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.

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In recent years, surface phenomena have attracted a lot of interest. Particularly, the interface between liquid crystals and solid substrates displays a rich variety of behaviors: orientational wetting and spreading memory effects, surface melting, Kosterlitz-Thouless transitions, quasi-critical behavior of surface energies, surface anchoring transitions, 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, at high temperatures the preferred surface orientation is usually either parallel or perpendicular to the substrate, tilted orientations are difficult to achieve, and temperature-driven anchoring transitions systematically occur immediately below the bulk isotropic transition temperature. 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 non-polar direction called the nematic director. At a molecular level, nematics exhibit large orientational fluctuations and usual 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. 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 to each molecule; then the probability of observing a given instantaneous microscopic configuration is proportional to the Boltzmann factor, where is a complex microscopic free-energy and is the inverse temperature. At macroscopic scales the bulk free-energy is well described by a simple elasticity involving only the average molecular orientation and its gradient. The quantity gives the probability of observing a given smooth director configuration, whatever the details of its rapidly varying components. One therefore obtains the coarse-grained free-energy by summing the microscopic probabilities over all the Fourier components with wavevector and where is some macroscopic cutoff, the components with being fixed and denoted by . The resulting free-energy, which corresponds to the Frank elasticity, is therefore meaningful only for the slowly varying Fourier components whose coefficients depend on and are expected to scale as powers of the range of the molecular interactions. This is why, for , it is justified to retain in only the lowest-order gradient terms.

Using the Frank elasticity 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 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. 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 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 , of the order of the nematic coherence length at the isotropic transition, up to a scale at least a few times larger than . Our results, based on perturbation theory, are valid for weak anchorings, in
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 \( \theta, \phi \) centered on the \( z \)-axis. we start with a bulk elasticity already coarse-grained on a mesoscopic length \( a \approx \xi_{N1} \), such that it can be expressed in the usual Frank form. in the one-constant approximation \( \xi_{N1}^2 \), its surface energy naturally acquires a temperature dependence of the surface harmonics. they can also shift the minimum of the anchoring energy measured by Jägemalm et al. \[12\]. it turns out that the oblique-to-homeotropic anchoring energy. our results fit well the quasi-critical temperature dependence of the surface harmonics. 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 quasi-critical temperature dependence of the azimuthal anchoring energy measured by Faetti et al. \[11\], the oblique-to-homeotropic anchoring transition measured by Patel and Yokoyama \[12\], and the bistable oblique-to-planar anchoring transition measured by Jägemalm et al. \[13\]. 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 \[10\].
where, for $\Lambda a \ll 1$,

$$t = \langle \phi^2(r) \rangle > = \kappa_b T \int_\Lambda \frac{d^3 q}{(2\pi)^3} \frac{1}{Kq^2} \approx \frac{\kappa_b T}{\pi K a} \quad (7)$$

Note that $\langle \phi^2(r) \rangle > = t/\sin^2 \theta_0$ 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. [1] 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

$$V = W_0 \sin^2 \phi = W_{0z} \cos 2\phi + \text{const.} \quad (8)$$

Setting $\theta_0 = \pi/2$, $\phi_0 = 0$, we have fitted their data with (8), i.e., $W_{0z}^{\rm ef}(t) = W_{0z}^{\rm ef} \exp(-2t)$, in which we have assumed a Landau-de Gennes form for the temperature dependence of $K$ [21], yielding

$$t = \frac{\kappa_b t_{\rm N1}}{\pi K_{\rm N1} a} \left( \frac{4}{3 + \sqrt{9 - 8\tau}} \right)^2 \quad (9)$$

where $\tau = (T - T^*)/(T_{\rm N1} - T^*)$ is the reduced temperature, $T_{\rm N1}$ the nematic-isotropic transition temperature, $T^*$ the isotropic supercooling temperature, and $K_{\rm N1}$ the elastic constant at the transition. With $T_{\rm N1} \approx 306.8{\degree}K$, $T_{\rm N1} - T^* \approx 1.5{\degree}K$ [22], our best fit, shown in Fig. 2, yields $t_{\rm N1} = \kappa_b t_{\rm N1}/\pi K_{\rm N1} a = 2.1 \pm 0.1$ and $W_{0z}^{\rm ef}(t_{\rm N1}) = (-2.08 \pm 0.08) \times 10^{-4}$ erg/cm$^2$. For an extrapolated $K_{\rm N1} \approx 0.5$ pN [23], the value of $t_{\rm N1}$ yields $a \approx 13$ Å,

which roughly compares with $\xi_{\rm N1}$ for a first-order phase transition.

Close to the nematic-isotropic transition of the nematic compound E7, Patel and Yokoyama [23] 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.,

$$V = W_{20}^{c} \cos 2\theta + W_{40}^{c} \cos 4\theta \quad (10)$$

Minimizing (10) with respect to $\theta$ yields the anchoring phase diagram shown in the inset in 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 $T_{\rm N1} \approx 57.7{\degree}C$ and $T_H = 54.48{\degree}C$ [24], where $T_H$ is the homeotropic-to-oblique transition temperature, we fit closely the temperature dependence of the easy-axis direction $\theta$ with $T_{\rm N1} - T^* \approx 1.62{\degree}C$ and $t_{\rm N1} = 1.2 \pm 0.04$ (Fig. 3).

Using the same values of $T_{\rm N1}$, $T_{\rm N1} - T^*$ and $t_{\rm N1}$, which depend only on the nematic material, we can fit equally well the bistable oblique-to-planar anchoring transition observed by Jægemalm et al. [25] at $T = T_p = 49.7{\degree}C$ 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

$$V = W_{20}^{c} \cos 2\theta + W_{40}^{c} \cos 2\phi + W_{21}^{c} \sin 2\theta \cos \phi \quad (11)$$

Setting $W_{\theta} = W_{20}^{c}/W_{02}^{c}$ and $W_{\phi} = |W_{21}^{c}/W_{02}^{c}|$, 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), homeotropic (H), and planar orthogonal to the evaporation plane (P). Once fixed the values of $T_{NI}$, $T_{NI} - T^*$, and $t_{NI}$, the fit on $\theta$ has no adjustable parameter, while for the fit on $\phi$ there remains the only free parameter $w_{21}^c/w_{02}^c$, best adjusted to the value $6.76 \pm 0.05$.

To estimate the validity of our first-order perturbative expansion in the surface potential, we have calculated the second-order correction to $W_{40}^c$ coming from $w_{20}^c$ [24]. For $\Lambda a \ll 1$, we find

$$\frac{\delta W_{40}^c}{w_{20}^c} \approx \frac{2 w_{20}^c}{\pi A K} \exp(-4t),$$

(12)

which is negligible for $\Lambda^{-1} \ll \ell$, where $\ell = K/w_{20}^c$ 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 $\Lambda^{-1} > \xi_{NI}$, our model is insensitive to the variations of the scalar order-parameter $S$. 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 $\xi_{NI}$—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 $\xi_{NI}$ becomes critically large.

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[1] P. G. de Gennes and J. Prost, The Physics of Liquid Crystals (Clarendon Press, Oxford, 1993).
[2] P. Sheng, Phys. Rev. Lett. 37, 1059 (1976).
[3] K. Miyano, Phys. Rev. Lett. 43, 51 (1979).
[4] R. Lipowsky, Phys. Rev. Lett. 49, 1575 (1982).
[5] G. P. Crawford, R. Ondris-Crawford, S. Žumer, and J. W. Doane, Phys. Rev. Lett. 70, 1838 (1993).
[6] J. Xue, C. S. Jung, and M. W. Kim, Phys. Rev. Lett. 69, 474 (1992).
[7] M. P. Valignat et al., Phys. Rev. Lett. 77, 1994 (1996).
[8] Y. Ouchi, M. B. Feller, T. Moses, and Y. R. Shen, Phys. Rev. Lett. 68, 3040 (1992).
[9] R. Barberi and G. Durand, Phys. Rev. A 41, 2207 (1990).
[10] T. J. Sluckin and A. Poniewierski, Phys. Rev. Lett. 55, 2907 (1985).
[11] S. Faetti, M. Gatti, V. Palleschi, and T. J. Sluckin, Phys. Rev. Lett. 55, 1681 (1985).
[12] D.-S. Seo, Y. Limura, and S. Kobayashi, Appl. Phys. Lett. 61, 234 (1992).
[13] Y. Peng et al., Mol. Cryst. Liq. Cryst. 304, 253 (1997).
[14] B. Jérôme, Rep. Prog. Phys. 54, 391 (1991).
[15] G. Ryschenkow and M. Kléman, J. Chem. Phys. 64, 404 (1976).
[16] M. Monkade, M. Boix, and G. Durand, Europhys. Lett. 5, 697 (1988).
[17] B. Jérôme, P. Pieranski, and M. Boix, Europhys. Lett. 5, 693 (1988).
[18] J. Bechhoefer et al., Phys. Rev. Lett. 64, 1911 (1990).
[19] P. I. C. Teixeira and T. J. Sluckin, J. Chem. Phys. 97, 1498 (1992).
[20] J. S. Patel and H. Yokoyama, Nature 362, 525 (1993).
[21] Yang-Ming Zhu et al., Phys. Rev. Lett. 72, 2573 (1994).
[22] P. Jägemalm, G. Barbero, L. Komitov, and A. Strigazzi, Phys. Lett. A 235, 621 (1997).
[23] A. Rapini and M. Papoular, J. Phys. Coll. 30, C4-54 (1969).
[24] R. Filas and J. S. Patel, Appl. Phys. Lett. 50, 1426 (1987).
[25] P. M. Chaikin and T. C. Lubensky, Principles of Condensed Matter Physics (Cambridge University Press, Cambridge, 1995).
[26] $\mathcal{F}$ is formally obtained from the total Hamiltonian by integrating out all the microscopic degrees of freedom other than $m$.
[27] F. C. Frank, Disc. Faraday Soc. 25, 19 (1958).
[28] G. Barbero, Z. Gabbasova, and M. A. Osipov, J. Phys. II (France) 1, 691 (1991).
[29] A. K. Sen and D. E. Sullivan, Phys. Rev. A 35, 1391 (1987).
[30] See, e.g., L. Landau and E. Lifchitz, *Mécanique* (Mir, Moscou, 1982).

[31] E. B. Priestley, P. J. Wojtowicz, and P. Sheng, *Introduction to Liquid Crystals* (Plenum, New York, 1979).

[32] I. Lelidis and G. Durand, Phys. Rev. E 48, 3822 (1993).

[33] J. D. Bunning, T. E. Faber, and P. L. Sherrell, J. Phys. (Paris) 42, 1175 (1981).

[34] Actually, all orders can be calculated separately by means of Gaussian integrals.