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Effect of director fluctuations on the surface tension of nematic liquid crystals

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We discuss the surface tension of a thermotropic nematic liquid crystal near the nematic-isotropic temperature. We find that certain experimentally observed features of the temperature trend that present difficulties to mean-field theoretical approaches can be attributed to director fluctuations. Our main result is the possibility of a minimum below T_{NI} if the anchoring extrapolation length scales with reduced temperature in the spinodal limit as t^x, with $x<1$. We also show in the case of partial nematic wetting that dampening of director fluctuations at the surface by anchoring at the nascent interface can reverse the sign of the surface tension discontinuity at T_{NI}. [S1063-651X(99)50604-1]

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Experimental measurements of the surface-tension temperature dependence $\gamma(T)$ of nematic liquid crystals exhibit a number of interesting features in the vicinity of the nematic-isotropic transition temperature T_{NI} [1]. While globally the surface tension decreases monotonically with temperature in a generic fluidlike fashion, in some, though not all, of the available data, there is a region of positive gradient $d\gamma/dT$ on one or both sides of T_{NI}, and there is almost always a discontinuity at T_{NI} itself.

Anomalous behavior of the gradient on the T_{NI}^{+} side of the discontinuity has a straightforward wetting thermodynamics interpretation. Insofar as a nematic wetting layer constitutes negative surface excess orientational entropy, it contributes positively to the temperature derivative of the Gibbs adsorption equation,

$$\partial\gamma/\partial T=-s_s, \tag{1}$$

where s_s is the surface excess entropy per unit area. If the nematic phase completely wets the surface, then $d\gamma/dT$ diverges at T_{NI}, since an ordered wetting layer diverging in thickness is tantamount to diverging surface excess orientational entropy. At some temperature not too far above T_{NI}, a *maximum* must therefore appear as the surface tension recovers the negative-slope characteristic of the isotropic phase [2].

A pretransitional *minimum* below T_{NI} is also commonly observed, but does not have a straightforward orientational wetting thermodynamics interpretation. Recent attempts to explain this feature have applied density-functional techniques [3–5], in which detailed microscopic surface structure is calculated from molecule-molecule interactions in mean-field approximation. Certain carefully chosen interactions are found to induce smecticlike structure just below the surface in the region T_{NI}^{-}, and this may lead to a surface tension minimum driven by surface excess entropy deriving primarily from translational, as opposed to orientational, degrees of freedom.

A drawback of these studies is that they rely on rather specific anisotropic attractive interactions, constructed by superposing terms of the spherical-harmonics expansion with at best conjectural physical contingency. Moreover, the conclusion arrived at, that smecticlike subsurface structure is responsible for the surface-tension minimum, begs the question of why, qualitatively speaking, smectic order should be increasing as temperature increases *away* from the bulk *Sm-N* transition. This is a counterintuitive state of affairs, in view of the wetting paradigm, obfuscated in the models by subtle coupling effects that lend it the character of a less-than-compelling numerical artifact.

The present discussion is motivated in part by the inconclusiveness of the density-functional approach. We argue that the swing in negative surface entropy driving the surface-tension minimum might derive alternatively from enhanced director fluctuations near T_{NI}. This is a critical effect, substantiating a suggestion made long ago by Gannon and Faber [6] that the surface-tension minimum might be somehow related to the nearly continuous nature of the nematic-isotropic transition. Density-functional models are unable to explore this avenue, since they are constrained by mean-field approximation.

We also address an issue raised recently by Martínez-Ratón *et al.* [5] concerning the sign of the discontinuity at T_{NI} when the surface is partially wetted by the nematic phase. The observable surface tension above T_{NI} is then related to that of the nematic-air interface ($N\alpha$) and the nematic-isotropic (NI) interface by

$$\gamma(T_{NI}^{+})=\gamma_{N\alpha}+\gamma_{NI}\cos\theta_c, \tag{2}$$

where the contact angle θ_c is finite for partial wetting, and goes to zero in the limit of complete wetting. Approaching T_{NI} from below when there is no wetting layer, one has simply $\gamma(T_{NI}^{-})=\gamma_{N\alpha}$, so for complete wetting one expects a positive discontinuity

$$\Delta\gamma=\gamma(T_{NI}^{+})-\gamma(T_{NI}^{-})=\gamma_{NI}. \tag{3}$$

Martínez-Ratón *et al.* assume a more general expression encompassing partial nematic wetting:

$$\Delta\gamma=\gamma_{NI}\cos\theta_c. \tag{4}$$

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However, there is an apparent contradiction in trying to resolve this equation with experimental $\gamma(T)$ behavior sometimes observed in which a negative discontinuity appears in conjunction with a surface-tension maximum above T_{NI} (e.g., [7]). Given that the presence of a surface-tension maximum indicates nematic wetting, the sign of the discontinuity should, according to Eq. (4), be positive.

We show that in fact an additional term deriving from director fluctuations should be included in Eq. (4), which may explain the negative sign of the discontinuity. The correction can be regarded as a signature of the director-fluctuation-induced effective interaction between nematic walls recently discussed by several authors [8,9].

First, however, we give an account of the surface-tension minimum below T_{NI}, assuming there is no isotropic wetting film. The fluctuations we consider are polar fluctuations $\theta_s = \cos^{-1}(\mathbf{n}\cdot\mathbf{d})$ about a homeotropic equilibrium in which the director $\mathbf{n}$ is preferentially oriented along the surface normal $\mathbf{d}$. As we remark below, the overall effect turns out to be similar at a planar anchoring surface.

Writing for surface area A,

$$\theta_s(\mathbf{r}) = \frac{1}{A}\sum_{\mathbf{q}} \tilde{\theta}_s(\mathbf{q})\exp(i\mathbf{q}\cdot\mathbf{r}), \tag{5}$$

where $\mathbf{r}$ denotes the spatial coordinates in the plane of the surface, our starting point (following [10]) is the Berreman–de Gennes ''one-constant'' elastic response $\tilde{v}(q) = Kq/4$ to a mode $\tilde{\theta}_s(\mathbf{q})$ [11].

This unusual q dependence reflects the penetration of elastic deformation below the surface. With the proviso that the response is instantaneous (we ignore the dynamics), and that there is no coupling between the modes, there is an associated contribution to the Hamiltonian of the system

$$\frac{1}{A}\sum_{\mathbf{q}} |\tilde{\theta}_s(\mathbf{q})|^2 \tilde{v}(q).$$

In real space this is equivalent to

$$\frac{1}{2}\int\int \theta_s(\mathbf{r}) v(|\mathbf{r}-\mathbf{r}'|)\theta_s(\mathbf{r}') d\mathbf{r} d\mathbf{r}',$$

where the effective interaction $v(r)$; the inverse Fourier transform of $\tilde{v}(q)$, falls off as r^{-3}.

Implementing a Rapini-Papoular-type anchoring potential $W\theta_s^2/2$, we have in addition

$$\frac{W}{2A}\sum_{\mathbf{q}} |\tilde{\theta}_s(\mathbf{q})|^2,$$

and hence a partition function

$$Z_\theta \sim \Pi_{\mathbf{q}} \int d\tilde{\theta}_s(\mathbf{q}) \exp\left[-\frac{\beta}{2A}|\tilde{\theta}_s(\mathbf{q})|^2 (W + Kq/2)\right], \tag{6}$$

where $\beta = 1/k_B T$.

A Hamiltonian term linear in q is not altogether unfamiliar. In the wetting-layer-spreading scenario of [12] the same general partition function in one dimension describes thermal contact line displacements in the presence of a pinning potential. The r^{-3} tail of the effective interaction also presents an analogy with a monolayer of homeotropically anchored dipoles, as studied in [13], although the focus there is on the interplay between the linear term and a term in q^2 deriving from short-range interactions in the monolayer.

From Eq. (6) we obtain the average

$$\langle |\tilde{\theta}_s(\mathbf{q})|^2 \rangle = A[\beta(W + Kq/2)]^{-1}, \tag{7}$$

and hence, in the limit $A \to \infty$, the mean-square director fluctuation,

$$\langle \theta_s^2 \rangle = \frac{k_B T}{2\pi W}\int_0^{q_c} dq \frac{q}{1+\xi q/2}, \tag{8}$$

where $\xi = K/W$ is the anchoring extrapolation length of de Gennes [11], and q_c is a wave-number cutoff defining the limit of the continuum formulation.

The corresponding contribution of polar fluctuations to the surface tension is

$$\gamma_\theta = -k_B T \frac{\partial \ln Z_{\theta_s}}{\partial A} = \frac{W}{4}\langle \theta_s^2 \rangle - \frac{3 k_B T}{16\pi} q_c^2. \tag{9}$$

For stronger anchoring, $W \sim \gamma_{N\alpha}$, director fluctuations are coupled to capillary wave fluctuations z_s in the position of the surface,

$$z_s(\mathbf{r}) = \frac{1}{A}\sum_{\mathbf{q}} \tilde{z}_s(\mathbf{q})\exp(i\mathbf{q}\cdot\mathbf{r}). \tag{10}$$

In the limit of rigid coupling $\theta_s \sim \nabla z_s$, we have to effectively consider a modified capillary wave Hamiltonian,

$$\frac{1}{2}\sum_{\mathbf{q}} |\tilde{z}_s(\mathbf{q})|^2 \left(\overline{\gamma_{N\alpha}} q^2 + \frac{K}{2} q^3\right), \tag{11}$$

where $\overline{\gamma_{N\alpha}}$ is the ''bare'' surface tension in the absence of capillary wave fluctuations (see, e.g., [14]).

Equivalently, we can write

$$\frac{1}{2}\sum_{\mathbf{q}} |\tilde{\theta}_s(\mathbf{q})|^2 \left(\overline{\gamma_{N\alpha}} + \frac{K}{2} q\right), \tag{12}$$

which gives, by straightforward analogy to the weak anchoring derivation,

$$\gamma_\theta \sim \frac{\overline{\gamma_{N\alpha}}}{4}\langle \theta_s^2 \rangle, \tag{13}$$

with $K/\overline{\gamma_{N\alpha}}$ replacing ξ in Eq. (8).

In the region T_{NI}^-, the close proximity to the spinodal temperature T^* can lead to strong critical effects. By way of illustration, Maier-Saupe theory predicts decay of the elastic constant K with reduced temperature $t = (T^* - T)/T$, as $K \sim t^{1/2}$. Assuming that W remains finite in the critical limit, we have then $\xi \sim t^{1/2}$ correspondingly. Expanding Eq. (8) up to first order in ξ and substituting into Eq. (9),

$$\gamma_\theta \simeq -\frac{k_B T q_c^2}{8\pi}(1 + \xi q_c/6). \tag{14}$$

Writing $q_c = 2\pi/\sigma$ and $\xi \sim \sigma$, with σ a molecular dimension, γ_θ is of the order of $k_B T/\sigma^2$, i.e., a few dyn/cm, as compared with typically 20–30 dyn/cm for $\gamma_{N\alpha}$.

With increasing temperature T just below T_{NI} (i.e., decreasing t), we see that the singular part $\sim t^{1/2}$ drives a positive divergence in the gradient,

$$\frac{\partial \gamma_\theta}{\partial T} \sim t^{-1/2}. \tag{15}$$

In order for a minimum to appear in $\gamma_{N\alpha}(T)$, this has to overcome the generic density-driven ''background'' negative trend we mentioned at the outset, which only happens if T_{NI} is sufficiently close to T^*. Although it is obviously feasible in this theory, the minimum is by no means a *necessary* signature, as is also found to be the case experimentally.

The ansatz $\xi \sim t^{1/2}$ that we have made here is not definitive, since it ignores possible scaling of W. More generally, the gradient divergence is associated with decay of the anchoring extrapolation length as t^x with $x<1$. Beyond Maier-Saupe theory, which fails to predict W, the more sophisticated density-functional approaches discussed above might be helpful in yielding detailed predictions for x. Alternatively, grazing-incidence scattering experiments at the surface might allow extrapolation of ξ in the critical region by probing the unusual q dependence of the director structure factor Eq. (7).

One reaches similar conclusions in considering polar fluctuations about a planar anchoring equilibrium. The only modification is that the elastic-free-energy response picks up a factor $\cos^2\varphi$, where φ is the angle between $\mathbf{q}$ and the average azimuthal orientation of the director in the surface plane [11]. The effect on Eq. (14), for example, is merely to reduce the singular part by a factor of 2. Note, however, that in the planar case, there is an azimuthal counterpart to the polar contribution we have focused on here.

There are more interesting modifications to the elastic response term in the case of a nematic film above T_{NI}, due to finite film thickness l and the anchoring conditions at the nascent NI interface. For negligible anchoring energy, we have

$$\frac{K}{2}\int_0^l (\nabla\theta_{ss})^2 dz = \frac{Kq}{4}|\tilde{\theta}_s(\mathbf{q})|^2[1-\exp(-2ql)],$$

where $\theta_{ss}(\mathbf{r},z) = \tilde{\theta}_s(\mathbf{q})\exp(i\mathbf{q}\cdot\mathbf{r}-qz)$ is the subsurface ($z>0$) director deformation in response to a surface director fluctuation $\mathbf{q}$ (see [11]).

This lowering of the fluctuation Hamiltonian leads to an increase in $\langle\theta_s^2\rangle$. On the other hand, a fixed anchoring boundary condition at the NI interface has a dampening effect on the surface director fluctuations,

$$\theta_{ss}(\mathbf{r},z) = \tilde{\theta}_s(\mathbf{q})\exp(i\mathbf{q}\cdot\mathbf{r})\left(\frac{\exp(-qz)-\exp(-ql)}{1-\exp(-ql)}\right), \tag{16}$$

giving an elastic-response free energy

$$\frac{Kq}{4}|\tilde{\theta}_s(\mathbf{q})|^2\left(\frac{1-\exp(-2ql)}{1-\exp(-ql)}\right).$$

We now reformulate the nematic wetting expressions, Eqs. (2) and (3), taking these considerations into account:

$$\gamma(T_{NI}^+) = \overline{\gamma_{N\alpha}} + \gamma_\theta(l) + \gamma_{NI}\cos\theta_c,$$

$$\gamma(T_{NI}^-) = \overline{\gamma_{N\alpha}} + \gamma_\theta(\infty), \tag{17}$$

$$\Delta\gamma = \gamma_\theta(l) - \gamma_\theta(\infty) + \gamma_{NI}\cos\theta_c. \tag{18}$$

The condition for a negative discontinuity is

$$\langle\theta_s^2\rangle_\infty - \langle\theta_s^2\rangle_l > \frac{4\gamma_{NI}\cos\theta_c}{W}. \tag{19}$$

For homeotropic anchoring, the limit described by Eq. (12), in which the director is rigidly coupled to capillary waves, sets a lower bound $4\gamma_{NI}\cos\theta_c/\overline{\gamma_{N\alpha}}$ on the right-hand side.

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