Memory-Free Conic Anchoring of Liquid Crystals on a Solid Substrate

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We show that the anchoring memory of liquid crystals on solid substrates can be completely removed by grafting highly mobile polymer chains. Using grafted polystyrene, we obtain uniform, stable, and reproducible memory-free and conically degenerated anchoring of the nematic 5CB. The symmetry of the conic anchoring enables two different zenithal anchoring breakings, towards homeotropic and planar states. Under external torques we observe both of them, with weak thresholds.

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Nematic liquid crystals (LC) are anisotropic liquids with elongated molecules, on average parallel to a local symmetry axis $\mathbf{n}$, called director. Sample boundaries usually impose orientation of the surface director $\mathbf{n}_s$ along some "easy" axis $\mathbf{n}_e$. This "anchoring" phenomenon is described by an anchoring energy $W_s(\mathbf{n}_e, \mathbf{n}_s)$, minimized for $\mathbf{n}_s \parallel \mathbf{n}_e$. The symmetry and the strength of the anchoring depend on the surface anisotropy. All surfaces are strongly anisotropic along their normal, resulting in relatively strong zenithal (out-of-plane) anchoring. The azimuthal (in-plane) anchoring is usually weaker and is expected even to vanish on isotropic substrates. The anchoring then is degenerated [1], with easy axis replaced by an "easy surface," in general a cone of revolution (Fig. 1).

This azimuthal degeneration is typical for LC interfaces with isotropic fluids. On isotropic solids, however, the anchoring degeneration is removed by the orientational memory [2]. These surfaces are really isotropic only before the first contact with the LC. On contact, the initial random orientation of $\mathbf{n}_s$ is *memorized* on the surface, mostly by adsorption of an oriented layer of nematic molecules [3]. The adsorbed layer behaves as a new, strongly anisotropic substrate [3,4], imposing ill defined monostable anchoring. Recently, Bryan-Brown *et al.* [5] have shown that doping of the LC with oligomeric impurities makes the surface "slippery"—the segregation of the dopant close to the substrate gives a thin isotropic layer, screening the memory. The resulting anchoring is azimuthally degenerated, with weak zenithal energy. However, this liquid anchoring layer of impurities could diffuse in the bulk and to the other surface, modifying their properties. At long term it could be unstable mechanically and chemically, especially under strong fields and hydrodynamic flows.

Here we demonstrate that memory-free, azimuthally degenerated anchorings can be realized also on solid surfaces. To eliminate the memory we "lubricate" the anchoring by a thin layer of highly mobile, fluid polymer chains, grafted to the surface. This enables the nematic molecules to reorient with the chains themselves and we observe conically degenerated and memory-free anchoring, with weak zenithal strength and long-term stability. We show that the symmetry of the conic anchoring enables two different anchoring breakings under applied torque, toward homeotropic and planar states, respectively. We observe experimentally both these breakings.

To remove the anchoring memory, one has to avoid the adsorption of the LC, e.g., by saturating the adsorption sites on the surface by some "passivation" layer, consisting of nonmesogenic molecules [6]. However, it is difficult to avoid the adsorption on the passivation layer itself, giving rise again to a memory induced anchoring. Another possible approach is to cover the surface with highly flexible, "fluid" polymer chains. The LC molecules, even adsorbed on the chains, can reorient freely—the fluid chains lubricate the anchoring, removing any memory.

Throughout this study we use the nematic pentylcyanobiphenyl (5CB). We started our experiments with spin-coated layers of polyisoprene (PI), chosen for its low glass transition temperature (−70 °C). As expected, the 5CB anchoring on PI was azimuthally degenerated and memory-free (see below the observation technique), due to the high mobility of the polymer chains. In another anchoring "lubrication" experiment we used substrates spin coated with isotropic polystyrene (PS) film. At first contact with 5CB we observe flow alignment patterns on the surface indicating that the initial local $\mathbf{n}_s$ direction is memorized. A few minutes later the memory disappears, leaving degenerate conic anchoring. In this case, 5CB

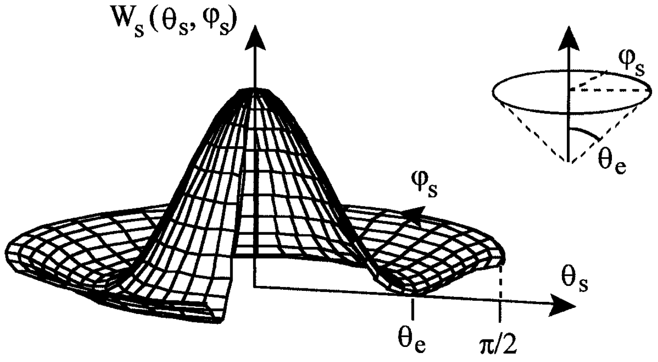

FIG. 1. "Easy cone" and surface energy for conic degenerate anchoring.

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penetrates progressively into the film and the PS chains, initially in the glassy state, become mobile, resulting in memory-free alignment layer.

These two polymer treatments show that the anchoring memory lubrication can be achieved. However, their stability is poor—at long term they dissolve in the nematic and migrate. We can stabilize the PI films by UV cross-linking, but then the conic anchoring is transformed in a trivial memory-dominated alignment. This confirms the importance of the chain fluidity for the memory elimination (the cross-linking reduces drastically the chain mobility).

To resolve this stability problem, we attach chemically the polymer to the surface. Self-assembled films [7] and grafted polymers have already been shown to align LC. In particular, wetting and ellipsometry studies indicate [8] an almost planar orientation of 5CB on a polystyrene brush, grafted to silicon wafer. Using the same technique, we graft monodisperse, trichlorosilane terminated polystyrene to glass plates [9], bare or covered with indium-tin oxide (ITO). We thus obtain a dry polymer brush, with an average thickness d in the range 25–500 Å. The anchoring depends only weakly on d and here we focus on data for $d \cong 460$ Å.

In contact with the brush, the 5CB molecules penetrate into it. Ellipsometry studies [9] show that d increases up to an equilibrium value corresponding to 42% of 5CB (volume fraction) in the brush at room temperature. The swollen film of highly mobile PS chains (firmly bound to the surface by one end) behaves as a disordered fluid interface, inducing memory-free degenerate anchoring similar to the one observed for spin-coated PS or PI layers. However, the film is now stable mechanically and chemically, insoluble in the nematic. It can be washed in toluene and reused, and the anchoring does not change even in two-year-old samples. Unlike fluid surfaces [1] or impurity interfaces [5], our grafted solid substrates enable independent control of the anchorings on the two plates of the cell, easy application of electric fields, and variation of the cell thickness and geometry without change of the anchoring properties. In the following we present mainly the study of these grafted PS layers, only briefly comparing them with the PI anchorings.

The microscopic observations of small nematic drops deposited at room temperature on the PS brush reveal a finite but very small contact angle (a few degrees). At the air-5CB interface the anchoring is homeotropic ($\theta_e = 0$), free of azimuthal torques. The radial $\mathbf{n}_s$ distribution at the substrate [Fig. 2(a)] shows anchoring degeneration. Upon cooling down from the isotropic phase, we observe texture instabilities [Fig. 2(b)], already reported for hybrid nematic cells [10]. Around the defects φ_s varies continuously, without pinning at the surface, showing no anchoring memory.

We confirm these observations in sandwich cells, with 5CB filled between the substrate under study and a standard counterplate with strong monostable anchoring, at choice homeotropic, planar ($\theta_e = \pi/2$), or tilted ($0 < \theta_e < \pi/2$). The cell holder enables a variation of the gap D in the range 1–100 μm and azimuthal rotation of the plates. With homeotropic counterplate the sample shows *schlieren* texture, typical of degenerate alignment [2]. Under weak perturbations the $\mathbf{n}_s$ pattern varies freely, without memory. Planar or tilted alignment on the counterplate gives uniform (U) textures, without twist. These U-textures remain unchanged when the substrate is rotated at arbitrary azimuthal angle. To twist the texture, we apply an in-plane ac ($f > 10$ kHz) electric field $\mathbf{E} \perp \mathbf{n}$, using two parallel conductive ITO electrodes, deposited on one of the plates. This field favors orientation along $\mathbf{E}$ and above the Frederiks threshold, renormalized for the sample geometry, we observe a twisted texture. When the field is removed, the texture relaxes back to the U-state with typical bulk relaxation times, showing no surface elasticity. We estimate the residual azimuthal anchoring strength, if any, to be less than 3×10^{-10} N/m, 5 orders of magnitude weaker than the usual monostable value. Similar anchoring memory lubrication is observed for PI or PS spin-coated films and we expect it for any polymer layer swollen by LC molecules, with fluid enough chains.

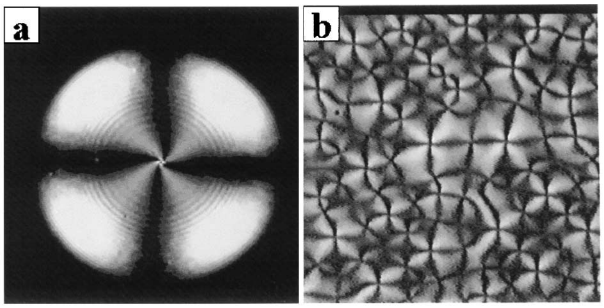

FIG. 2. (a) Radial texture of a 5CB drop on grafted PS at room temperature, showing the azimuthal anchoring degeneration. (b) Texture instabilities close to T_c, showing memory-free anchoring.

The anchoring degeneration could be planar ($\theta_e = \pi/2$) or conic ($0 < \theta_e < \pi/2$). Qualitatively, we can distinguish these two cases using a planar counterplate. For $\theta_e = \pi/2$ the equilibrium texture is unique ($\theta = \pi/2$ throughout the cell). For $\theta_e < \pi/2$ the equilibrium texture is splayed and twofold degenerated—two opposite tilts are possible on the conic plate, with opposite signs of the splay in the cell. We always observe coexistence of twin-splay domains, showing *conic* degeneration. We measure the tilt θ_e from the birefringence variation with the thickness in a free drop [9], or as a function of a weak electric field, applied in a sandwich cell [11]. At room temperature we obtain typically $\theta_e \approx 72°$ for grafted PS and $\theta_e \approx 74°$ for PI. This conic tilt angle varies weakly with temperature, but we never observe temperature driven conic to planar transition.

To study the zenithal energy of the conic anchoring, we need first to consider its symmetry, drastically different from the usual tilted monostable case. Because of the degeneration, the anchoring energy $W_s = W_s(\theta_s)$ is independent of φ_s. Because of the inversion symmetry of the nematic and the revolution symmetry of the easy cone, $W_s(\theta_s)$ is symmetric around *both* $\theta_s = 0$ and $\theta_s = \pi/2$ and should have *extrema* in these two points. In both monostable or degenerate planar cases, $W_s(\theta_s)$ has a minimum for $\theta_s = \theta_e = \pi/2$ and a maximum for $\theta_s = 0$ [Fig. 3(a)]. In first approximation these two planar cases can be described in the usual Rapini-Papoular approximation [12]:

$$W_s(\theta_s) = \tfrac{1}{2}A\cos^2\theta_s\,, \tag{1}$$

where $A > 0$ is the anchoring strength coefficient. Around the energy maximum at $\theta_s = 0$, the anchoring torque vanishes and an anchoring *breaking* can be achieved, when an external torque favors homeotropic alignment—θ_s becomes *exactly* zero under finite field [13,14].

For conic degeneration, however, the anchoring symmetry is incompatible with Eq. (1). Now $W_s(\theta_s)$ presents a minimum for $\theta_s = \theta_e$ and two *maxima* for $\theta_s = 0$ and $\pi/2$ [Fig. 3(b)]. In lowest approximation, we expect an anchoring energy quartic in $\cos\theta_s$:

$$W_s(\theta_s) = \tfrac{1}{2}A\cos^2\theta_s + \tfrac{1}{4}B\cos^4\theta_s + \text{const}\,. \tag{2}$$

This energy should have a minimum for $\theta_s = \theta_e$. This implies $B > -A > 0$, $\cos^2\theta_e = -A/B$ and the energy becomes

$$W_s(\theta_s) = \tfrac{1}{4}B(\cos^2\theta_s - \cos^2\theta_e)^2. \tag{3}$$

Equation (3) is similar to the azimuthal energy [15], already proposed for bistable anchorings. The anchoring torque from Eq. (3) vanishes for *both* maxima, $\theta_s = 0$ and $\theta_s = \pi/2$, showing that *two different anchoring breakings* are possible, toward homeotropic or planar state. For comparison, *neither* of these breakings exist for monostable tilted anchorings.

Around the extrema, the anchoring strength is described by $W_s'' = d^2W_s/d\theta^2$. Comparing W_s'' with the bulk elasticity, we define an anchoring extrapolation length $L = |K/W_s''|$ for each extremum (in one-constant approximation $K_{11} = K_{33} = K$). For planar alignment this reduces to the usual de Gennes' definition [1] and from Eq. (1) $L = K/A$ is the same for both extrema. For conic anchoring, Eq. (3) gives *three different* extrapolation lengths: $L_e = K/(2B\sin^2\theta_e\cos^2\theta_e)$ for $\theta_s = \theta_e$, $L_\perp = K/(B\sin^2\theta_e)$ for $\theta_s = 0$, and $L_\parallel = K/(B\cos^2\theta_e)$ for $\theta_s = \pi/2$.

We measure the anchoring strength from the anchoring breaking thresholds. In a first experiment, we use a thin wedge sample ($D < 1$ μm), with homeotropic alignment on the opposite boundary. This boundary is either the air surface of a free liquid crystal drop, or silane treated spherical glass lens. We measure the thickness locally from the known lens curvatures or from the optical interference pattern in the free drop [9]. A strong mechanical torque $\Gamma_b = K\theta_s/D$ is transmitted from the distorted bulk to the conic substrate. Below a critical thickness $D_\perp = L_\perp$, the anchoring torque $\Gamma_s \cong K\theta_s/L_\perp$ cannot equilibrate Γ_b and the anchoring is broken. We observe the breaking from the vanishing birefringence of the sample at $D = D_\perp$. In a separate experiment we break the anchoring in a sandwich cell, applying an electric field E [11]. In this case the breaking condition is $\xi_E = L_\perp$, where $\xi_E = \sqrt{K/(\varepsilon_0\varepsilon_a E^2)}$ is the electric field correlation length [1]. The values of $L_\perp$, measured by anchoring breaking under mechanical and electric fields (Fig. 4), are in good agreement between them. The corresponding anchoring strength B ($B = 6 \times 10^{-5}$ N/m at 23 °C, $B = 8 \times 10^{-6}$ N/m at $T_c \cong 35$ °C) is 1 order of magnitude weaker than the usual monostable value [16]. The critical electric field is quite weak, $E_c \cong 2.1$ V/μm for PI and $E_c \cong 2.3$ V/μm for PS at room temperature (for comparison, $E_c \geq 10$ V/μm for 5CB on SiO [16]).

Applying a torque from a planar counterplate, close to T_c we observe also the breaking toward planar state ($\theta_s = \pi/2$), at a critical thickness $D_\parallel = L_\parallel$. In this case,

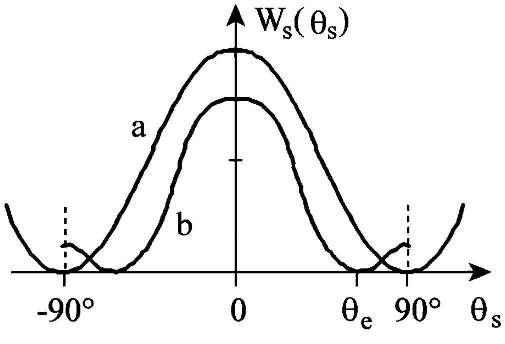

FIG. 3. Zenithal energy of the degenerate anchoring. Curve *a*, planar case: only one minimum ($\theta_s = \pm\pi/2$) and one maximum ($\theta_s = 0$) exist. Curve *b*, conic case: there are one minimum ($\theta_s = \theta_e$) and two maxima ($\theta_s = \pm\pi/2$ or 0).

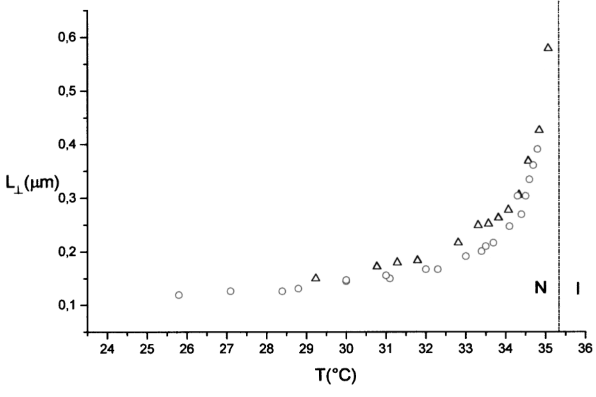

FIG. 4. Temperature dependence of the extrapolation length $L_\perp = K/(B\sin^2\theta_e)$ for anchoring breaking from conic to homeotropic, measured under mechanical constraint (○) and electric field (△).

for decreasing thickness we expect the birefringence not to vanish but to saturate to a fixed value. Experimentally, $D_{\parallel}$ is difficult to observe in wedge cells and we use fixed thickness cell, observing electro-optically [11] the disappearance of the conic tilt at some critical temperature, thickness dependent. In a separate experiment we observe the same breaking applying an in-plane electric field, with $\xi_E = L_{\parallel}$. The values of B, calculated from $L_{\parallel}$ and $L_{\perp}$ are similar ($B \cong 1.4 \times 10^{-5}$ N/m at $T_c - T = 2\,^{\circ}\mathrm{C}$), showing the validity of Eq. (3).

How can this conic anchoring be understood? Close to the surface, the mesogen molecules are disordered by the isotropic polymer chains and the nematic order S decreases. The strong order gradient ∇S creates an ordoelectric polarization $\mathbf{P}_0$, which self-energy is proportional to $(\nabla S)^2(\cos^2\theta_s - \frac{1}{3})^2$ and vanishes [17] at $\theta_s = \theta_m$, the magic angle defined by $\cos^2\theta_m = \frac{1}{3}$. In this way, the surface disorder favors tilted alignment. This ordoelectric effect has already been invoked to explain the tilt at fluid interfaces [5,17] and on SiO layers [18]. We note that the ordoelectric contribution to the coefficients in Eq. (2) is always negative for A and positive for B, as needed to obtain a transition from planar to conic degeneration. The strong polar electro-optic response of our cells also suggests an ordoelectric origin of the conic tilt. The ordoelectric polarization depends on θ_s and couples with the polarity of the applied field, favoring either a decrease or an increase of θ_s. In the latter case we observe polar anchoring breaking from the conic to the planar state with $U_c \sim 0.2$ V. This polar response is 1 order of magnitude stronger than the one expected from the 5CB flexoelectric polarization [19] and we attribute it to ordoelectricity.

The anchoring memory lubrication, achieved in our conic anchorings, seems promising for both basic science and applications. The vanishing azimuthal anchoring energy is interesting for improving the optical characteristics and switching voltages of existing nematic displays [5,6]. The degeneration makes it possible for us to realize sandwich LC cells without any anchoring constraints, enabling us to study the spontaneous bulk properties with free boundary conditions [20]. The weak zenithal anchoring will be useful for the realization of the recently proposed monostable and bistable devices with fast switching by anchoring breaking [6,16,21,22]. The memory removal by anchoring lubrication, if applied to *anisotropic* substrates like rubbed polymers, can resolve some problems of existing LC devices, such as image sticking. More important, this opens the way for realization of uniform, reproducible and stable in time weak or moderately strong anchorings, needed for fast nematic bistable devices [6,16,21,22]—indeed, weak anchorings are usually dominated by anchoring memory, which makes them stronger, sensitive to flow alignment and other perturbations, with easy axis gliding under applied external torques.

In conclusion, we have shown that highly mobile polymer chains, such as polyisoprene or polystyrene, can remove completely the anchoring memory on solid substrates ("anchoring lubrication"). Polystyrene chains, grafted to glass plates and swollen by the LC, give memory-free and azimuthally degenerated conic anchorings, reproducible, uniform and stable mechanically and chemically. Under applied torques, two different anchoring breakings, toward planar or homeotropic states, are observed.

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