Coarse-Grained Surface Energies and Temperature-Induced Anchoring Transitions in Nematic Liquid Crystals

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We introduce a coarse-grained description of the surface energy of a nematic liquid crystal. The thermal fluctuations of the nematic director close to the surface renormalize at macroscopic scales the bare surface potential in a temperature-dependent way. The angular dependence of the renormalized potential is dramatically smoothed, thus explaining the success of the Rapini-Papoular form. Close to the isotropic phase, the anchoring energy is strongly suppressed and the change of its shape allows for anchoring transitions. Our theory describes quantitatively the temperature dependence of the anchoring energy and the temperature-induced anchoring transitions reported in the literature. [S0031-9007(99)09369-2]

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In recent years, surface phenomena have attracted a lot of interest. Particularly, the interface between liquid crystals [1] and solid substrates displays a rich variety of behaviors: orientational wetting [2–5] and spreading [6,7], memory effects [8], surface melting [9], Kosterlitz-Thouless transitions [10], quasicritical behavior of surface energies [11–13], surface anchoring transitions [14–22], etc. Despite the complexity and the diversity of the interactions between nematic liquid crystals and solid substrates, some simple—though unexplained—ubiquitous aspects emerge from the experiments: the angular dependences of the surface potentials are extremely smooth and well described by the so-called Rapini-Papoular law [23], at high temperatures the preferred surface orientation is usually either parallel or perpendicular to the substrate, tilted orientations are difficult to achieve [24], and temperature-driven anchoring transitions systematically occur immediately below the bulk isotropic transition temperature [20]. In this Letter, we show that all these effects can be explained in terms of a renormalization of the surface energy by the short-wavelength orientational fluctuations in the bulk.

Nematic liquid crystals are fluid mesophases made of elongated molecules displaying a broken orientational symmetry along a nonpolar direction called the nematic director $\mathbf{n}$ [1]. At a molecular level, nematics exhibit large orientational fluctuations and usually some degree of short-range biaxial and positional order. The link between the microscopic and the macroscopic description can be established by means of a coarse-graining procedure [25]. Before determining the consequences of this procedure on the surface behavior, let us briefly discuss how it is carried out in the bulk. One can associate a local orientation $\mathbf{m}$ with each molecule; then the probability $p[\mathbf{m}]$ of a given instantaneous microscopic configuration $\mathbf{m}(\mathbf{r})$ is proportional to the Boltzmann factor $\exp(-\beta\mathcal{F}[\mathbf{m}])$, where $\mathcal{F}[\mathbf{m}]$ is a complex microscopic free energy [26] and $\beta = 1/k_{\mathrm{B}}T$ is the inverse temperature. At macroscopic scales the bulk free-energy $F[\mathbf{n}]$ is well described by a simple elasticity involving only the average molecular orientation $\mathbf{n}$ and its gradient [1,27]. The quantity $\exp(-\beta F[\mathbf{n}])$ gives the probability of observing a given smooth director configuration $\mathbf{n}(\mathbf{r})$, whatever the details of its rapidly varying components. One therefore obtains the coarse-grained free-energy $F[\mathbf{n}]$ by summing the microscopic probabilities $\exp(-\beta\mathcal{F}[\mathbf{m}])$ over all the Fourier components $\mathbf{m}(\mathbf{q})$ with wave vector $|\mathbf{q}| > \Lambda$, where Λ is some macroscopic cutoff, the components $\mathbf{m}(\mathbf{q})$ with $|\mathbf{q}| < \Lambda$ being fixed and denoted by $\mathbf{n}(\mathbf{q})$. The resulting free-energy $F[\mathbf{n}]$, which corresponds to the Frank elasticity [27], is therefore meaningful only for the slowly varying Fourier components $|\mathbf{q}| < \Lambda$ of $\mathbf{n}$. Such a coarse-graining procedure yields a renormalized elasticity expanded in power series of the derivatives of $\mathbf{n}$, whose coefficients depend on T and are expected to scale as powers of the range b of the molecular interactions. This is why, for $\Lambda b \ll 1$, it is justified to retain in $F[\mathbf{n}]$ only the lowest-order gradient terms.

Using the Frank elasticity $F[\mathbf{n}]$ implicitly entails a coarse graining in the bulk. For the sake of consistency, this procedure should also be performed on the surface. The latter will then be effectively transformed into a blurred layer of width Λ^{-1} acquiring some properties of the bulk. Such a coupling between surface and bulk is usually introduced in a phenomenological way by means of Landau expansions in the tensorial nematic order-parameter $\mathbf{Q}$ [2–4,9–14,28,29]. However, modeling surface properties in this way is rather complicated, since one has to deal with spatially varying tensorial fields, and also somewhat arbitrary, since high powers of $\mathbf{Q}$ should be included due to the first-order character of the nematic-isotropic transition.

We have calculated the renormalization of the surface energy by coarse graining the director orientation from a mesoscopic length a, of the order of the nematic coherence length ξ_{NI} at the isotropic transition [1], up to a scale Λ^{-1} at least a few times larger than a. Our results, based on perturbation theory, are valid for weak anchorings, in the sense $\ell \gg \xi_{\mathrm{NI}}$, where ℓ is the anchoring extrapolation length [1]. Calling θ and ϕ the director's polar angles and starting from a "bare" surface anchoring energy expanded in Fourier harmonics of the form $\mathrm{cs}(2n\theta)\ \mathrm{cs}(m\phi)$ (cs being either cos or sin), we find that each harmonic is independently renormalized by a Debye-Waller factor $\exp(-\alpha_n - \beta_m)$, with $\alpha_n, \beta_n \propto n^2 k_{\mathrm{B}} T/Ka$, where K is a bulk nematic elastic constant. At scales larger than Λ^{-1}, the high-order harmonics are thus strongly suppressed by the director thermal fluctuations: this explains the success of the Rapini-Papoular form [23]. Moreover, the anchoring energy naturally acquires a temperature dependence through the elastic constant $K(T)$. The surface energy is thus reduced close to the nematic-isotropic transition—where K is lowered—in agreement with experiments [11–13]. The different temperature dependences of the surface harmonics allow for anchoring transitions: as the temperature increases, the suppression of the high-order harmonics shifts the minimum of the anchoring energy towards some symmetry axis of the surface. Our results fit well the quasicritical temperature dependence of the azimuthal anchoring energy measured by Faetti *et al.* [11], the oblique-to-homeotropic anchoring transition measured by Patel and Yokoyama [20], and the bistable oblique-to-planar anchoring transition [16] measured by Jägemalm *et al.* [22]. It turns out that the effective macroscopic anchoring, whose minimum gives the coarse-grained director orientation at the surface, can significantly differ from the mesoscopic surface potential (Fig. 1). The director fluctuations within the coarse-grained region dramatically smooth the fine details of the anchoring energy. They can also shift the average equilibrium position of the director at the surface, similarly to the amplitude-dependent shift of the average position of an anharmonic oscillator [30].

Precisely, we consider a semi-infinite nematic slab in the $z \geq 0$ half-space, and we describe the nematic director by its spherical coordinates θ, ϕ centered on the z axis. We start with a bulk elasticity already coarse grained on a mesoscopic length $a \approx \xi_{\mathrm{NI}}$, such that it can be expressed in the usual Frank form. In the one-constant approximation [1], its harmonic part, expanded about an arbitrary direction (θ_0, ϕ_0), takes the form

$$\mathcal{H}_0 = \frac{1}{2} K(T) \int d^3r[(\nabla\theta)^2 + \sin^2\theta_0(\nabla\phi)^2]. \qquad (1)$$

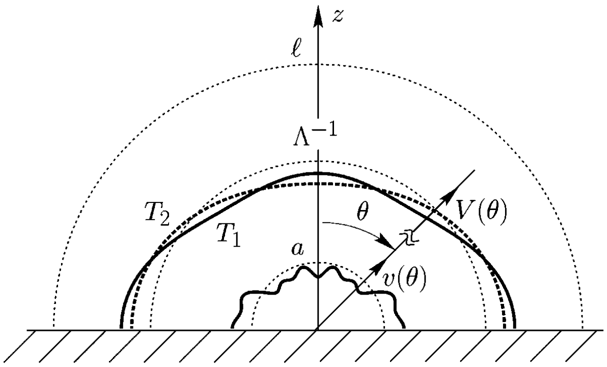

FIG. 1. Schematic representation of the surface and its anchoring potential at the mesoscopic scale a and coarse-grained scale Λ^{-1}. The mesoscopic potential $v(\theta)$ and its corresponding effective coarse-grained potential $V(\theta)$ are plotted in polar coordinates in arbitrary units. The renormalized potential $V(\theta)$, which depends on temperature, favors here an oblique anchoring at T_1 and an homeotropic one at $T_2 > T_1$.

At the length scale a, the bare surface potential $\mathcal{H}_s$ is given by some local functional of the mesoscopic director's orientation at the surface

$$\mathcal{H}_s = \int d^2r_\perp\, v(\theta, \phi). \qquad (2)$$

The total free-energy F_t of the nematic slab is given by the path integral

$$\exp(-\beta F_t) = \int \mathcal{D}[\theta]\mathcal{D}[\phi] \times \exp[-\beta(\mathcal{H}_0 + \mathcal{H}_{\mathrm{nh}} + \mathcal{H}_s)], \qquad (3)$$

where $\mathcal{H}_{\mathrm{nh}}$ contains the nonharmonic bulk terms. To further coarse grain on a length scale $\Lambda^{-1} > a$, we put $\theta(\mathbf{r}) = \theta^{<}(\mathbf{r}) + \theta^{>}(\mathbf{r})$ and $\phi(\mathbf{r}) = \phi^{<}(\mathbf{r}) + \phi^{>}(\mathbf{r})$, where $\theta^{<}(\mathbf{r})$, $\phi^{<}(\mathbf{r})$ have Fourier components with wave vectors $|\mathbf{q}| \leq \Lambda$, and $\theta^{>}(\mathbf{r})$, $\phi^{>}(\mathbf{r})$ have Fourier components with $\Lambda < |\mathbf{q}| < 2\pi/a$. Integrating out $\theta^{>}$ and $\phi^{>}$ yields the renormalized Hamiltonian $\mathcal{H}^{<}$ at length scales Λ^{-1}; to lowest order in perturbation theory, it is given by [25]

$$\mathcal{H}^{<} = \mathcal{H}_0 + \langle \mathcal{H}_{\mathrm{nh}} + \mathcal{H}_s \rangle_{>}, \qquad (4)$$

where $\langle \cdots \rangle_{>}$ indicates the statistical average over the high-wave vector components, weighted by the Gaussian Hamiltonian $\mathcal{H}_0$. At first order, the bulk and the surface are therefore renormalized independently.

Because of the $\mathbf{n} \rightarrow -\mathbf{n}$ invariance, the bare surface energy density can be Fourier expanded as

$$v(\theta, \phi) = \sum_{n,m}{}' \cos n\theta[w_{nm}^{\mathrm{cc}} \cos m\phi + w_{nm}^{\mathrm{cs}} \sin m\phi] + \sum_{n,m}{}'' \sin n\theta[w_{nm}^{\mathrm{sc}} \cos m\phi + w_{nm}^{\mathrm{ss}} \sin m\phi], \qquad (5)$$

where n runs over all even integers, and m runs over all even (respectively, odd) integers in the first (respectively, second) sum.

Even though (5) is nonlinear, the renormalized Hamiltonian (4) can be transformed into Gaussian integrals by writing the trigonometric functions as complex exponentials. We obtain a renormalized surface energy density $V(\theta^{<}, \phi^{<})$ whose Fourier components $W_{nm}^{\alpha\beta}$ (α, β being either c or s) are separately renormalized,

$$W_{nm}^{\alpha\beta}(t) = w_{nm}^{\alpha\beta} \exp\left[-\frac{1}{2}\left(n^2 + \frac{m^2}{\sin^2\theta_0}\right)t\right], \qquad (6)$$

where, for $\Lambda a \ll 1$,

$$t = \langle \theta^{>}(\mathbf{r})^2 \rangle_{>} = k_B T \int_{\Lambda}^{2\pi/a} \frac{d^3q}{(2\pi)^3} \frac{1}{Kq^2} \simeq \frac{k_B T}{\pi K a}. \tag{7}$$

Note that $\langle \phi^{>}(\mathbf{r})^2 \rangle_{>} = t/\sin^2\theta_0$ also appears in (6).

It follows from (6) that for large t, i.e., in the vicinity of the nematic-isotropic transition, where K is reduced, the effective surface potential should be very well described by its first harmonics. This is indeed what was measured by Faetti *et al.* [11] using the nematic liquid crystal 5CB, planarly anchored on a glass plate treated by oblique evaporation of SiO: exploring the azimuthal anchoring energy in regions far away from the parabolic minimum, they could not detect any deviation from the simple form

$$V = W_0 \sin^2\phi = W_{02}^{\rm cc} \cos 2\phi + \text{const.} \tag{8}$$

Setting $\theta_0 = \pi/2$, $\phi_0 = 0$, we have fitted their data with (6), i.e., $W_{02}^{\rm cc}(t) = w_{02}^{\rm cc} \exp(-2t)$, in which we have assumed a Landau–de Gennes form for the temperature dependence of K [31], yielding

$$t = \frac{k_B T_{\rm NI}}{\pi K_{\rm NI}\, a} \left(\frac{4}{3 + \sqrt{9 - 8\tau}} \right)^2, \tag{9}$$

where $\tau = (T - T^*)/(T_{\rm NI} - T^*)$ is the reduced temperature, $T_{\rm NI}$ the nematic-isotropic transition temperature, T^* the isotropic supercooling temperature, and $K_{\rm NI}$ the elastic constant at the transition. With $T_{\rm NI} \simeq 306.8$ K, $T_{\rm NI} - T^* \simeq 1.5$ K [32], our best fit, shown in Fig. 2, yields $t_{\rm NI} \equiv k_B T_{\rm NI}/\pi K_{\rm NI}\, a = 2.1 \pm 0.1$ and $W_{02}^{\rm cc}(t_{\rm NI}) = (-2.08 \pm 0.08) \times 10^{-4}$ erg/cm^2. For an extrapolated $K_{\rm NI} \simeq 0.5$ pN [33], the value of $t_{\rm NI}$ yields $a \simeq 13$ Å, which roughly compares with $\xi_{\rm NI}$ for a first-order phase transition.

Close to the nematic-isotropic transition of the nematic compound E7, Patel and Yokoyama [20] have observed a tilted-to-homeotropic anchoring transition on a fluoropolymer-coated surface. Again, we can explain it by retaining in V the first two harmonics allowed by symmetry, i.e.,

$$V = W_{20}^{\rm cc} \cos 2\theta + W_{40}^{\rm cc} \cos 4\theta. \tag{10}$$

Minimizing (10) with respect to θ yields the anchoring phase diagram shown in the inset of Fig. 3, which displays the following regions separated by second-order transition lines: conical oblique (O), homeotropic (H), degenerated planar (P), and metastable homeotropic/planar (H/P). According to (6) and (9), as temperature increases, the easy axis of the anchoring follows the typical path shown in the phase diagram. Setting $T_{\rm NI} \simeq 57.7$ °C and $T_{\rm H} = 54.48$ °C [20], where $T_{\rm H}$ is the homeotropic-to-oblique transition temperature, we fit closely the temperature dependence of the easy-axis direction θ with $T_{\rm NI} - T^* \simeq 1.62$ K and $t_{\rm NI} = 1.2 \pm 0.04$ (Fig. 3).

Using the same values of $T_{\rm NI}$, $T_{\rm NI} - T^*$, and $t_{\rm NI}$, which depend only on the nematic material, we can fit equally well the bistable oblique-to-planar anchoring transition observed by Jägemalm *et al.* [22] at $T = T_{\rm P} = 49.7$ °C for the same compound E7 (Fig. 4). This anchoring transition also appears close to the nematic-isotropic transition, in the presence of a glass substrate treated by an oblique evaporation of SiO. Here, by symmetry, the lowest-order expansion of V is

$$V = W_{20}^{\rm cc} \cos 2\theta + W_{02}^{\rm cc} \cos 2\phi + W_{21}^{\rm sc} \sin 2\theta \cos\phi. \tag{11}$$

Setting $\overline{W}_\theta = W_{20}^{\rm cc}/W_{02}^{\rm cc}$ and $\overline{W}_{\theta\phi} = |W_{21}^{\rm sc}/W_{02}^{\rm cc}|$, the corresponding anchoring phase diagram, shown in the inset of Fig. 4, displays the four regions, separated by second-order transition lines, that are observed experimentally [16,17]: oblique in the evaporation plane (O), bistable symmetric with respect to the evaporation plane (B),

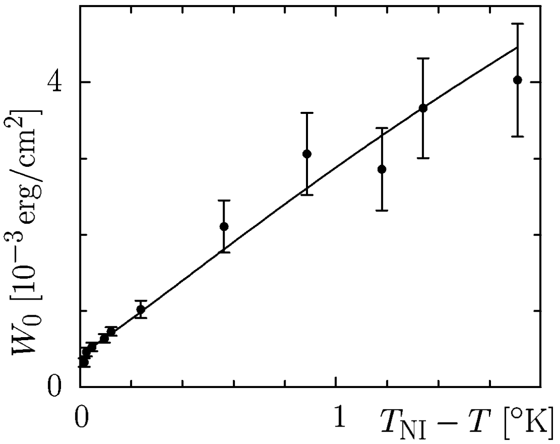

FIG. 2. Azimuthal anchoring energy W_0 vs temperature T according to Faetti *et al.* [11]. Points: experimental data; solid line: our fit.

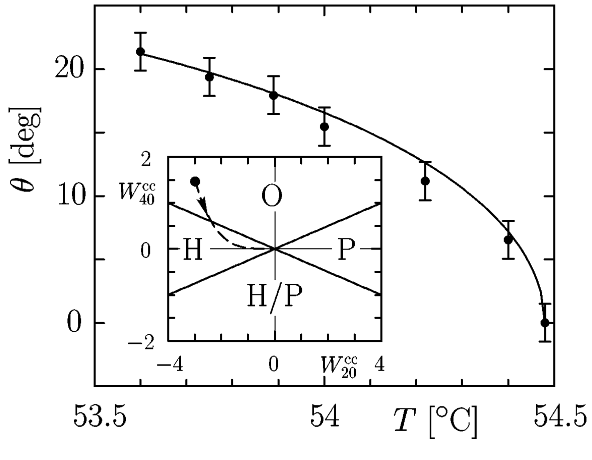

FIG. 3. Surface easy-axis θ (measured with respect to the surface normal) vs temperature T according to Patel and Yokoyama [20]. Points: experimental data; solid line: our fit. Inset: Anchoring phase diagram (in arbitrary units) corresponding to Eq. (10).

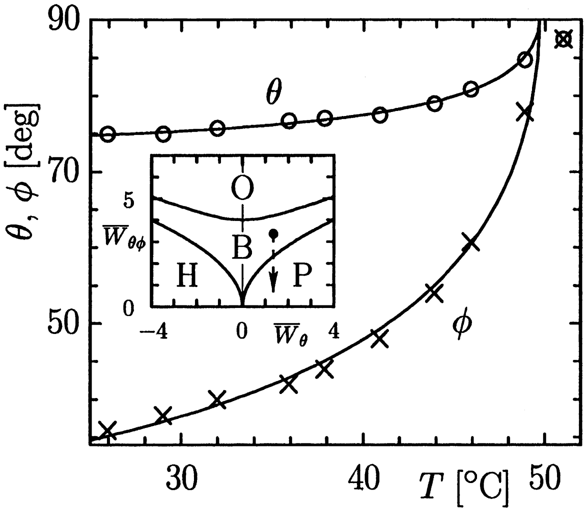

FIG. 4. Surface easy-axis (θ, ϕ) vs temperature T according to Jägemalm *et al.* [22]. Points: experimental data; solid line: our fit. Inset: anchoring phase diagram corresponding to Eq. (11); the arrow indicates the path followed as T increases.

homeotropic (H), and planar orthogonal to the evaporation plane (P). Once fixed the values of $T_{\rm P}$, and, by the previous fit, of $T_{\rm NI}$, $T_{\rm NI} - T^*$, and $t_{\rm NI}$, the fit on θ has no adjustable parameter, while for the fit on ϕ there remains the only free parameter $w_{21}^{\rm sc}/w_{02}^{\rm cc}$, best adjusted to the value 6.76 ± 0.05.

To estimate the validity of our first-order perturbative expansion in the surface potential, we have calculated the second-order correction to $W_{40}^{\rm cc}$ coming from $w_{20}^{\rm cc}$ [34]. For $\Lambda a \ll 1$, we find

$$\frac{\delta W_{40}^{\rm cc}}{w_{20}^{\rm cc}} \simeq \frac{2\, w_{20}^{\rm cc}}{\pi \Lambda K} \exp(-4t)\,, \qquad (12)$$

which is negligible for $\Lambda^{-1} \ll \ell$, where $\ell = K/w_{20}^{\rm cc}$ is a bare anchoring extrapolation length; this sets the limit of validity of our analysis. Coarse graining on a length $\Lambda^{-1} \gtrsim \ell$ effectively reduces the anchoring for purely elastic reasons, as will be described elsewhere.

Finally, note that, since we coarse grained on a length $\Lambda^{-1} > \xi_{\rm NI}$, our model is insensitive to the variations of the scalar order-parameter S [1]. This does not imply, however, that S must be uniform throughout the sample: any substrate inducing a surface variation of S will still be described—at length scales larger than $\xi_{\rm NI}$—by some potential $v(\theta, \phi)$ depending only on the director's orientation. Our analysis simply disregards the underlying surface variations of S: this is a limitation only when $\xi_{\rm NI}$ becomes critically large.

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