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Rapid Note

Fluctuations at the domain edges of nematic liquid crystals in two dimensions

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Abstract. Capillary waves and director fluctuations reduce the surface tension of a non-anchoring unbound nematic surface by comparable amounts. These are relatively small effects in three dimensions, but in two dimensions they become more significant. We examine the conditions in two dimensions under which they dominate explicitly within the framework of a model of the Maier-Saupe type. We find that for reasonable physical parameters of the model the onset of the fluctuation dominated regime generally preempts the nematic-isotropic transition. We conclude that processes which are sensitive to line tension, such as Ostwald ripening during two-dimensional liquid-gas phase separation, are much more strongly coupled to anisotropic molecular interactions and associated nematic ordering than in three dimensions.

PACS. 64.70.Md Transitions in liquid crystals – 68.10.Cr Surface energy (surface tension, interface tension, angle of contact, etc.) – 61.30.Cz Theory and models of liquid crystal structure

There have been several recent theoretical investigations of director fluctuation effects at nematic surfaces. On the one hand, coupling of director modes to capillary wave displacements of the surface can mean that although the generic roughness of unbound surfaces in both two and three dimensions remains (due to the low thermal excitation energies of long wavelength capillary waves), a nematic surface is less rough than its isotropic counterpart [1]. Elastic coupling to the bulk leads to to an unusual non-Gaussian form for the associated fluctuation spectrum, a possible direct consequence of which [2] is the oddly mean-field-like character of the second-order oblique-homeotropic anchoring transition observed at some free surfaces. Another avenue concerns the temperature dependence of the surface tension at a free surface. Critically enhanced surface director fluctuations explain experimental observations of a surface tension minimum in the approach to the nematic-isotropic transition $T_{\rm NI}$ from below [3]. Moreover, under nematic wetting conditions, the sign and magnitude of experimentally observed discontinuities in the surface tension trend at $T_{\rm NI}$ itself appears to be sensitive to a director fluctuation-induced effective interaction between the surface and the nascent nematic-isotropic interface [3–5].

These effects only feature, however, in the presence of a surface anchoring potential. In the absence of such a potential, director fluctuations contribute to the surface tension an amount similar to the capillary wave contribution. In three dimensions, one has respectively $-3k_{\rm B}Tq_{\rm c}^2/16\pi$ [3] and $-k_{\rm B}Tq_{\rm c}^2/4\pi$ (see *e.g.* [6]), where $q_{\rm c} = 2\pi/\sigma$ is a high wavelength cutoff imposed by the molecular lengthscale σ. The capillary wave contribution is well documented in a general fluids context [6], and is known to be a small effect at temperatures relevant to the nematic phase. In three dimensions, therefore, we do not expect significant director fluctuation effects at a non-anchoring free surface.

Here we comment on the less transparent situation in a two-dimensional nematic. Given that director fluctuations are well known to be stronger in bulk two dimensions than in bulk three dimensions, we are interested in how they are manifest at a non-anchoring domain edge.

A suitable perspective is the familiar Maier-Saupe approach which is a celebrated non-anchoring scenario. The idea in the following is to demonstrate that for a reasonable choice of parameters in such a description, it is feasible for the nematic-isotropic transition to be preempted by the onset of a fluctuation dominated regime, the fluctuations in question being capillary waves and director modes in more or less equal measure.

The parameters of the model are positive energy coefficients $\epsilon_{\rm iso}$, $\epsilon_{\rm ani}$ governing a balance between isotropic and anisotropic components of the microscopic interaction

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potential

$$\Phi(\mathbf{r}_i - \mathbf{r}_j, \phi_i, \phi_j) = -v(|\mathbf{r}_i - \mathbf{r}_j|) \times \{\epsilon_{\rm iso} + \epsilon_{\rm ani}\cos 2(\phi_i - \phi_j)\}, \quad (1)$$

where $\mathbf{r}$ and ϕ specify position and orientation of the particles. For the $r-$dependence we adopt $v(r) = (\sigma/r)^m$ at separations $r > \sigma$; zero otherwise. The positive exponent m sets the range.

Mean-field approximation predicts a second-order nematic-isotropic transition at (see [7,8])

$$k_{\rm B}T_{\rm NI} = \frac{\rho\epsilon_{\rm ani}}{2}\int v(r){\rm d}\mathbf{r} = \frac{\pi\rho\sigma^2\epsilon_{\rm ani}}{m-2} \quad (2)$$

for given particle density ρ (note the condition $m > 2$).

The hyperscaling critical dimension is higher than two for this model. Hence mean-field theory misrepresents the free energy density and equation (2) is a rather weak approximation. It is also preempted, although not too drastically, by the Kosterlitz-Thouless mechanism [7]. For the present purpose a rough estimate is sufficient, and we disregard these shortcomings.

In order to self-consistently determine ρ at a thermodynamically stable edge at $T_{\rm NI}$, we treat the particles as isotropically interacting hard disks. This is permissible because at $T_{\rm NI}$ there is no net free energy contribution from the anisotropic part of the interaction in the above approximation. Implementing the scaled particle result for the bulk pressure of the hard disk fluid [9],

$$\frac{p_{\rm hd}}{k_{\rm B}T} = \frac{\rho}{(1-\zeta)^2}, \quad (3)$$

we obtain for the grand potential per unit area A in the bulk

$$\frac{\Omega}{A} = \rho k_{\rm B}T\left\{\frac{\zeta}{1-\zeta} - \log(1-\zeta)\right\} - \frac{\pi\rho^2\epsilon_{\rm iso}}{m-2} - \mu\rho, \quad (4)$$

where $\zeta = \pi\rho\sigma^2/4$ is the disk packing fraction, and μ is the chemical potential. The term in $\epsilon_{\rm iso}$ is again mean-field.

The condition for thermodynamic equilibrium is that Ω is a minimum with respect to ρ. Assuming there are no particles outside the edge, we also require for stability that the pressure exerted by the bulk on the edge is zero, *i.e.*, $p = -\Omega/A = 0$. Substituting equation (2) and applying these conditions, we obtain at $T_{\rm NI}$,

$$\frac{\zeta(3-2\zeta)}{(1-\zeta)^2} - \log(1-\zeta) = \frac{\epsilon_{\rm iso}}{\epsilon_{\rm ani}}\cdot \quad (5)$$

The solution, shown in Figure 1, affords an estimate of the line tension [10] in the well-known Fowler approximation (neglect of fluctuations),

$$\tau = \rho^2\epsilon_{\rm iso}\int_0^\infty r^2 v(r){\rm d}r = \frac{\rho^2\sigma^3\epsilon_{\rm iso}}{m-3}\cdot \quad (6)$$

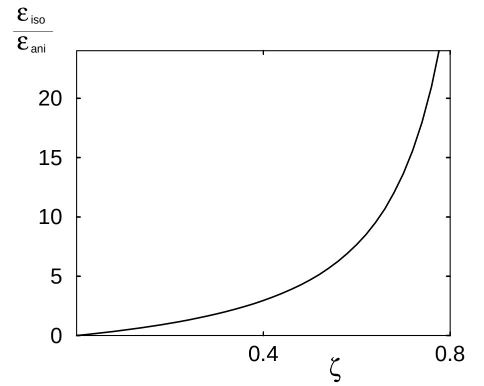

Fig. 1. Graphical solution of equation (5).

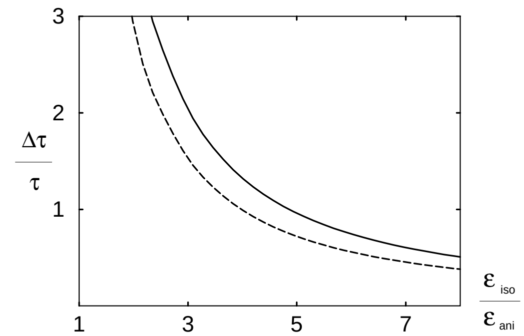

Fig. 2. Breakdown of the criterion equation (8), substituting ζ from the previous figure. Solid and dashed lines correspond respectively to $m = \infty$ and $m = 6$.

We can now set up a criterion $|\Delta\tau|/\tau \ll 1$ guaranteeing the validity of the Fowler approximation, where $\Delta\tau$ is the fluctuation renormalization at $T_{\rm NI}$.

The director and capillary wave contributions to $\Delta\tau$ are respectively $-k_{\rm B}Tq_{\rm c}/2\pi$ [11] and $-3k_{\rm B}Tq_{\rm c}/4\pi$ [6]. Hence,

$$\Delta\tau = -\frac{5k_{\rm B}T}{4\pi}q_{\rm c}, \quad (7)$$

and $|\Delta\tau|/\tau \ll 1$ corresponds to

$$\frac{5\pi^2}{8\zeta}\left(\frac{m-3}{m-2}\right)\frac{\epsilon_{\rm ani}}{\epsilon_{\rm iso}} \ll 1. \quad (8)$$

As shown in Figure 2, the left hand side diverges as $\epsilon_{\rm iso}/\epsilon_{\rm ani} \to 0$, the criterion becoming untenable below $\epsilon_{\rm iso}/\epsilon_{\rm ani} \sim O(10)$. Introducing a temperature scale by setting $\epsilon_{\rm iso}/k_{\rm B} \sim 2000$ K from the Lennard-Jones context, this is tantamount to fluctuation dominance for a nematic-isotropic transition as low as ~ 150 K.

Hence, in this model, we can say that generally the line tension of a non-anchoring 2D nematic edge is dominated by fluctuations. This is not surprising in itself, given the well-known affinity of fluctuation effects to reduced dimensionality. A less intuitively evident corollary is the significance of liquid crystallinity in determining the line tension: recall that the specifically liquid-crystalline contribution (from director fluctuations) is *comparable* in magnitude to the dominant capillary wave contribution. By contrast, in three dimensions, when the Fowler approximation is reasonably accurate, nematic surface tension differs from its isotropic counterpart only by a factor $(1 + \eta^2 \epsilon_{\rm ani}/\epsilon_{\rm iso})$, where $\eta = \langle \cos 2\phi \rangle$ is the distribution averaged order parameter.

There are no experimental templates with which to directly compare these remarks. However, the "robust" conclusion, which is that the balance between isotropic and anisotropic interactions can govern a dramatic increase in the sensitivity of line tension to bulk orientational ordering, might be relevant to certain experimentally studied complex fluid systems.

Examples include liquid-gas phase separation in Langmuir monolayers, during which domain morphology [12] and dynamics [13] are characterized by the line tension. Recent experimental studies (*e.g.*, [14]) have established that in monolayers exhibiting high molecular tilt with respect to the monolayer plane, positional and bond orientational order is negligible. As discussed in [7], such a system can be mapped into a 2D nematic or polar-nematic phase by freezing out the tilt degree of freedom. Ostwald ripening of domains apparently exhibiting polar-nematic order floating in the gas phase at room temperature and low pressure has been observed in [14], and might be a circumstance where director fluctuations are important in the way we describe.

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