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Liquid-crystal monolayers in high magnetic fields: a second-harmonic generation study

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Abstract

We present the first experimental results on the molecular orientation of LC monolayers in high magnetic fields. The influence of the external magnetic field on the in-plane molecular orientation of 4-n-octyl-4'-cyanobiphenyl (8CB) molecules on rubbed polymer surfaces is studied with the use of second-harmonic generation. It is found that the orientation of the LC molecules is fixed with respect to the rubbing axis upto magnetic fields of 20 T. These results are in-line with the previously proposed model for surface-induced LC alignment based on a LC bulk interacting with a fixed interfacial LC monolayer. It can also be concluded that hardly any collective behaviour of the LC molecules, constituting the first monolayer, is present.

1. Introduction

It is well-known that the orientational behaviour of liquid crystals (LCs) in a cell can vary greatly in the vicinity of interfaces (see e.g. Ref. [1]). By applying proper surface treatments, such as the application of surfactant-layers or rubbing polymer layers etc., preferential orientations in the bulk of a LC ranging from parallel to perpendicular to the surface can be obtained (see e.g. Ref. [2]). Almost all applications of LCs in devices are based on this phenomenon. In those switching LC devices, the second preferential orientation, different from the surface-induced one, usually is obtained by applying an external electric field. Both the surface-induced LC alignment and the switching behaviour of LC cells have been studied in great detail over the past decades [1, 2]. However, the absence of detailed information on the LC orientation in the proximity of the interface, being the

boundary conditions of this problem, has been a major problem in a great number of those studies. For this reason, a wide variety of techniques have been employed over the past years to study the LC alignment in such detail that some information on the surface region could be obtained [1, 2]. However, sufficient surface sensitivity is seldom obtained to study the interactions at the surface at the microscopic level.

In the last decade second-harmonic generation (SHG), which is intrinsically surface specific, has proven to be an excellent tool to study the molecular orientation of the LC molecules at interfaces [3–7]. In those studies, a wealth of detailed information on the interfacial LC orientation has been obtained, yielding novel insights in the phenomenon of surface-induced LC alignment. It has been found that the polar orientation of LC molecules at surfactant-covered interfaces need not be directly correlated to the resulting LC bulk alignment [8, 9]. Yet, it appeared possible to influence the interfacial LC alignment by applying different boundary conditions to the interfacial LC molecules, either by using different

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preparation techniques for the silane-surfactant layers [9] or by increasing the surface pressure in mixed LC/surfactant layers on a Langmuir–Blodgett trough [10]. Furthermore, the industrially important process of rubbing-induced LC alignment has been studied in some detail with SHG [4, 6, 11, 12]. From those studies, it has been found that the interfacial LC alignment completely determines the resulting LC bulk alignment. Also, the formation of a pretilt angle, i.e., the angle between the average molecular orientation in the bulk of the cell and the surface, and the discrepancy between the interfacial and the polar bulk orientation has been clarified by interpretation of the SHG experiments [11]. From all SHG experiments it can be concluded that the conventional model of a LC bulk interacting with some treated surface should be interchanged with a model of a surface strongly interacting with the first LC monolayer, which acts as the boundary condition for the orientation of the LC bulk.

It should be noted here, that all SHG studies have been focussed on the interactions between the surface and the interfacial LC molecules. In the interpretation, the interfacial orientation and the resulting bulk orientation have been correlated. Although the switching behaviour of LCs by applying external fields is greatly influenced by the exact boundary conditions, no SHG investigations have been made on the influence of *external* fields on the interfacial LC alignment.

The absence of such studies is mainly due to the lack of experimental facilities to combine the application of sufficiently strong external fields with the SHG technique. The application of strong electric fields perpendicular to the surface can easily be obtained by using semi-transparent electrodes over a complete LC cell. However, in this way not only the external field is acting on the interfacial LC molecules, but also the reoriented bulk of the LC is acting on the molecules at the interface. A second problem in such a geometry is the interpretation of the SHG data due to the mixed contribution to the SH signal of LC monolayer, LC bulk and electrodes. Application of large in-plane electric fields over an area that can be probed by SHG, minimizing the influence of the electrodes on the SH signal, is much more difficult; And, in this geometry the effects of the LC bulk are still present.

Therefore, the use of magnetic fields seems more promising. Here, the main problem is the strength of such fields. From a simple calculation it can be shown that a fairly high magnetic field should be applied, which imposes novel experimental difficulties. In this communication, we present the first experimental SHG studies on the orientation of interfacial LC molecules in an external magnetic field. The in-plane orientation of the LC molecules adsorbed on rubbed polyimide layers has been

determined for magnetic fields upto 20 T. The results indicate the absence of strong collective behaviour of the LC monolayer and are in-line with the earlier obtained model for surface-induced LC alignment [11].

2. Theory

For surface SHG, the signal at the second-harmonic frequency 2ω is generated by the induced surface nonlinear polarization

$$\mathbf{P}^{(2)}(2\omega) = \chi^{(2)}(-2\omega; \omega, \omega): \mathbf{E}(\omega) \mathbf{E}(\omega).$$

Here, $\mathbf{E}(\omega)$ denotes the excitation field at the fundamental frequency ω and $\chi^{(2)}$ is the surface nonlinear susceptibility tensor. It can be shown that the observed SH intensity $I(2\omega)$ can be related to the induced polarization via [7]

$$I(2\omega) \propto |\mathbf{P}^{(2)}(2\omega)|^2.$$

In our experimental geometry (see Fig. 1), the components of the optical excitation field at frequency ω are given by

$$\begin{aligned} E_x(\omega) &\propto \cos(\alpha - \alpha_0), \\ E_y(\omega) &\propto \sin(\alpha - \alpha_0)e^{i\Delta}, \\ E_z(\omega) &= 0, \end{aligned} \quad (1)$$

where α denotes the angle of the polarizer with respect to the \hat{x} -axis (as Fig. 1). Since the experiments have been conducted in high magnetic fields, the influence of the magnetic field on the polarization of the incident light cannot be neglected. The angle α_0 has been introduced to incorporate this effect, it denotes the angle over which the plane of polarization is rotated due to the Faraday rotation of the incident wave travelling through the entrance prism. The magnitude of $\alpha_0 = IVB$, where the Verdet constant $V = 2.8^\circ/\text{cm T}$, for light of 532 nm wavelength passing through BK7 glass. Δ is the phase difference between E_x and E_y introduced by the total internal reflection at the glass/air interface in the prism. Under our experimental conditions ($\lambda = 532$ nm, BK7 glass, angle of incidence 45°) $\Delta = 37^\circ$.

For the cyanobiphenyl LC molecules that have been used in this experiment, it has already been argued that the elements of the $\chi^{(2)}$ tensor can be related to the dominant element $\alpha_{ijk}^{(2)}$ of the hyperpolarizability tensor $\alpha^{(2)}$ of the adsorbed molecules by [7]

$$\chi_{ijk}^{(2)} = N_s \langle (\hat{i} \cdot \hat{\zeta}) (\hat{j} \cdot \hat{\zeta}) (\hat{k} \cdot \hat{\zeta}) \rangle \alpha_{ijk}^{(2)}. \quad (2)$$

Here, N_s is the surface density of the LC molecules, $\hat{i}, \hat{j}, \hat{k}$ refer to the sample coordinates, and the brackets denote an appropriate average over all molecular orientations. For surfaces exhibiting C_{1v} -symmetry along \hat{x} , with

independent polar Θ and azimuthal ϕ distributions of ζ , the following non-vanishing elements of $\chi^{(2)}$ can be discerned:

$$\begin{aligned}\chi_{xxx}^{(2)} &= N_s \langle \sin^3 \Theta \rangle \langle \cos^3 \phi \rangle \alpha_{\zeta\zeta\zeta}^{(2)}, \\ \chi_{xyy}^{(2)} &= \chi_{yxy}^{(2)} = \chi_{yyx}^{(2)} \\ &= N_s \langle \sin^3 \Theta \rangle \langle \cos \phi \sin^2 \phi \rangle \alpha_{\zeta\zeta\zeta}^{(2)}, \\ \chi_{xzz}^{(2)} &= \chi_{zxx}^{(2)} = \chi_{zxx}^{(2)} \\ &= N_s \langle \sin \Theta \cos^2 \Theta \rangle \langle \cos \phi \rangle \alpha_{\zeta\zeta\zeta}^{(2)}, \\ \chi_{zxx}^{(2)} &= \chi_{xzz}^{(2)} = \chi_{xzz}^{(2)} \\ &= N_s \langle \cos \Theta \sin^2 \Theta \rangle \langle \cos^2 \phi \rangle \alpha_{\zeta\zeta\zeta}^{(2)}, \\ \chi_{zyy}^{(2)} &= \chi_{yzy}^{(2)} = \chi_{yzy}^{(2)} \\ &= N_s \langle \cos \Theta \sin^2 \Theta \rangle \langle \sin^2 \phi \rangle \alpha_{\zeta\zeta\zeta}^{(2)}, \\ \chi_{zzz}^{(2)} &= N_s \langle \cos^3 \Theta \rangle \alpha_{\zeta\zeta\zeta}^{(2)}.\end{aligned}\quad (3)$$

Here, Θ denotes the polar angle between \hat{z} and ζ and ϕ is the azimuthal angle of the LC molecular orientation with respect to \hat{x} . Note that the angular brackets denote an average over all molecular orientations within the (macroscopic) probed area.

In the presented experiments, only the in-plane orientational distribution of the LC monolayer is of interest. The two independent elements $\chi_{xxx}^{(2)}$ and $\chi_{xyy}^{(2)}$, both directly related to the in-plane distribution, can be determined by measuring the SH response in transmission (see Fig. 1) upon rotation of the incident polarization α . In the experiment the SH response is measured upon rotation of the polarizer angle α over 180° at a series of different magnetic field strengths. Any change in the azimuthal distribution due to the presence of the magnetic field should appear in the SH response.

In the following we will discuss the interaction between a magnetic field \mathbf{B} and a monolayer of LC molecules. In general, the magnetization \mathbf{M} induced by an external magnetic field \mathbf{B} is given by

$$\mathbf{M} = \chi^M \cdot \mathbf{B}, \quad (4)$$

where χ^M is the magnetic susceptibility tensor. The resulting torque can be found via

$$\mathbf{T} = \mathbf{M} \times \mathbf{B}. \quad (5)$$

For one individual LC molecule with orientation (Θ, ϕ) in a magnetic field \mathbf{B} along \hat{y} , where the first-order magnetic polarizability tensor χ^M is dominated by a single component $\alpha_{\zeta\zeta}^M$ along the long molecular axis ζ^1 ,

¹ Usually, the value of $\Delta\chi^M$ is used, where $\Delta\chi_{\parallel}^M = \chi_{\parallel}^M - \chi_{\perp}^M$. For simplicity we only adopted the element along ζ .

the following azimuthal torque T_ϕ towards the magnetic field axis can be found:

$$T_\phi = \mu_0^{-1} \alpha_{\zeta\zeta}^M \cos \phi \sin \phi \cos \Theta B^2, \quad (6)$$

where μ_0 is the permeability of free space. From Eq. (6) it can be seen that the strength of the interaction depends on the molecular orientation (Θ, ϕ) and is quadratically dependent on magnetic field strength. Note that for the surface studied, $\Theta \simeq 70^\circ$.

Next, the effect of the magnetic field on the resulting molecular distribution will be discussed. Fig. 2 shows a plot of the azimuthal orientational distribution of the LC molecules on a rubbed polyimide surface as determined by SHG [5]. The rubbing direction is along the positive \hat{x} -axis. The result explicitly shows that rubbing causes the molecules to lie preferentially parallel and anti-parallel to the rubbing direction, more parallel than anti-parallel. Details on the variation of the molecular distribution with the different parameters, like the polymers and the rubbing strength have been discussed elsewhere [4, 5, 11]. The magnetic field \mathbf{B} is directed along the \hat{y} -axis.

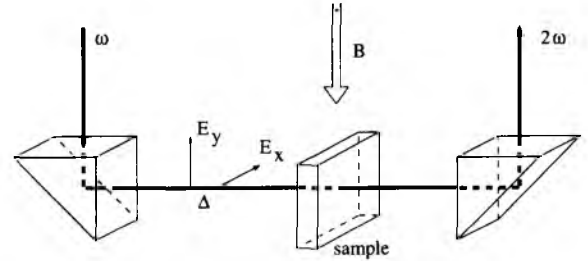


Fig. 1. Experimental geometry for the SHG experiments performed in a 20 T magnet. Details are discussed in the text.

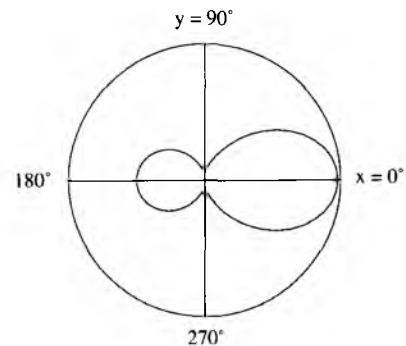


Fig. 2. Azimuthal orientational distribution of 8CB liquid crystal molecules adsorbed on a rubbed polyimide surface, as determined by SHG.

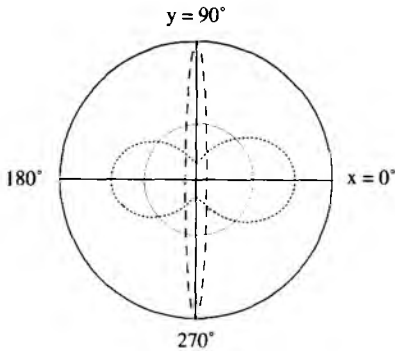


Fig. 3. Azimuthal orientational distribution of LC molecules adsorbed on a rubbed polyimide surface under application of different magnetic field strengths along the y -axis.

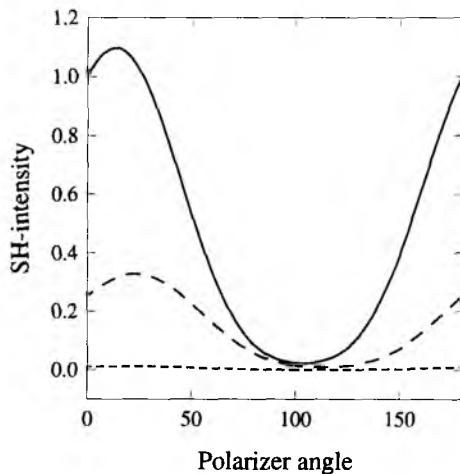


Fig. 4. Simulated SH response of the LC monolayers with the azimuthal orientational distributions of Fig. 3.

To show the effect of the field B on the molecular distribution presented in Fig. 2, three possible situations have been plotted in Fig. 3. The dotted line refers to the case when no magnetic field is applied, the dashed line refers to the case when a very strong magnetic field is applied, while the solid line refers to the intermediate situation. In order to obtain information on the sensitivity of the employed SH experiment, the simulated SH responses related to the three distributions are shown in Fig. 4. For low magnetic fields ($B \approx 0$) the distribution is C_{1v} -symmetric around the x -axis, resulting in a maximum SH signal as the excitation polarization is along this axis ($\alpha - \alpha_0 = 0$). In the other extreme ($B \approx \infty$), the distribution is nearly C_{2v} -symmetric. In this case the SH response is symmetry-forbidden. It can also be seen that for an intermediate case the SH response has been changed substantially.

3. Experimental

The experiments were performed with the frequency-doubled output of a Q-switched Nd:YAG-laser producing 532 nm light pulses of 8 ns duration at a repetition rate of 30 Hz with a pulse energy of 10 mJ. The laser beam (cross-section 15 mm^2) is directed at normal incidence on the sample which is mounted in the bore of a 20 T Bitter magnet of the Nijmegen High Magnetic Field Laboratory (see Fig. 1). In the experiment the SH intensity is measured upon rotation of the incident polarization over 180° with the use of a half-wave plate. The detection of the SH photons is performed after appropriate spectral filtering by a photomultiplier with gated electronics. No polarization discrimination is done.

The samples used in the experiments were produced by spin coating a solution of polyimide onto 1.1 mm thick Corning 7059 glass plates. The average thickness of the resulting polymer films was 110 nm after a thermal curing step. The preferential orientation of the polyimide surface was imposed by rubbing and was carried out on a rubbing machine similar to the one published by Becker et al. [13]. In this way the rubbing process is performed with excellent reproducibility. The 8CB monolayers were deposited by evaporation [9], using SHG as an in situ monitor. The resulting surface density of the molecules is $2 \times 10^{14} \text{ cm}^{-2}$, ensuring that the complete SHG signal is generated by the LC molecules. Further details on the sample preparation and characterization have been published elsewhere [5, 6, 11].

4. Results

As has been shown by the simulations in Fig. 4, the effect of changes in the molecular orientation due to external fields do show up in the SH response. In the reported experiments we have measured the SH response of LC monolayers evaporated onto rubbed polyimide surfaces, where the molecules are preferentially aligned along the rubbing direction. Before mounting the samples in the bore of the magnet, it has been verified that the molecular orientation after rubbing is identical to those published before and shown in Fig. 3. After mounting the samples, the experimental setup has been tested by comparing the zero magnetic field data with the original recordings.

In Fig. 5 the raw SH response upon rotation of the input polarization is shown for a LC monolayer sample exposed to magnetic fields of $B = 0, 10$ and 20 T . The solid lines represent a fit to the data points for the different data sets. From these data it can be observed that application of a magnetic field shifts the curves but does not affect the line shape according to Fig. 4. As has

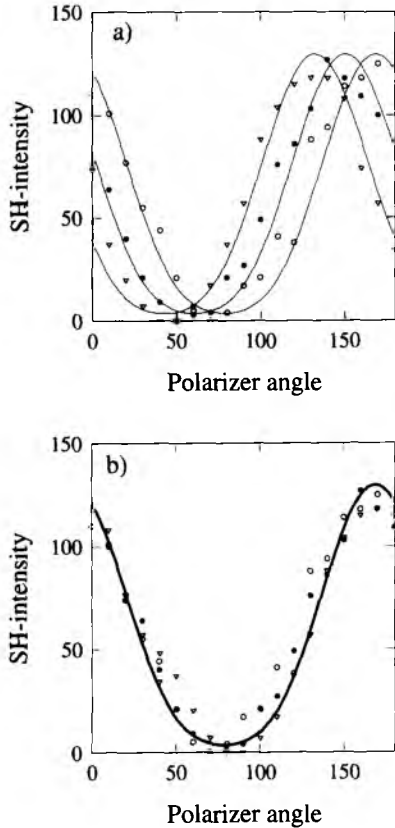


Fig. 5. Experimentally determined SH response of an 8CB monolayer on a rubbed polyimide surface in the presence of different magnetic fields. (a) The raw data for $B = 0, 10$ and 20 T have been depicted. (b) All data points have been corrected for the known amount of Faraday rotation.

been indicated in the theory section, the Faraday rotation of the excitation light when passing through the glass prism before hitting the sample, has to be incorporated in the analysis of the data. For our experimental setup this effect can be calculated easily.

In Fig. 5(b) the same data points corrected for the known amount of Faraday rotation have been shown. All data sets now seem equal within the experimental errors, which implies that the azimuthal orientation distribution remains unaffected up to $B = 20$ T. Also data obtained with the magnetic field in the opposite direction and at intermediate values of B , once corrected for the Faraday rotation, are equal to the curves presented in Fig. 5(b).

5. Discussion

In the azimuthal alignment of LCs with magnetic fields two parameters are of primary interest. First, the energy

difference ΔE_M between alignment parallel and perpendicular to the direction of the magnetic field. Second, the energy difference between alignment along or perpendicular to the rubbing-induced easy axis, the so-called azimuthal anchoring energy ΔE_ϕ . A prerequisite for field-induced alignment is the collective behaviour of a great number of molecules, since ΔE_M for one molecule is much less than the thermal energy

$$\frac{\Delta E_M}{k_B T} \ll 1. \quad (7)$$

Experiments show that weakly coupled LCs in cells can be switched at field strengths of the order of 0.1 T. From this it can be concluded that 10^9 molecules work in unison. To this number a volume is related, characterized by a coherence length $l_{\text{coh}} \approx 1 \mu\text{m}$. So, in LC cells usually the surface anchoring has been overcome at field strengths of the order of a few tenths of a Tesla. At that field elastic and magnetic interactions are comparable in magnitude. For the surfaces studied, the polar anchoring energy is reported to be 10^{-7} J/cm^2 , independent of rubbing strength [4]. For these surfaces azimuthal anchoring energies are of the order of 10^{-10} J/cm^2 , for the different rubbing conditions. Therefore, in the experiment a magnetic field was applied in the plane of the substrate.

Next, we consider a 2D system. It should be noted here that the above-mentioned values for the surface anchoring energies are based on continuum models, simply extrapolating the bulk LC parameters towards the substrate. Therefore, we firstly suppose that the coherence length of the LC material is the same in all dimensions. This implies that a total N_{tot} of $N_s l_{\text{coh}}^2$ molecules work in unison. From a simple calculation it can be found that for $B = 3.3$ T, $\Delta E_M^{\text{tot}} = N_{\text{tot}} \Delta E_M \approx k_B T$, allowing for a field-induced reorientation of the LC monolayer. At this stage, a comparison with the anchoring energy is still necessary. With our magnetic field strengths up to 20 T, the magnetic energy difference between parallel and perpendicular orientation is maximally $7.6 \times 10^{-11} \text{ J/cm}^2$. This is of the same order of magnitude as the anchoring energy and due to the collective behaviour also the thermal energy barrier should have been overcome in the experiment. From the above presented first-order approach it can be concluded that a LC monolayer should reorient in magnetic fields of 20 T.

At this point the question arises: why is the azimuthal orientation of an LC monolayer fixed in the present experiment? To understand this, it should be noted that all arguments given above are based on the assumption that parameters determined for a 3D system can be translated into 2D parameters. The anchoring energy determined from measurements on bulk LCs, can be

related to the distortion of the molecules near the interface. However, in former SHG experiments it has been shown that the bulk is not directly interacting with the polymer surfaces. In SHG experiments on LC cells it was found that the azimuthal orientational distribution of the LC molecules at the interface was not isotropic if the polyimide orienting layer was rubbed before assembling the LC cell. This orientational distribution of the interfacial LC monolayer was not greatly affected by the status of an adjacent LC bulk and was similar to that of a single LC monolayer at a polyimide/air interface. The azimuthal orientation could be influenced dramatically by changing the polymer surface itself. From those experiments, it was concluded that the orientation of the LC bulk is determined by the interaction of the bulk with a more or less fixed LC monolayer in close contact with the polyimide substrate.

So, here we have a proof that in the present experiment on a single LC monolayer, the value for the anchoring energy can therefore not be regarded as being representative. This value describes the interaction of the LC bulk with a LC monolayer and not that of the interfacial LC molecules and the substrate. From other SHG experiments, a better value for the anchoring of individual LC molecules on polymer surfaces can be obtained. Ouchi et al. [14] have performed SHG experiments on the surface memory effect (SME). In those experiments a LC cell was assembled of non-rubbed, i.e. azimuthally isotropic, polymer substrates. The cell was filled with 8CB and subsequently aligned via an external magnetic field while the LC was in the smectic phase. It was observed that the alignment of the LC persisted in the absence of the external field, even after the LC had been heated to the isotropic phase and cooled back to the nematic phase again. It was believed that the smectic LC had impressed its ordering on the LC/polyimide interface. The resulting, very limited, anisotropy in the interfacial LC alignment was ascribed to the orientation of a limited number of interfacial LC molecules in local surface potential wells. By measuring the decay of the alignment as a function of temperature a value of 2.1 eV has been found for the surface potential barrier height. This implies that the aligned molecules can only be reoriented after climbing this potential barrier. The value of this barrier seems to be unrealistically high, since the desorption energy of a LC molecule from a polyimide surface is of the order of 1.3 eV. After being desorbed of the surface a random orientation of the molecule seems to be certified. As a result, the azimuthal surface potential barrier can never exceed the desorption energy. The discrepancy may be attributed to the unnaturally high value (10^{26} s^{-1}) for the pre-exponential factor that Ouchi has found. Usually, a value of the order of 10^{16} s^{-1} is used. With this value, also 1.3 eV is found for the surface potential barrier.

Consequently, a value of 1.3 eV might be taken as the surface anchoring energy. With this value for the azimuthal anchoring energy of a single molecule it can be estimated that magnetic fields of the order of a few thousand Tesla are needed.

6. Conclusion

In conclusion, the first experimental results on the molecular orientation of LC monolayers in high magnetic fields have been presented. By studying the influence of the external magnetic field on the in-plane molecular orientation of 8CB molecules on rubbed polymer surfaces it is found that the orientation of the LC molecules is fixed with respect to the rubbing axis upto magnetic fields of 20 T. Based on a simple scaling of experimentally determined values for LC cells to values for a 2D LC monolayer, magnetic fields of 20 T should have been sufficient to induce magnetic field induced reorientation. However, the novel results are in-line with the previously proposed model for surface-induced LC alignment based on a LC bulk interacting with a fixed interfacial LC monolayer. From the presented observations it can be concluded that hardly any collective behaviour of the LC molecules constituting the first monolayer is present.

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