C18). The monolayers were deposited at a surface pressure of 20 mN m$^{-1}$ and at an area-per-molecule of 0.2 nm$^2$. Transfer ratio of deposition was close to one.

Stearic acid is shown in Figure 2 where the deposition conditions are indicated. The monolayers were deposited with a transfer ratio close to one.

The cells were filled with 5CB (NCΦΦC$_5$H$_{11}$) in the nematic phase (5CB exhibits a nematic phase between 24°C and 35°C). During capillary flow the NLC adopts a quasi-planar alignment with splay-bend deformation and preferred orientation along the flow direction (Figure 1). As in the case of MBBA [9], the flow-induced alignment is metastable and transforms into homeotropic via nucleation and expansion of homeotropic domains. An example of how the homeotropic domains expand in the quasi-planar one after the capillary flow has ceased is shown in Figure 3. 5CB also possesses a dominating hyperpolarizability along the long molecular axis $\xi$, which makes it suitable for SHG studies.

The filling and relaxation processes were monitored with a Nd:YAG laser ($\lambda_\omega = 1064$ nm, $\lambda_2\omega = 532$ nm). Angles and coordinate system are shown in Figure 4. The SH output was detected by a photomultiplier. A typical output data-file is shown in Figure 5. The procedure was repeated for all in-out polarization combinations, and for several angles $\Phi$. Since once a cell is filled it cannot be used any longer, a different cell was used for each measurement.
Figure 3: Cell between crossed polarizers. The 5CB flow has ceased and the homeotropic domain (black) expands in the quasi-planar one (gray). The cell thickness is 10 µm. The three pictures are taken at a time interval of 20 s. Magnification 10.

Figure 4: Schematic representation of the experimental geometry. $\theta_i$ is the incidence angle (55 deg). The flow is along the x-direction. $\theta$ and $\phi$ are the polar and azimuthal angles, respectively of the LC monolayer molecules. $\Phi$ is the angle between the plane of incidence and the direction of the flow. The $xy$-plane is the substrate plane and the z direction is the “homeotropic direction”.

Figure 5: Example of datafile. SHG is monitored before, during, and after filling. Polarization combination and azimuthal sample orientation with respect to the flow direction, $\Phi$, are specified.

The cell thickness were measured previos filling with a spectrophotometer ($\pm 0.1 \mu m$).

4 Results

Figure 6 shows the intensity of the SH light generated during capillary flow of 5CB at room temperature (nematic phase) as a function of the angle $\Phi$ between the flow direction, $x$ (Figure 4), and the plane of incidence for the four different polarization combinations. All signals show a substantial anisotropy. The different SH response for $\Phi = 0$ and $\Phi = 180$ in the PP plot reflects the preferential alignment of the molecules along the filling direction, that is, the LC molecules are tilted preferentially along the flow direction.

The electric quadrupole nonlinearity of the LC might also contribute to the SHG [19]. This contribution is generally many orders of magnitude smaller that the dipolar one and proportional to the thickness of the nematic layer [20,21]. To ensure that the SH signal of Figure 6 was only coming from the NLC surface monolayer the SHG intensity was measured as a function of the cell thickness for some polarization combinations (Figure 7).

The data in Figure 6 could be fitted following [15] to find the values of the second-order nonlinear susceptibilities that yeald the coefficients of the distribution functions $f_\theta$ and $g_\phi$ (Equations 7-8 and 11, respectively). The calculated values of $\theta_{0,\text{flow}}$, $\sigma_{\text{flow}}$, and of the $a_{n,\text{flow}}$ coefficients are listed in Table 1. The azimuthal orientational distribution $g_{\phi,\text{flow}}$ of the monolayer during...
Figure 6: SHG signal (arbitrary units) as a function of the angle $\Phi$ (Figure 4) during 5CB capillary flow. $\Phi = 0$ corresponds to the flow direction. The open circles are the data with error bars, and the lines are the fits following [15]. The input-output polarizations are shown. S-polarization is perpendicular to the plane of incidence. P-polarization is parallel to the incidence plane. The thickness of the cells used was 10 $\mu$m.

Table 1: Polar tilt angle and azimuthal orientation distribution coefficients of 5CB during flow.

| Distribution   | $\theta_{0,\text{flow}}$ [deg] | $\sigma_{\text{flow}}$ [deg] | $a_{1,\text{flow}}$ | $a_{2,\text{flow}}$ | $a_{3,\text{flow}}$ |
|----------------|-------------------------------|-------------------------------|---------------------|---------------------|---------------------|
| $\delta(\theta)$ | 78                            | 0                             | 0.121               | 0.081               | 0.044               |
| Gaussian       | 78                            | 3                             | 0.098               | 0.081               | 0.062               |
capillary flow was calculated from the $a_{n,\text{flow}}$ coefficients listed in Table 1 and is shown in Figure 8. The distribution is highly anisotropic and shows that flow causes the molecules to lie preferentially parallel to the flow direction with a pretilt angle $\theta_{0,\text{flow}} = 78$ degrees. The surface order parameter, as calculated from $a_{2,\text{flow}}$, is quite small, $S_{s,\text{flow}} = 0.04$.

After the capillary flow has ceased the metastable quasi-planar alignment relaxes to homeotropic and the SHG signal changes (as in the Figure 5). A measurable signal, almost isotropic in $\Phi$, was detected for SP and PP polarization combinations (Figure 9), while no detectable signal was generated for SS and PS polarization combinations. These two facts suggest that, after relaxation, the monolayer is isotropically oriented in the $xy$ plane. S-out conversions are forbidden by symmetry in such a case [15], whereas the allowed conversions should produce a signal which is azimuthally isotropic.

The values of the tilt angle $\theta_{0,\text{hom}} \pm \sigma_{\text{hom}}$, and of the $a_{n,\text{hom}}$ coefficients calculated from the fits in Figure 9 are listed in Table 2 and the azimuthal distribution function $g_{\phi,\text{hom}}$ of the relaxed LC monolayer is shown in Figure 10. The coefficient $a_{2,\text{hom}}$ of the relaxed monolayer is zero, which implies that the in-plane order parameter $S_{s,\text{hom}} = 0$. A zero surface order parameter corresponds to an isotropic azimuthal distribution of the NLC molecules in the monolayer. However, the value of $S_{s,\text{hom}}$ is questionable because it is within the experimental accuracy of our setup. We can only conclude that
Figure 8: Azimuthal orientational distribution function $g_{\phi, \text{flow}}$ of the first NLC layer during capillary flow.

Figure 9: SHG signal (arbitrary units) vs $\Phi$ angle from a 5CB cell after flow. Only SP and PP polarization combination generated detectable signal.

Table 2: Polar tilt angle and azimuthal orientation distribution coefficients of 5CB after relaxation to the bulk homeotropic alignment.

| Distribution | $\theta_{0, \text{hom}}$ [deg] | $\sigma_{\text{hom}}$ [deg] | $a_{1, \text{hom}}$ | $a_{2, \text{hom}}$ | $a_{3, \text{hom}}$ |
|--------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| $\delta(\theta)$ | 39              | 0               | 0.107           | 0               | 0.049           |
| Gaussian     | 38              | 7               | 0.111           | 0               | -0.010          |
Figure 10: Azimuthal orientational distribution function $g_{\phi,\text{hom}}$ of the NLC molecules in the first layer after the flow has ceased and the nematic layer has relaxed from the flow-induced alignment to the homeotropic one.

$S_{s,\text{hom}}$ must indeed be very small.

The azimuthal distribution function $g_{\phi,\text{hom}}$ shows memory of the flow: the NLC molecules are tilted an angle $\theta_{0,\text{hom}} = 39$ degrees almost isotropically, with a slight preference for the flow direction ($\Phi = 0$).

The relaxed state was studied by conoscopy and the homeotropic alignment was found to be very good.

5 Discussion and conclusions

During capillary flow the first NLC monolayer in contact with the aligning LB film results to be oriented in the direction of the flow with a quite large pretilt ($\theta_{0,\text{flow}} = 78$ degrees). If the CN groups of the 5CB molecules are oriented towards the surface, then during flow the molecules are tilted as in Figure 11. This suggests that the LB film itself is affected by the flow. Once the flow ceases the stearic acid alkyl chains relax to their equilibrium orientation with a pretilt $\theta_{0,\text{hom}} = 38$ degrees almost isotropically distributed in the cell plane, with a preference for the flow direction. The NLC monolayer in contact with the surface follows the fast relaxation of the LB film and propagates the homeotropic alignment into the LC bulk via the long-range nematic and the elastic interactions. This interpretation is in agreement with the observed dependence of the relaxation speed on the LB monolayer [10].
In polarizing microscopy one observes circular domains of homeotropic alignment expanding in the quasi-planar structure (see also Ref. [9]). This regular circular form is indication of the isotropic character of the surface relaxation process, which is confirmed by the isotropic azimuthal distribution of the NLC molecules after realaxation. Even though after relaxation the LB film presents a substancial pretilt, the NLC bulk is homeotropically oriented because the pretilt is distributed almost isotropically (conical degeneracy) in the cell plane and the overall effect on the LC bulk is that of inducing homeotropic alignment.

Some authors refer to this phenomenon as subsurface deformation [2, 22]. In general, the bulk NLC alignment differs from that of the first monolayer(s) and a subsurface distortion exists for any tilted anchoring [23]. However, the analysis is made assuming that the surface tilt is confined to the $xz$ plane and that the anchoring at the surface is strong (infinite). In this case the largest distortion, estimated to be about 1–2 degrees of polar orientation, is localized over the first molecular layers and it has a tail decaying as the inverse distance from the surface which makes it to extend over a microscopic length. However, NLCs in general align weakly on surfactants. The anchoring strengths are on the order of $10^{-6}$ J m$^{-2}$ [24], up to three orders of magnitude smaller than what is generally considered strong anchoring. For such weak anchorings one would expect the surface and the bulk orientations to differ more substantially than in the case of strong anchoring, which is in fact what we observed in this work (the bulk and surface tilts differ by 39 degrees).

The LB monolayer preserves a memory of the flow, which is visible through the anisotropic azimuthal distribution of the first nematic layer, which shows that the surfactant molecules have a slight preference to be oriented in the direction of the previous flow. This flow memory is not directly visible in the equilibrium homeotropic alignment, but it has been
observed in the case of MBBA homeotropically aligned by stearic acid [12]: after electric-field–induced breaking of the anchoring the homeotropic alignment is not immediately restored, but the sample presents a quasi-planar orientation along the direction of the previous flow.

In conclusion, we have directly shown that capillary flow influences considerably the orientation of the first monolayer of nematic liquid crystal in contact with the surfactant LB film, and, indirectly, that the flow affects the surfactant layer as well.

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