Positional Anchoring of Smectic Liquid Crystals

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Positional anchoring of the smectic-A (S_A) liquid crystal 4O.8 at a glass plate interface is measured with a micromechanical technique: stress oscillations at layer thickness scale are observed under shear normal to the layers. Similar oscillations are observed on its smectic-B phase, and previously in plastic crystals. These oscillations are explained by shear-induced surface melting and recrystallization. The corresponding S_A positional anchoring energy is $\sim 10^{-8}$–10^{-9} J/m^2. This unidimensional periodic melting is a model for solid friction in soft matter.

Anchoring properties of liquid crystals on solid surfaces are not yet completely understood. The nematic (N) phase presents bulk *orientational* ordering. If a glass plate is also ordered, e.g., by surfactant coating, rubbing, evaporation, etc., it can orient the surface molecules along an easy direction [1]. Bulk orientation is then controlled by the surface. Disoriented surface molecules are subjected to restoring torques from an angular anchoring energy. The smectic phase presents bulk *positional* ordering. A solid crystalline surface would be able to induce by epitaxy a positional anchoring; molecules displaced from their easy position would then be subjected to restoring forces, from a positional anchoring energy. In principle, positional anchoring of a smectic crystal seems to be impossible on an amorphous surface, invariant by translation, which cannot induce periodic ordering. On an amorphous surface, however, the bulk smectic ordering can induce a weak periodic surface order. If we shear the surface normal to the layers with an infinitely low rate, the surface smectic order should be continually recreated. The smectic would glide on the surface, with viscous but not elastic anchoring forces. If the shear movement is rapid enough, the smectic surface ordering could be frozen and a positional anchoring force should be measurable. In this paper, we present the first experimental evidence of positional anchoring of smectic layers in contact with a glass plate, obtained through a micromechanical technique.

To analyze the anchoring properties, let us consider a smectic-A (S_A) crystal in contact with a glass plate, in "planar" orientation, i.e., with molecular long axis parallel to the interface and smectic layers parallel to the Oz direction, normal to the glass plate (Fig. 1). In the Landau–de Gennes description [2], we can describe the surface smectic ordering induced by the bulk by a nonzero order parameter Ψ_S. Ψ_S has an arbitrary phase: The anchored molecules have different positions from one sample to another, but $|\Psi_S|$ is defined for a given sample. A likely profile of $\Psi(z)$ is sketched in Fig. 1(a): Ψ decreases from the bulk value Ψ_B to Ψ_S, on the smectic coherence length ξ. In this continuous model, Ψ becomes zero *outside the smectic* at $z = -z_0$. Imagine that layers

are shifted on a distance x along the glass surface, perpendicular to the layers. We suppose that the surface molecules of order Ψ_S are strongly fixed on the glass. For an arbitrary x, in the regions where the surface molecules were initially aligned with the bulk molecules, the layers are subjected to anchoring forces towards their equilibrium position and thus slightly oblique from Oz. Whenever $x = nm$, where $m \sim 20$ Å is the layer thickness and n an integer, the bulk layers are in phase with the surface molecules and an equilibrium state is reached. On the con-
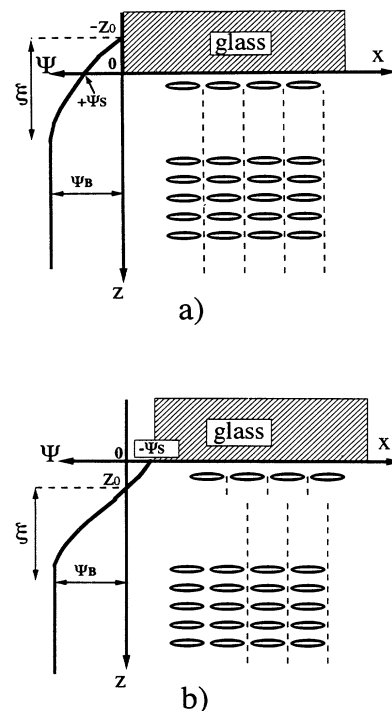

FIG. 1. Variation of the smectic order Ψ close to an amorphous surface. (a) In absence of shear; the $\Psi = 0$ point is virtual, inside the glass. (b) For a half layer shear; the $\Psi = 0$ point must appear inside the smectic material, increasing the surface energy.

trary [Fig. 1(b)], for $x = (2n+1)m/2$, the bulk Ψ_B is out of phase with the surface Ψ_S. In this unstable equilibrium position, no anchoring force exists but the texture costs some free energy E_S. The positional anchoring energy is thus expected to oscillate as $E_S(1 - \cos 2\pi x/m)$. We now calculate E_S.

The free energy density may be written [2]

$$f(\Psi) = a\Psi^2 + \tfrac{1}{2} b\Psi^4 + c(\nabla\Psi)^2 + \cdots , \qquad (1)$$

where $a = \tfrac{1}{2} a(T - T_c)$. T is the temperature and T_c is the second order transition temperature. To simplify, we deal with an algebraic rather than a complex Ψ. Far from the interface, in the bulk, Ψ is uniform and given by $\Psi_B^2 = -a/b$ with $f(\Psi_B) = -a^2/2b$. In the nonuniform case, Ψ is a solution of

$$a\Psi + b\Psi^3 - c\frac{\partial^2\Psi}{\partial z^2} = 0 , \qquad (2)$$

which has the first integral

$$a\Psi^2 + \frac{1}{2} b\Psi^4 - c\left(\frac{\partial\Psi}{\partial z}\right)^2 = a\Psi_B^2 + \frac{1}{2} b\Psi_B^4 . \qquad (3)$$

The surface energy is defined by

$$W_S = \int_0^\infty [f(\Psi) - f(\Psi_B)]dz = \int_0^\infty 2c\left(\frac{\partial\Psi}{\partial z}\right)^2 dz . \qquad (4)$$

E_S is half the variation of W_S between the stable and unstable equilibrium positions. When the layers are sheared by $m/2$ [Fig. 1(b)], $\Psi(z)$ appears with an out of phase value $-\Psi_S$ at the surface and a zero value *inside the smectic* at $z = +z_0 \sim \xi(\Psi_S/\Psi_B)$. The new Ψ profile is $\Psi'(z) = \Psi(z + z_0)$ and thus

$$E_S = \frac{1}{2}\int_0^\infty 2c\left[\left(\frac{\partial\Psi'}{\partial z}\right)^2 - \left(\frac{\partial\Psi}{\partial z}\right)^2\right]dz$$

$$= \int_0^{z_0} 2c\left(\frac{\partial\Psi}{\partial z}\right)^2 dz \sim 2c\frac{\Psi_B^2}{\xi^2}z_0 , \qquad (5)$$

with $\xi = (-c/2a)^{1/2} = (c/2b)^{1/2}\Psi_B^{-1}$. With $\Psi_B \sim 0.5$, $b \sim k_B T/m^3$, and $c \sim k_B T/m$ (k_B the Boltzmann constant), the anchoring energy per unit area is finally

$$E_S \sim (8bc)^{1/2}\Psi_B^2\Psi_S \sim (k_B T/m^2)\Psi_S . \qquad (6)$$

We have performed an experiment to check these ideas. We apply a continuous shear strain on a smectic liquid-crystal–glass-plate interface in the geometry of Fig. 1. We measure the shear stress transmitted through the sample. We use butyloxy-benzylidene-octylaniline (4O.8) which presents, between the crystal (K) and the isotropic (I) phases, the following transitions:

$$K \xrightarrow{33\,°C} S_B \xrightarrow{49.5\,°C} S_A \xrightarrow{63.7\,°C} N \xrightarrow{79\,°C} I .$$

A S_A single crystal is obtained between two glass plates,

with a thickness $d = 10$ μm and an area ~ 1 cm^2. The planar orientation is created in the N phase by an oblique SiO evaporation on the glass plate. The mechanical setup has been previously described [3]. We use as transducers piezoelectric ceramics, cemented on each glass plate. A time-dependent shear displacement $\delta(t)$, along Ox or Oy (normal to Ox and Oz), is imposed on one plate; the stress $\sigma(t)$ is measured on the other plate transducer. The mechanical holder is placed in a temperature-regulated oven, stable within $10^{-2}\,°$C. The sample, kept at $T = 54.3\,°$C in the S_A phase, is submitted to a periodic triangular time shape shear, of peak to peak amplitude $2\delta_0$ ($0 < 2\delta_0 < 400$ Å) at a frequency v ($0.1 < v < 1000$ Hz). The plate velocity is $|V| = 4\delta_0 v$. We first shear along Oy, parallel to the smectic layers with $2\delta_0 = 80$ Å and $v = 10$ Hz: No measurable stress is obtained. We expect $\sigma = \eta_s V/d$ ($\eta_s \sim 10^{-1}$ Pa s is a shear viscosity inside the layers) $\sim 10^{-3}$ N/m^2, lower than our sensitivity $\sim 10^{-1}$ N/m^2. We now shear the surface along the Ox, normal to the layers, with the same δ_0 and v: The measured $\sigma(t)$ is shown in Fig. 2. We observe two effects: stress oscillations superimposed on a viscoelastic relaxation.

To analyze the viscoelastic relaxation, we measure first the elastic constant C_{44} from the slope of $\sigma(t)$ at small times. We find $C_{44} = 2 \times 10^5$ N/m^2. We change V, increasing v from 1 Hz to 100 Hz; C_{44} is unchanged. For large times, $\sigma(t)$ tends towards an asymptotic value $\sigma(\infty)$ proportional to the plate velocity V: $\sigma(\infty) = 1.5 \times 10^9 V$ N/m^2. For intermediate times, $\sigma(t)$ relaxes towards $\sigma(\infty)$ with a relaxation time $\tau = 0.2$ s, independent of V. To explain C_{44}, we suppose that the sheared molecules remain parallel to the interface, from viscous forces. Calling θ the angle between the sheared layers and Oz, an elastic energy $\tfrac{1}{2} B_\perp \theta^2$ is stored in the bulk, where $B_\perp \sim (c/m^2)\Psi_B^2 \sim 10^5$ N/m^2 is the usual smectic shear elastic constant. $B_\perp$ corresponds to C_{44}. With this cor-
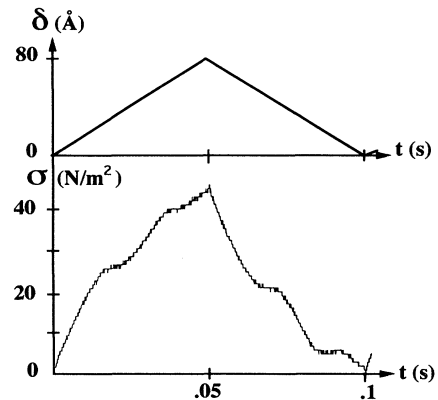

FIG. 2. Shear behavior of 4O.8 in the S_A phase ($T = 54.3\,°$C). Upper curve: triangular shear vs time, applied after a rest time ($\delta = 0$) of 2 min. Lower curve: transient shear stress.

respondence, we expect a viscoelastic response with a molecular relaxation time $\tau_t = \eta_t/B_\perp \sim 10^{-6}$ s ($\eta_t \sim 10^{-1}$ Pa s is a bulk tilt viscosity). The measured τ is much larger than τ_t. To explain it, we imagine a macroscopic mechanism: At large δ, molecules must flow through the layers, by permeation [4]. The permeation is easier where Ψ^2 is weak, i.e., the shear flow must be localized near the surface on the thickness ξ. A simple model can now describe the $\sigma(t)$ shape. The imposed $\delta = Vt$ can be divided into (i) a viscous displacement δ' within ξ, near each interface, with a viscosity η_p, and (ii) an elastic displacement $\delta - 2\delta'$ in the bulk, with the elastic constant $B_\perp$. Stress equilibrium gives $(\eta_p/\xi)(d\delta'/dt) + (B_\perp/d)\delta' = (B_\perp V/2d)t$, i.e.,

$$\sigma = \frac{\eta_p V}{2\xi}(1 - e^{-t/\tau}) \quad \text{with} \quad \tau = \frac{\eta_p d}{B_\perp \xi}. \quad (7)$$

From $\sigma(\infty)$ and τ, (7) gives coherent values for the ratio η_p/ξ equal, respectively, to 3×10^9 and 4×10^9 Pa s/m. Estimating $\xi = \xi_\perp \sim 30$ Å from x-ray diffraction on similar smectics [5], one finds $\eta_p \sim 10$ Pa s, 2 orders of magnitude larger than in usual nematics but acceptable for smectics.

In Fig. 2, superimposed on the viscoelastic relaxation, we observe two weak oscillations of σ, reminiscent of the previously observed stress oscillations in plastic crystals [6], but much weaker. These oscillations are not easy to obtain: It is necessary to anneal the sample in the S_A phase for one day and to record the first stress curves after a rest time. The shear displacement measured between two successive oscillations is 28 ± 2 Å. The same experiment made under a larger strain $2\delta_0 = 160$ Å gives a similar response with five stress oscillations of weaker amplitude, periodic and again with a displacement 28 ± 2 Å between them. This distance corresponds to the layer spacing of 28.6 Å measured on the same material by x-ray diffraction [7]. We associate the stress oscillations with the jump of smectic layers on one molecular distance above the fixed surface molecules. From our experiment, we can deduce the amplitude $\Delta\sigma$ of the stress oscillations, by the stress deviation from the mean viscoelastic $\sigma(t)$ curve on the observed molecular period $d(\delta)$, and the energy $E_S \sim \Delta\sigma d(\delta)$ of the shear oscillation. We find $E_S \sim 10^{-8}$ J/m^2. From (6), with $\Psi_B^2 \sim (T_c - T)/T = 3 \times 10^{-2}$, we obtain $E_S \sim 10^{-4}\Psi_S$ J/m^2. Assuming the sample is a single crystal over the whole surface, we obtain $\Psi_S \sim 10^{-4}$. The same experiment, performed at a higher temperature $T = 57.9$ °C, corresponding to $\Psi_B^2 \sim 2 \times 10^{-2}$, gives $E_S \sim 10^{-9}$ J/m^2, resulting in a lower $\Psi_S \sim 2 \times 10^{-5}$. The T dependence of Ψ_S is qualitatively correct. Its small value could be due to a possible polycrystalline surface structure, so that Ψ_S may be locally much larger than its average value. These small values of Ψ_S explain the relatively small amplitude of the stress oscillations compared to the plastic crystals.

We repeat the experiment in the S_B phase, with the

same layer geometry but a three-dimensional (3D) positional ordering. At $T = 45$ °C, under periodic shear strain parallel to the smectic layers, $\sigma(t)$ presents an elastic part with $C_{44} = 1.5 \times 10^7$ N/m^2, followed by an elastic limit and a linear plastic deformation without any oscillation. Stress oscillations can be obtained under a different experimental procedure: The sample is first submitted during 20 s to a low strain deformation in the elastic regime ($2\delta_0 = 2$ Å). A few seconds later, $\sigma(t)$ is recorded with $2\delta_0 = 23$ Å (Fig. 3). Two stress oscillations are then visible, separated by a distance equal to 8.6 ± 0.5 Å. The crystallographic structure in the smectic-B layers is a hexagonal lattice with parameter $a_0 = 5.0$ Å [7]. A local orientational ordering in the layers is superimposed on this lattice [8]: Molecules have the same orientation on a rectangular network with parameters a_0 and $a_0\sqrt{3}$. The measured distance 8.6 Å $= 5\sqrt{3}$ Å corresponds to this last value. The smectic-B oscillations can thus be interpreted as surface jumps on the distance between molecules with the same orientation. The preliminary elastic deformation probably helps to extend the local surface orientational ordering over the interface plane.

We now shear the glass interface along Ox, normal to the smectic layers. A response similar to the S_A one is obtained, but only at frequencies $\nu \geq 100$ Hz and close to the S_B-S_A transition in the range 48 °C $< T <$ 49.5 °C. The response is viscoelastic with weak superimposed stress oscillations, at a period 27 ± 3 Å. Although the sample is a 3D crystal, a shear flow must appear as in S_A, which can be explained with the same model. At $T = 48.4$ °C and $\nu = 100$ Hz, we measure $C_{44} = 1.7 \times 10^5$ N/m^2, $\sigma(\infty) = 10$ N/m^2, and $\tau = 2 \times 10^{-3}$ s. Using (7), with $d = 35$ μm and $V = 1.5 \times 10^{-6}$ m/s, calling ξ_B the S_B coherence length, we obtain $\eta_p/\xi_B = 10^7$, 2 orders of magnitude lower than in S_A. Since the S_B-S_A transition is first order, ξ_B cannot diverge much at this transition, so that η_p is probably much lower in the S_B phase.

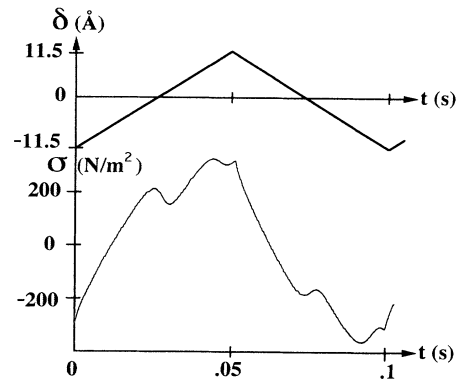Stress oscillations at molecular period have been al-

FIG. 3. Same as Fig. 2 for 4O.8 in the S_B phase ($T = 45$ °C). The shear is now periodic and the stress is accumulated on 16 periods.

ready observed in cubic plastic crystals [6]: Under the same experimental conditions, plastic crystals present deep periodic stress oscillations with a period equal to 1 or 2 times the lattice parameter. These observations were explained by a coherent slip of molecular planes at the crystal-glass interface. The common behavior of sheared S_A, S_B, and plastic crystals suggests now a common explanation. For S_A, the oscillations are explained by periodic melting and recrystallization of the layers near the interface. We propose the same model for the three kinds of structure: Some molecules are anchored at the surface, with a weak surface ordering imposed by the bulk; under shear stress, in a thin zone near the interface, a unidimensional melting and recrystallization occurs in the direction normal to the solid surface; in the perturbed zone, the one-dimensional (1D) S_A crystal is completely melted, but the 3D ordered S_B and plastic crystals keep a 2D ordering. The common observed periodic stress oscillations of these relatively soft materials close to a solid interface suggest that the model of periodic melting and recrystallization could be a general description of solid friction.

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