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Rotational friction at the molecular level

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Abstract. – We use second-harmonic generation measurements to follow the reorientation of liquid-crystal molecules in the first few molecular layers in contact with a surface. These measurements reveal four molecular relaxation times differing by orders of magnitude arising from different dissipation processes taking place at the interface with a solid. The slowest processes are due to the direct interaction of molecules with the solid, while the others concern molecules located just above this surface layer. This position-dependent dynamics explains some of the discrepancies previously observed in measurements of the surface reorientation dynamics of liquid crystals.

A flowing liquid remains at a macroscopic scale at rest in the vicinity of a solid surface, yet molecules do slide along solid walls and therefore dissipate energy in microscopic friction processes [1]. In the case of anisotropic molecules, the friction processes associated with molecular reorientations play an essential role in the surface dynamic behaviour. This rotational friction is most important for liquid crystals and their display applications in which the liquid-crystal orientation switches between different configurations.

While most experiments show that the reorientation dynamics at the surface is slower than the bulk dynamics, there are significant differences on the reported size of the surface effect. The ratio between surface and bulk relaxation times varies from 2 to 10^3 [2–17] and the value of the surface viscosity associated with the reorientation of the so-called surface director, *i.e.* the mean molecular axis just outside the interface between the limiting wall and the bulk (see fig. 1a), varies from 0.33 $\mathrm{N\,s\,m^{-1}}$ to 8×10^{-10} $\mathrm{N\,s\,m^{-1}}$ [3–5].

All these experimental studies probe average dynamic properties. Some experiments probe the dynamics of the surface director [2, 4, 7, 17, 18] while others probe the dynamics of liquid crystals confined in pores with techniques that are not surface specific [3, 5, 6, 8–16]. These confined systems also exhibit dynamic effects due to the confinement geometry [8–10, 19] making the effect of the surfaces themselves difficult to distinguish. Even more puzzling is the observation of the so-called surface memory effect, *i.e.* the fact that isotropic surfaces,

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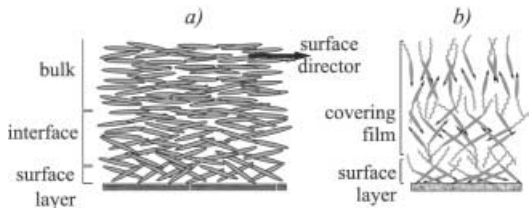

Fig. 1 – a) Schematic representation of a liquid crystal in contact with a solid wall. The mean orientation of the molecules in the bulk just outside the interfacial region corresponds to the "surface" director probed by optical experiments. b) Schematic representation of the structure of a thin liquid-crystal film used as model system in our experiments.

which induce *a priori* no preferred orientation of the director, preserve the orientation of the surface director first adopted by the liquid crystal [20–22]. This suggests that the surface molecules are very strongly adsorbed and that their dynamics is even much slower than what is measured in the experiments mentioned above. This seems to be confirmed by the observed slow reorientation of the surface director (with angular velocities down to 0.1°/hour) under the application of an external field [4, 7].

There is obviously a need for a better understanding of the rotational dynamics close to surfaces. To achieve this, it is essential to know which microscopic friction processes take place in the vicinity of a surface when molecules reorient. To get this piece of information, we have studied thin liquid-crystal films (a few molecular layers) consisting of polar molecules deposited onto isotropic fused-quartz plates in between two electrodes providing a DC electric field parallel to the substrate. In a way similar to the poling of side-chain polymer liquid crystals to make non-linear optical materials [23], 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 applied field is subsequently switched off and the evolution of the orientational distribution of the molecules is followed in time using optical second-harmonic generation measurements [24]. This gives information on the reorientation dynamics of the molecules in the immediate vicinity of the surface.

In the experiments reported here, the liquid-crystal films are made of 4-heptyloxy-4′-cyanobiphenyl (7OCB, melting temperature 55 °C, clearing temperature 75 °C) in which the nematic liquid crystalline phase can easily be supercooled down to room temperature (this liquid crystal exhibits no smectic phase). The films are deposited by evaporation from a hot source and condensation on amorphous quartz plates [25] in a gap of 1 mm between two gold electrodes coated on the plates. The electrodes produce an electric field (up to 2 $\mathrm{kV\,mm^{-1}}$) parallel to the surface that is essentially uniform in the middle of the gap where the measurements have been performed. The applied field is 2 $\mathrm{kV\,mm^{-1}}$ in the present measurements; there is no observable dependence of the relaxation times on the applied field. A green (532 nm) s-polarised radiation is incident on the sample (the optical set-up is depicted in [24]), generating from each molecule an s-polarised second-harmonic signal. If there is no in-plane order, however, all these signals interfere destructively and the measured signal is zero. If there is an in-plane polar order and for an angle of 90° between the poling field and the incidence plane of the light, the square root of the resulting signal is proportional to the average $\langle \sin^3\theta \cos^3\phi \rangle$, where (θ, ϕ) are the spherical coordinates defining the axis of a given molecule [26]. The ss second-harmonic signal is therefore a direct measure of the degree of field-induced polar ordering and of the time evolution of this order after the field is switched

off. In the presence of the applied field, this signal contains in principle an electric-field–induced contribution (EFISH) [27]. This contribution is however two orders of magnitude smaller than the ordinary signal and can be neglected.

The films used in our study can be divided into two regions (fig. 1b). There is first *the surface layer*, *i.e.* 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 and make an angle of approximately 70° with respect to the substrate normal [25]. They have, however, no preferred in-plane orientation. The rest of the film forms what we call *the covering film*. In the absence of electric field, this part of the film has a quadrupolar ordering, with as many molecules pointing in one direction as in its opposite. The in-plane distribution is then isotropic as in the surface layer.

If an electric field is applied in the plane of the substrate, an in-plane anisotropy is induced both in the surface layer and in the covering film by orienting the molecular dipoles along its own direction. The field-induced polar ordering generates a non-zero second-harmonic signal. With static second-harmonic generation measurements using different polarisations of the in-coming and out-going beams [26], we can determine the orientational distribution of the molecules with the poling field on. These measurements show that the poling field does not affect the tilt of the molecules but only their azimuthal orientation. So the reorientations we observe are in-plane rotations. Note that the free surface does not affect this type of reorientation.

The decay of the *ss* second-harmonic signal in time after the electric field is switched off, is a direct measure of the disappearance of the in-plane polar order as the molecules relax towards their equilibrium orientational order. We observe that the decay of the second-harmonic signal takes place in four steps, revealing four different relaxation processes. There is first a jump occurring at $t = 0$ in less than the time-resolution of our experiments ($\approx$ ms). Then we observe two relaxation processes, one that we call fast with a decay time of approximately 10 s (at room temperature) and another that we call slow, which takes a few hundred seconds. 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 room temperature, this signal ("background") becomes undetectable in approximately ten hours at room temperature.

The dependence of the different relaxation processes on film thickness allows us to determine in which part of the film the different processes take place. The first jump corresponds to approximately 20% of the square root of the signal independently of the film thickness and can therefore be attributed to a very fast relaxation process taking place in the whole film.

We have examined in more detail the fast and slow relaxation processes. Typical decays of the square root of the second-harmonic signal as a function of time (for $t > 1$ ms) at 20 °C are shown in fig. 2. To characterise the two relaxation processes, we have fitted the square root of the signal with a sum of two exponential functions:

$$\sqrt{S(t)} = \sqrt{S_0} + \exp[t/\tau_\mathrm{f} + l_\mathrm{f}] + \exp[t/\tau_\mathrm{s} + l_\mathrm{s}]\,, \tag{1}$$

where S_0 is the background level of the signal, τ_f characterises the fast relaxation and τ_s the slow relaxation. $\exp[l_\mathrm{f}]$ and $\exp[l_\mathrm{s}]$ are prefactors giving the signal intensity corresponding to each component at $t = 0$. For all samples, $[\exp[l_\mathrm{s}]]^2$ 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 films only consisting of a surface layer exhibits a single slow relaxation regime (fig. 2b). This shows that the fast relaxation corresponds to the relaxation of the covering film and the slow relaxation to that of the surface layer. The two relaxation times τ_f and τ_s do not depend on the thickness of the film (in the range up to 50 Å that we have

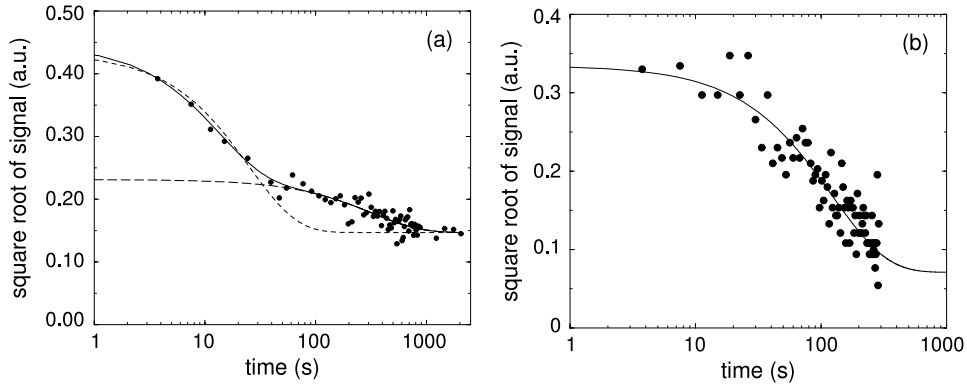

Fig. 2 – Typical decay of the square root of the second-harmonic signal at 20° after the poling field is switched off at time $t = 0$ (a) for a multilayer of thickness 50 Å (surface layer + covering film) and (b) for a monolayer (only surface layer with thickness 11 Å). The solid line is a fit with eq. (1). In (b) $\exp[l_{\mathrm{f}}]$ has been set to 0 and in (a) the long-dashed line shows the slow component in the fit (characteristic decay τ_{s}) and the short-dashed line a fit with a single exponential.

studied). The temperature dependence of τ_{f} and τ_{s} appears to follow an Arrhenius law (fig. 3) similar to bulk translational and orientational viscosities far enough from phase transitions. The apparent activation energies are $19 \pm 5kT$ and $24 \pm 7kT$ for the fast and slow relaxation, respectively.

The fact that we observe several relaxation processes in molecularly thin films shows that the reorientation dynamics of anisotropic molecules close to surfaces is quite complex and cannot be described by a single surface viscosity or friction coefficient. Since we can attribute different relaxation processes to different parts of the films, we can obtain information about the friction processes responsible for the slowing-down of the molecular reorientation dynamics in the vicinity of surfaces.

We can distinguish three populations of molecules with a slow dynamics (we leave out the molecules responsible for the first jump not studied in our experiments):

a) *Molecules above the surface layer:* in our model system, these are the molecules in the covering film. They are responsible for the fast exponential relaxation process with characteristic time τ_{f}. At the time scale of τ_{f}, the molecules in the surface layer are immobile with the orientational order imposed by the applied electric field. The anisotropy of this order, as determined from static second-harmonic generation measurements (see above), is however too small to promote a preferred polar orientation in the covering film and affect its reorientation dynamics once the electric field is switched off.

The molecules in the covering film feel a bulk-like viscous torque Γ_{visc} due to the rotational viscosity γ_{F} of the material in the vicinity of the surface: $\Gamma_{\mathrm{visc}} = -\gamma_{\mathrm{F}}\dot{\phi}V$, where V is the volume of a molecule and $\dot{\phi}$ is the angular velocity of the molecules in the surface plane. The relaxation time τ_{f} of the molecules in the covering film is related to the viscous torque Γ_{visc} by $\tau_{\mathrm{f}} = -\Gamma_{\mathrm{visc}}/2kT\dot{\phi} = \gamma_{\mathrm{F}}V/2kT$ [28]. Assuming that the molecules reorient individually ($V = 5\times5\times25$ Å^3), we find $\gamma_{\mathrm{F}} \approx 10^8$ N s m^{-2} at room temperature. This is significantly larger than the bulk value of the rotational viscosity in this kind of liquid crystals (≈ 0.1 N s m^{-2}). Assuming that the motion is correlated over a number n_{c} of molecules only reduces γ_{F} by a factor n_{c}. Since n_{c} cannot be larger than the number of molecules in a volume h^3 (where h is the thickness of the film), γ_{F} is at least of the order of 10^6 N s m^{-2}.

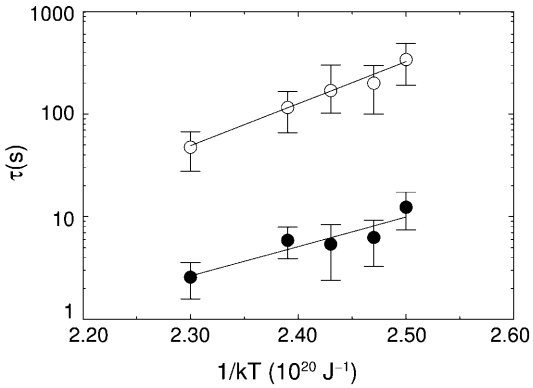

Fig. 3 – Arrhenius plot of the relaxation times τ_{f} (•) and τ_{s} (∘).

b) *Unpinned surface molecules:* these molecules in the surface layer are responsible for the slow exponential relaxation process with characteristic time τ_{s}. The unpinned surface molecules feel a friction torque exerted by the substrate $\Gamma_{\mathrm{surf}} = -\gamma_{\mathrm{S}}\dot{\phi}A$, where A is the contact area of the molecules with the substrate and γ_{S} is a surface rotational viscosity. As the molecules in the covering film, the unpinned surface molecules also feel the viscous torque Γ_{visc} due to the rotational viscosity γ_{F} in the film: $\Gamma_{\mathrm{visc}} = -\gamma_{\mathrm{F}}\dot{\phi}V$. The relaxation time τ_{s} of these molecules is related to the different viscosities by: $\tau_{\mathrm{s}} = (\gamma_{\mathrm{S}}A + \gamma_{\mathrm{F}}V)/2kT$, from which we deduce the value of the true surface rotational viscosity corresponding to the friction of liquid-crystal molecules on a fused quartz substrate: $\gamma_{\mathrm{S}} \approx 2\ \mathrm{N\,s\,m^{-1}}$ at room temperature.

c) *Surface molecules pinned at defects on the substrate:* These molecules are responsible for the slowly decaying background signal. These molecules only represent a small fraction of the surface molecules since the background signal is only a fraction of the signal coming from the surface layer before it relaxes ($\exp[l_{\mathrm{s}}]$ in eq. (1)). As all molecules in the vicinity of the surface, they feel the bulk-like viscous torque $\Gamma_{\mathrm{visc}} = -\gamma_{\mathrm{F}}\dot{\phi}V$. The significant slowing-down of these molecules with respect to the others is due to their adsorption at pinning sites. Since these sites are not all the same, we expect the corresponding adsorption energy to take values within a certain interval. We can only follow the initial decay of the background signal till it disappears in the noise. This corresponds to the relaxation of the molecules that are the most loosely pinned with an adsorption energy $E_{\mathrm{pin}}^{\mathrm{min}}$ with $\tau_{\mathrm{back}} = \tau_{\mathrm{f}} \exp[E_{\mathrm{pin}}^{\mathrm{min}}/kT]$, leading to $E_{\mathrm{pin}}^{\mathrm{min}} \approx 8kT$.

Our finding that different categories of molecules in the vicinity of surfaces are subject to different friction processes leading to very different characteristic relaxation times allows us to explain some of the contradictory results reported so far on the surface reorientation dynamics in liquid crystals. Generally speaking, the "surface" dynamics probed by a given technique will depend on how close to the surface of the limiting wall the dynamics is observed. At distances from the surface that are larger than the ones we have explored, the viscosity should evolve towards its bulk value. This implies a significant speeding-up of the dynamics taking place over the thickness of the interface between the solid wall and the bulk liquid crystal, estimated to be a few 100 Å.

Experiments probing the dynamics of the liquid-crystal director close to surfaces give information on the average dynamics just outside the interface (fig. 1a). This dynamics probed by dynamics light scattering in pores has given a surface viscosity of $8 \times 10^{-10}\ \mathrm{N\,s\,m^{-1}}$,

essentially equal to the bulk rotational viscosity times the interface thickness [5, 29]. The "same" director dynamics probed via the reorientation of the director under an electric field has given a surface viscosity of the order of $0.3\,\mathrm{N\,s\,m^{-1}}$ [4]. This discrepancy can be explained by the fact that the director fluctuations probed by light scattering occur at such short time scale that they only involve the interfacial molecules located far enough from the solid surface (where the viscosity is essentially that of the bulk). In contrast, the slow reorientation (or gliding) of the surface director under the application of a constant electric field must be the result of a change in the orientational distribution of molecules in the surface layer, that we have shown to be orders of magnitude slower than bulk dynamics.

Our measurements also show that the surface memory effect mentioned at the beginning is not due to the adsorption of all surface molecules on the substrate, as implicitly assumed so far, but to the pinning of a small fraction of the surface molecules. The dynamics of the other surface molecules (that we have called unpinned) is too fast to cause a long-term memory effect. The little information collected so far through the memory effect on the surface adsorption of liquid-crystals molecules [22] actually concerns the small fraction of the surface molecules that are pinned at specific sites.

Our results and the examples just discussed show that the reorientation dynamics of anisotropic molecules at surfaces involve very different relaxation processes. Depending on the type of system, the degree of confinement, the considered dynamic property and time scale, one particular process will generally dominate and dictate the behaviour of the system. To be able to predict this behaviour, it is essential to have information on the microscopic friction processes and molecular rotational dynamics as the one provided by our experiments.

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