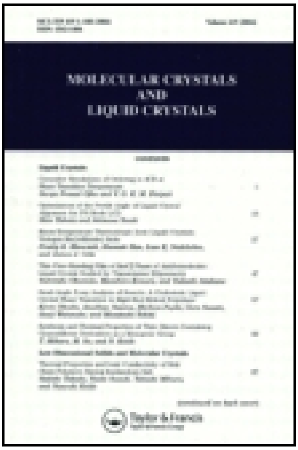

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Reorientation Dynamics of Liquid Crystal Molecules at Solid Surfaces

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Reorientation Dynamics of Liquid Crystal Molecules at Solid Surfaces

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We have studied the reorientation dynamics of liquid crystal molecules in the immediate vicinity (within a few molecular lengths) of fused quartz substrates. For this we apply a high-voltage DC electric field to create a polar ordering of the molecules. If this field is switched off, the reorientation dynamics of the molecules involves different relaxation regimes associated with relaxation times varying from less than 1ms to several hours. We discuss the origin of these different regimes.

Keywords: liquid crystals; surfaces; interfaces; dynamics

1. INTRODUCTION

Most electro-optical applications of liquid crystals are based on the switching of the orientation of the liquid crystal between different states [1]. The macroscopic observation of this switching phenomenon proves that the average alignment of the bulk molecules changes orientation. On the other hand, the director has a preferred orientation close to the surfaces (the anchoring direction) arising from the orientation of the molecules in the surface layer by their interaction with the surface [2]. This means that the reorientation of the bulk of the liquid crystal is in competition with the orienting effect of the surfaces. This raises several questions:

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- Do the molecules in contact with the substrate also reorient if the bulk reorients and how much energy does it cost? These questions have indirectly been addressed by measurements of the anchoring energy associated with reorientations of the director in the bulk [3-5]. This macroscopic anchoring energy is however a property of the whole interfacial region between the surface and the bulk [2,3]. We need rather to measure the microscopic anchoring energy of the molecules in the surface layer.
- Are the molecules adsorbed onto the substrate and what is the energy associated with this adsorption? There have been several experimental observations showing that once a liquid crystal has taken a given orientation on a substrate, this orientation becomes favoured with respect to the others. For instance, an azimuthal anchoring strength can be measured on isotropic substrates after that the bulk is aligned by an external field [6,7]. This alignment is also retained if the sample is heated well in the isotropic phase and cooled down in the absence of external field [8,9]. However, if a second external field is applied for a long time (hours) in a different direction than the original orienting field, the surface director slowly rotates (glides) towards the second field [10]. The anchoring strength measured on an undulated substrate was also found [11] to be one order of magnitude larger than expected from the topographic anchoring mechanism proposed by Berreman [12]. The pretilt angle at a rubbed polymer surface also appears to be affected by the history of the sample [13]. These observations suggest that the molecules in the surface layer get adsorbed onto the substrate in the orientation they adopt. The anisotropic part of this adsorption energy provides an additional contribution to the microscopic anchoring energy.
- What is the reorientation dynamics of the surface molecules? How fast do they reorient when a distortion is applied and how fast do they relax towards their equilibrium order when the distortion is removed? This dynamics is expected to be strongly influenced by the adsorption we have just mentioned. One way to get information on surface dynamics is to study the effect of confinement of the dynamics of liquid crystals. In a confined system, the proportion of molecules whose dynamics is affected by surfaces is large, and the dynamics of the whole system is strongly affected by the surfaces. There have been a number of studies performed according to this principle using optical techniques [14-23], dielectric spectroscopy [24,25] or NMR [26-28]. Theses techniques are not surface specific but with the last two the

distinct behaviour of molecules close to surfaces can be distinguished. However other effects such as interpore correlations [17,18], random potentials [19], and fluctuations of wetting layers [29,30] also influence the dynamics of confined systems, making the effect of the surfaces themselves difficult to distinguish. There have also been some studies of the director dynamics in the vicinity of surfaces over distances of at least 100nm [31-34].

To address the above questions at the molecular level, we have studied the behaviour of molecules in ultra-thin films made of a few molecular layers when they are forced to reorient away from their equilibrium order. This had already been tried by applying a strong magnetic field but no reorientation was seen [35]. One way to induce such a reorientation is to apply a high DC electric field. This process is used in particular for the poling of side-chain polymer liquid crystals to make nonlinear optical materials [36,37]. Electric fields ranging between $1\mathrm{kVmm}^{-1}$ and a few $100\mathrm{kVmm}^{-1}$ are able to induce a polar ordering of the liquid crystalline side-groups (in particular cyanobiphenyl groups) of these polymers.

We have therefore studied the following model system: a thin liquid crystal film consisting of polar molecules deposited onto the considered substrate in between two electrodes providing an electric field parallel to the substrate. The applied field tends to align the dipoles carried by the molecules along its own orientation, inducing a polar anisotropy in the plane of the substrate. The resulting orientational distribution of the molecules arises from a balance between the anchoring energy of the molecules onto the substrate and the energy of the molecular dipoles in the applied electric field. This orientational distribution gives therefore information on the anchoring energy of the molecules onto the substrate. We will not discuss this aspect here and concentrate on the dynamic behaviour of the surface molecules. The time evolution of the orientational distribution of the molecules when switching the applied field on and off gives information on the reorientation dynamics of the molecules in the vicinity of the surface. To measure the degree of electric-field-induced polar ordering of the molecules and its time dependence, we have used second-harmonic generation that is specifically sensitive to polar ordering.

In the present article, we present results concerning fused quartz plates as a substrate. This substrate is isotropic in its plane (symmetry C_∞), so that it does not induce a preferred azimuthal orientation of the liquid crystal molecules. In the following sections, we first discuss the expected electric-field-induced order in a thin liquid crystal film and the corresponding second-harmonic signal (section 2.). After describing the experimental conditions (section 3.), we present the observed dynamical behaviour (section 4.) and discuss its origin (section 5.).

2. EFFECT OF ELECTRIC FIELD ON MOLECULAR ORIENTATION

2.1 Structure of films

To examine the effect of an electric field on the orientational distribution of liquid crystal molecules in a thin film, we use the following considerations. A film of polar molecules (as cyanobiphenyl molecules) deposited on a substrate can be divided into two regions:

a) *The surface layer*: this is the polar layer of molecules in contact with the substrate. In the absence of electric field, it is known that these molecules preferentially point with their polar head towards the substrate (Figure 1) and make an angle of approximately 70° with respect to the substrate normal [38]. On fused quartz however, they have no preferred azimuthal orientation. If an electric field is applied in the plane of the substrate, it induces an in-plane anisotropy by orienting the molecular dipoles along its own direction.

b) *The covering film*: this is the rest of the film (Figure 1). In the absence of electric field, this part of the film has a quadrupolar

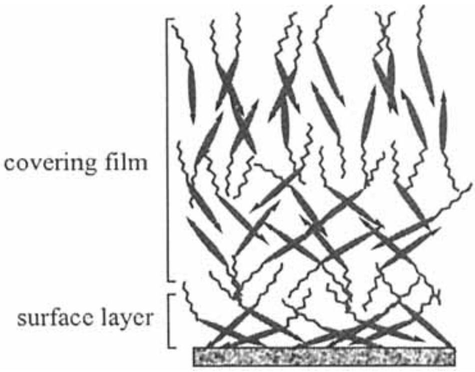

FIGURE 1 Schematic representation of the structure of a liquid crystal film.

ordering, with as many molecules pointing in one direction as in its opposite. The in-plane distribution is isotropic. Applying an electric field induces an in-plane polar anisotropy.

2.2 Second-harmonic generation from a poled liquid crystalline film

Since the thickness of all the films we have studied is at least ten times smaller than the wavelength of light, we consider our films as being infinitely thin. We can therefore apply the theory of surface second-harmonic generation presented in different articles [39-41]. The second-harmonic signal generated by our films is proportional to the square of the effective susceptibility:

$$\chi_{eff} = [\hat{e}(2\omega)\cdot\underline{L}(2\omega)]\underline{\chi} : [\hat{e}(\omega)\cdot\underline{L}(\omega)][\hat{e}(\omega)\cdot\underline{L}(\omega)]$$

which depends on the nonlinear susceptibility tensor $\underline{\chi}$ of the film, the polarisations $\hat{e}(\omega)$ and $\hat{e}(2\omega)$ of the in-coming and out-going beams and the local field factors $\underline{L}(\omega)$ and $\underline{L}(2\omega)$ relating the local electromagnetic field in the film to the fields of the in-coming and out-going waves. The main contribution to $\underline{\chi}$ is the dipolar term arising from a polar ordering in the system.

In the presence of an electric field, the film exhibits a mirror symmetry with respect to the (xz) plane containing the electric field (Figure 2). The nonlinear susceptibility tensor $\underline{\chi}$ of the film has then six non-zero independent components:

$$\chi_{xxx} = -N\alpha_{\xi\xi\xi} < \sin^3\theta \cos^3\phi >$$

$$\chi_{xyy} = \chi_{yxy} = \chi_{yyx} = -N\alpha_{\xi\xi\xi} < \sin^3\theta\,(\cos\phi - \cos^3\phi) >$$

$$\chi_{xzz} = \chi_{zxz} = \chi_{zzx} = -N\alpha_{\xi\xi\xi} < (\sin\theta - \sin^3\theta)\cos\phi >$$

$$\chi_{zxx} = \chi_{xzx} = \chi_{xxz} = N\alpha_{\xi\xi\xi} < (\cos\theta - \cos^3\theta)\cos^2\phi >$$

$$\chi_{zyy} = \chi_{yzy} = \chi_{yyz} = N\alpha_{\xi\xi\xi} < (\cos\theta - \cos^3\theta)(1 - \cos^2\phi) >$$

$$\chi_{zzz} = N\alpha_{\xi\xi\xi} < \cos^3\theta >$$

where N is the number density of the molecules in the film, $\alpha_{\xi\xi\xi}$ is the nonlinear polarisability of the molecules along the molecular axis ξ, and

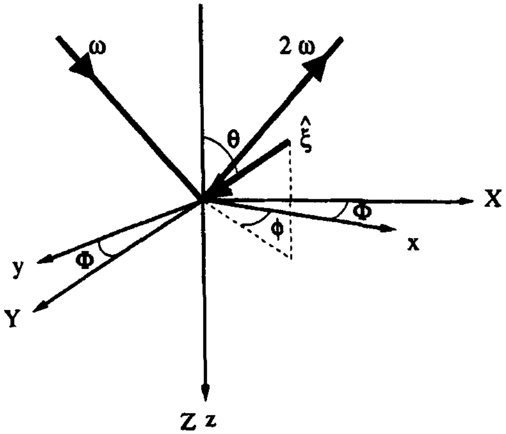

FIGURE 2 Reference frames (*xyz*) of the substrate surface and (*XYZ*) of the laboratory. (*XZ*) is the incidence plane of the laser beam and (*xz*) the mirror plane of the substrate surface containing the applied electric field. The molecular axis ξ is defined with respect to the substrate axes by the spherical coordinates (θ,ϕ).

(θ,φ) are the spherical coordinates defining the molecular axis (Figure 2):

$$\hat{\xi} = (-\sin\theta\cos\phi, -\sin\theta\sin\phi, \cos\phi)$$

When the applied electric field is switched off and the system relaxes towards the isotropic azimuthal orientational distribution induced by the substrate, the symmetry of the film remains unchanged till the orientational distribution of the molecules becomes perfectly isotropic. In this case χ becomes:

$$\chi_{xxx} = 0$$

$$\chi_{xyy} = \chi_{yxy} = \chi_{yyx} = 0$$

$$\chi_{xzz} = \chi_{zxz} = \chi_{zzx} = 0$$

$$\chi_{zxx} = \chi_{xzx} = \chi_{xxz} = N\alpha_{\xi\xi\xi} < \cos\theta - \cos^3\theta > / 2$$

$$\chi_{zyy} = \chi_{yzy} = \chi_{yyz} = N\alpha_{\xi\xi\xi} < \cos\theta - \cos^3\theta) > / 2$$

$$\chi_{zzz} = N\alpha_{\xi\xi\xi} < \cos^3\theta >$$

This shows that the first three components of χ are good measures of the degree of in-plane anisotropy induced by an applied electric field in the films and the degree ordering remaining in a film at a certain time after the applied field has been switched off. The component χ_{xxx} can directly be measured experimentally by measuring the second-harmonic signal with *s*-polarised in-going and out-coming beams with the incidence plane making an angle of 90° with the plane containing the applied electric field (Φ=90° in Figure 2). In this case the effective nonlinear susceptibility becomes [42]:

$$\chi_{ss} = \chi_{xxx} L_{yy}(2\omega) L_{yy}(\omega)^2$$

3. EXPERIMENTAL PROCEDURE

To perform our experiments, we have used substrates made of fused silica (amorphous quartz plates). The surface of these plates is isotropic (symmetry C_∞). On these substrates we coated two electrodes separated by a gap *d* of about 1mm. The electrodes were made of gold (1000Å - thick) attached to the quartz by a thin layer of chromium (100Å). The electrodes were connected to a high voltage power supply producing a DC voltage *V* of several kV; the current was limited to 10mA.

The electrodes produce an electric field that is parallel to the substrate surface at the surface [43]. The intensity of this field varies across the gap. It is minimum and equal to $E= 2V/\pi d$ in the middle of the gap. Around this minimum the profile of the field is very flat so that there is a region of width $d/5$=0.2mm in which the electric field is constant within 1%. All of our second-harmonic generation measurements were performed in this region with a laser spot of 100µm in diameter to ensure uniform field conditions.

The maximum electric field we could apply was typically 2kV/mm. Higher fields produced arcing between the electrodes, which destroyed the sample. Since this maximum field was lowered by the presence of water vapour, we kept our samples in a cell flushed by dry nitrogen. We switched the electric field with a circuit ensuring that the rise and fall times (2ms and 20ms respectivey) were minimum.

We deposited a multilayer of liquid crystal molecules in the gap on the substrate by evaporation from a hot source and condensation onto the substrate [38]. This deposition process makes very thin droplets of an extent of several mm in which the film thickness varies from less than a monolayer till several layers. For all results presented here, the deposition process was performed in the absence of electric field and the field was switched on afterwards. Depositing the films with the electric field on gave essentially the same results. The cell atmosphere of dry nitrogen preserved the samples from contamination. We have used 7OCB (T_m=55°C, T_{NI}=75°C) [44] as liquid crystal. Its nematic phase can easily be supercooled down to room temperature.

The measurements consisted in applying an electric field onto the sample until the molecules reached their new equilibrium order. Then the electric field was switched off at a time t=0 and the evolution of the second-harmonic signal was followed in time. For this we have used the usual set-up [39] with a frequency-doubled (λ=532nm) Q-switched, mode-locked Nd:YAG laser as light source. The time dependence of the electric potential applied onto the sample was also recorded to precisely determine the position of t=0.

We have measured the time dependence of the signal using two different ways of accumulating data:

- accumulation of laser pulses: the number of counted photons per laser pulse were averaged over a certain number of subsequent pulses. The time-resolution is then determined by the number of accumulated pulses and can be as low as a few seconds. These measurements are not limited in time.
- accumulation of time scans: the evolution of the signal after time t=0 was measured by the time dependence of the number of counted photons in each laser pulse. To obtain enough statistics, the same relaxation process was repeated around 100 times and the corresponding time scans were averaged. The time-resolution is then determined by the time interval between two laser pulses, which varies between 1.25ms for the maximum repetition rate of 800 Hz of the laser and 0.1s for a repetition rate of 10Hz. The measurements are then limited in time to 340 laser pulses because of the limited memory of the oscilloscope receiving the signal.

4. EXPERIMENTAL RESULTS

The overall decay of the second-harmonic signal in the *s*-in-*s*-out polarisation configuration when the electric field is switched off is schematically represented in Figure 3. The indicated time scales

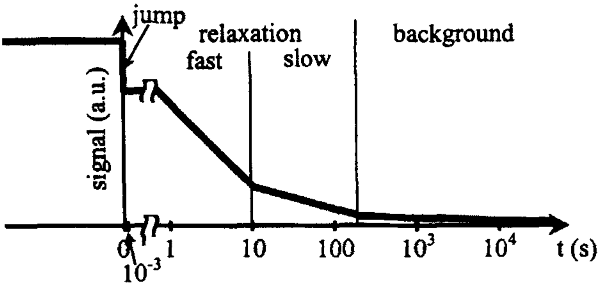

FIGURE 3 Schematic representation of the relaxation of the square-root of the signal at room temperature when the electric field is switched off.

correspond to a measurement at room temperature (T=20°C). We can distinguish four different relaxation processes. There is first a jump occurring at t=0 in less than the ms time-resolution of our experiments. Then we see two relaxation processes, one that we call fast with a decay time of approximately 10s and another that we call slow, which takes a few hundred seconds. At this point, we are left with a small background signal that decays over approximately 10 hours. In the following, we examine each of these regimes in more detail.

4.1 Jump

Even with our smallest time resolution, obtained by accumulating time scans measured for a repetition frequency of the laser of 800Hz, we cannot resolve the decay of the second-harmonic signal observed between times t=0 and t=1ms (Figure 4).

One could think that this jump is not due to the reorientation of the molecules in the film but to the disappearance of a contribution to the second-harmonic signal due to the application of an electric field. There are two possible mechanisms creating such a contribution.

In principle, a DC electric field can modify the intra-molecular potential in which the electrons of a molecule evolve. This would change the nonlinear polarisability $\alpha_{\xi\xi\xi}$ of the molecules. However this requires fields that are much larger than the ones we apply.

The other possible mechanism is electric field induced second-harmonic generation (EFISH). If a strong DC electric field is applied onto a non-polar medium, it can mix by a third-order nonlinear process with two waves at frequency ω to give a polarisation at frequency 2ω [45]:

$$\mathbf{P}^{\mathrm{EFISH}} = \underline{\chi}^{(3)}(2\omega = \omega + \omega + 0) : \mathbf{E}(\omega)\mathbf{E}(\omega)\mathbf{E}(0)$$

where $\chi^{(3)}$ is the third-order nonlinear susceptibility of the medium. The effective second-order susceptibility arising from this process is:

$$\chi_{ijkl}^{\mathrm{EFISH}} = \chi_{ijkl}^{(3)} E_l(0)$$

To compare the intensity of the EFISH signal with that of the pure second-order signal arising from the field-induced polar order, we have to compare the third-order polarisability γ of the molecules and the factor $\alpha_{\xi\xi\xi}\mu/kT$ [45]. For cyanobiphenyl molecules, γ is of the order of 10^{-35} esu $\approx 10^{-60}\mathrm{Cm}^4\mathrm{J}^{-3}$ [46], $\alpha_{\xi\xi\xi} \approx 10^{-29}$ esu $\approx 0.4\times10^{-49}\mathrm{C}^3\mathrm{m}^3\mathrm{J}^{-2}$ [46,47], and $\mu \approx 5\mathrm{D} = 15\times10^{-30}\mathrm{Cm}$. At room temperature this gives: $\alpha_{\xi\xi\xi}\mu/kT \approx 10^{-58}\mathrm{Cm}^4\mathrm{J}^{-3}$, which is two orders of magnitude larger than γ. We can therefore neglect the EFISH contribution.

So we can conclude that the jump in second-harmonic signal observed at short time scales is not an artefact due to the application of a field, but corresponds to a reorientation of part of the molecules towards an isotropic in-plane distribution.

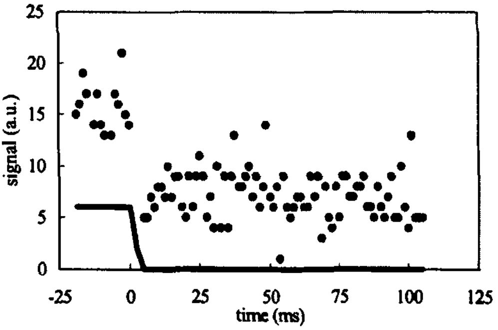

FIGURE 4 Jump of the second-harmonic signal after the electric field is switched off (at t=0). The points correspond to the signal, the solid line to the electric field (a.u.).

4.2 The fast and slow relaxations

A typical decay of the square root of the second-harmonic signal as a function of time (for t>1s) is shown in Figure 5. Displaying this signal against a logarithmic time scale clearly reveals two distinct relaxation regimes with two distinct relaxation times. To characterise these two regimes, we have fitted the square root of the signal with a sum of two exponential functions:

$$\sqrt{S(t)} = \sqrt{S_0} + \exp\left(\frac{t}{\tau_f} + l_f\right) + \exp\left(\frac{t}{\tau_s} + l_s\right) \tag{1}$$

where S_0 is the background level of the signal, τ_f characterises the fast relaxation and τ_s the slow relaxation. exp l_f and exp l_s are prefactors giving the signal intensity corresponding to each component at t=0.

For all samples, [exp l_s]^2 is equal (within the experimental errors) to the signal of the surface layer in the presence of the electric field. Moreover the decay of the signal generated by a film only made of a surface layer exhibits a single slow relaxation regime. This shows that the fast relaxation corresponds to the relaxation of the covering film and the slow relaxation to that of the surface layer.

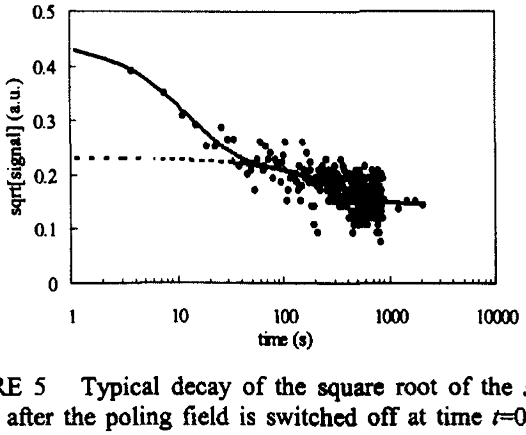

FIGURE 5 Typical decay of the square root of the *ss*-signal at Φ=90° after the poling field is switched off at time t=0. The solid line is a fit with Equation 1 and the dashed line the slow component in this fit (characteristic decay τ_s).

4.3 Background

At the end of the slow relaxation, the signal is not yet back at its noise level, although it is very small (less than 10 % of the signal with field on). At this point of the relaxation process, we have measured the dependence of the *ss*-signal on the azimuthal orientation Φ of the substrate. It indeed showed an anisotropy. At room temperature, this anisotropy becomes undetectable in approximately ten hours. However this does not mean that the anisotropy has totally disappeared in the surface layer, but only that we could not measure it. It has already been shown that an isotropic surface can induce a preferred orientation of a liquid crystal although the anisotropy of the orientational distribution at the surface is undetectable with second-harmonic generation [9]. The level of this background signal at the end of the slow relaxation depends on the history of the sample. In particular, it increases if the duration of the poling under electric field increases. Also, for a given duration of the poling, the level of the background increases for successive poling/relaxation cycles if the electric field is switched on again shortly after the slow relaxation ended.

V DISCUSSION

Our experimental results give the following picture of the relaxation of the electric-field-induced polar ordering in thin liquid crystal films when the electric field is switched off:

- In less than 1ms a first relaxation process (the "jump") takes place in the whole film. It probably arises from individual reorientations of molecules.
- The remaining polar ordering of the covering film relaxes in a characteristic time $\tau_f \approx 10$ s at room temperature. We call this the fast relaxation.
- The surface layer relaxes over longer time scales. Most of its order relaxes in a characteristic time $\tau_s \approx 300$s at room temperature (slow relaxation). The fast and slow relaxations correspond to the same type of relaxation process taking place in the covering film and the surface layer, with the dynamics of the latter being slowed down by the interaction of the surface molecules with the substrate.
- A residual polar ordering (background) remains in the surface layer for hours. This long time scale indicates that it is due to strong interactions of molecules with the substrate, as it can happen at defects.

Since these defects are not all the same, and therefore their interaction potential with the liquid crystal molecules might vary, we actually expect a relaxation of this background with a stretched exponential [48]. As in glasses, this type of dynamics gives rise to significant history-dependence of the dynamics, which we have indeed observed.

Let us now compare our result with the available information on the dynamics of liquid crystal molecules at interfaces. There have been several experiments showing that in the vicinity of a surface, the dynamics of a liquid crystal slows down with respect to that of the bulk [24,25,31,33]. They are however based on the measurements of quantities averaged over the whole interfacial region between the surface and the bulk. Their results are therefore difficult to compare directly with ours. The reported size of the effect varies a lot. The surface dynamics was found to be 1.7 times slower than bulk dynamics by evanescent wave photon correlation spectroscopy [31], 10 times slower in anchoring breaking experiments [33], and 10^3 times slower by dielectric spectroscopy [24,25] and NMR [26]. Our measurements show that several relaxation times differing by several orders of magnitude are involved within a distance of a few 100Å from a surface. Moreover it has been shown that in systems with sizes d between 0.1 and 1μm, the relaxation time τ of the director fluctuations varies according to $\tau^{-1}\sim d^{-1}$, because of confinement effects [21,22]. Obviously depending on the technique and system used, the dynamics is probed on different length scales close to surfaces and different relaxation mechanisms are seen, leading to large discrepancies between the reported results.

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