Spinodal dewetting of a nematic liquid crystal film

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We discuss spinodal dewetting of a nematic film destabilized by Van der Waals forces, focusing on the case of non-antagonistic anchoring conditions. Using physical parameters pertinent to low-molecular-weight thermotropic liquid crystals, we predict a small damping effect. In the presence of an antagonistic applied magnetic field, the anchoring conditions become more significant, and can influence the shape and dynamics of the unstable modes.

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Spinodal dewetting is a long-standing theoretical idea, relating to thin films of ~100 nm or less in which an effective disjoining pressure opposes wetting. In such a film, the time dependence of low-wave-number capillary wave fluctuation modes of the free surface is not oscillatory in the usual manner. Instead, these modes are predicted to grow exponentially, leading to eventual rupture of the film. Experimental evidence has been reported for a diverse range of systems, including polymer films [1], liquid metal films [2], and collagen films [3].

In this paper we comment on the phenomenon in nematic liquid crystalline (LC) films. An instructive point of departure is the experiment of Vandebrouck *et al.* [4] investigating spinodal dewetting of 5CB films spun of silicon wafers. These authors attributed the disjoining pressure to a balance of van der Waals forces versus a Frank elastic contribution due to antagonistic anchoring conditions at the respective film surfaces. Ziherl *et al.* [5] have suggested an alternative interpretation of the same experiment, in which the assumption of antagonistic anchoring conditions is retained, but the disjoining pressure is dominated by director fluctuations. The contrast between the two interpretations serves to illustrate that nematic order is capable of coupling to spinodal dewetting in a variety of ways. Here we examine the situation when the anchoring conditions are *nonantagonistic*, such that there is no Frank elastic contribution to the disjoining pressure in the manner of Ref. [4]. Moreover, we assume that van der Waals forces dominate over other LC contributions to the disjoining pressure such as the director fluctuation Casimir forces invoked in [5]. Instead, the emphasis will be on how nematic anchoring conditions influence spinodal dewetting by coupling to the curvature elasticity of the free surface.

We begin with a brief overview of the spinodal mechanism (for more detail, see Refs. [6,7]). Consider a Cartesian coordinate system in which the substrate surface and the free surface of the film lie perpendicular to the z axis at $z=l$ and $z=0$, respectively. Following Ref. [6], the capillary wave Hamiltonian governing inhomogenous displacement z_s of the free surface is

$$H=\tfrac{1}{2}\int\left\{\gamma(\nabla z_s)^2-\frac{d\Pi}{dl}z_s^2\right\}d\mathbf{r}, \tag{1}$$

where γ is the surface tension, $\mathbf{r}=(x,y)$, and Π denotes the disjoining pressure. For a mode $z_s(\mathbf{r})=\tilde{z}_s(\mathbf{q})\sin\mathbf{q}\cdot\mathbf{r}$, we have $H\sim\gamma q^2-d\Pi/dl$. Hence, if $d\Pi/dl>0$, modes of sufficiently low wave number $q^2<\lambda^{-2}=\gamma^{-1}d\Pi/dl$ are unstable. This is the generic instability which defines spinodal dewetting. When the disjoining pressure is dominated by van der Waals forces, as is assumed in the present discussion, we have (see Ref. [7])

$$\lambda\sim\frac{l^2}{a}, \tag{2}$$

where a is a molecular dimension.

Standard capillary hydrodynamics predicts exponential growth of the unstable modes, i.e., $\tilde{z}_s(\mathbf{q},t)=\tilde{z}_s(\mathbf{q},0)\exp[t/\tau(q)]$, with $\tau(q)$ real and positive. Following the formulation of Ref. [7], we write for the flux of liquid displaced locally as the surface deforms, $\mathbf{j}\sim-(l^3/\eta)\nabla p_s$, where η is an effective viscosity (we neglect director coupling) and

$$p_s=-\gamma\left(\nabla^2 z_s+\frac{z_s}{\lambda^2}\right) \tag{3}$$

is the local excess pressure on the film due to the deformation, from Eq. (1). Substituting into the volume conservation condition, $dz_s/dt=-\nabla\cdot\mathbf{j}$, and Fourier transforming, we obtain for the dispersion relation

$$\tau(q)\sim\frac{\eta\lambda^2}{l^3q^2\gamma}[1-\lambda^2q^2]^{-1}. \tag{4}$$

Minimization with respect to q yields the fastest growing modes (i.e., lowest τ)

$$q_m\sim\lambda^{-1}\sim a/l^2,\qquad \tau_m\sim\frac{\eta}{\gamma}\frac{l^5}{a^4}. \tag{5}$$

Consider now an anchoring potential of the Rapini-Papoular type, $W\theta_s^2/2$, where θ_s is the angle between the surface normal and the orientation of the nematic director at the surface. We assume that prior to surface displacement, the director in the film is uniformly oriented perpendicular to the surface, with $\theta_s(\mathbf{r})=0$.

Anchoring strength, for the purpose of the present discussion, is interpreted according to the anchoring extrapolation length $\xi=K/W$ (see Ref. [8]), where K is an approximate elastic coefficient governing director deformation.

At a weak anchoring surface, with $\xi \gg a$, elastic coupling to the bulk of the film prevents any director reorientation, and we have $\theta_s \sim \nabla z_s$. This has a trivial renormalizing effect on the surface tension term in the capillary wave Hamiltonian, i.e., $\gamma(\nabla z_s)^2 \rightarrow (\gamma+W)(\nabla z_s)^2$.

By contrast, a strong anchoring free surface, with $\xi \sim a$, maintains $\theta_s(\mathbf{r})=0$ via director reoriention commensurate with surface displacement. Director dynamics constrain the response to a rapid displacement, but we shall find below, *a posteriori*, that this is not significant during spinodal dewetting. The effect on the capillary wave Hamiltonian is to introduce an extra term derived from the associated subsurface director deformation. Following Ref. [9], we have, for the undulatory displacement modes we are interested in,

$$\delta H = \frac{1}{4}|\tilde{z}_s(\mathbf{q})|^2 K q^3 f(q,l) \tag{6}$$

per unit surface area.

The modulating factor $f(q,l)$ accounts for anchoring at the film-substrate interface. Limiting cases are [9]

$$\begin{aligned} f(q,l) &= 1-\exp(-2ql) \quad \text{(weak anchoring substrate)},\\ &= \frac{1-\exp(-2ql)}{1-\exp(-ql)} \text{(strong anchoring substrate)}. \end{aligned} \tag{7}$$

Going through the spinodal dewetting hydrodynamics again, with Eq. (6) implemented, we obtain a modified dispersion relation

$$\tau(q) \sim \frac{\eta \lambda^2}{l^3 q^2 \gamma}\left\{1-\lambda^2 q^2\left[1+\frac{1}{2}\left(\frac{K}{\gamma}\right) f(q,l) q\right]\right\}^{-1}, \tag{8}$$

from which the pertinent perturbation expansion parameter characterising the nematic correction to the important modes $q \simeq q_m$ is

$$\zeta = \frac{1}{2}\left(\frac{K}{\gamma}\right) f(q_m,l) q_m .$$

Using Eq. (5), and expanding Eqs. (7) in $q_m l \sim a/l$ ($\ll 1$), we have

$$\begin{aligned} \zeta &\sim \left(\frac{K}{\gamma}\right)\frac{a^2}{l^3} \quad \text{(weak anchoring substrate)},\\ &\sim \left(\frac{K}{\gamma}\right)\frac{a}{l^2} \quad \text{(strong anchoring substrate)}. \end{aligned} \tag{9}$$

Substituting typical low-molecular-weight thermotropic LC parameters $K \sim 10^{-7}$ dyn, $\gamma \sim 20$ dyn/cm, $a \sim 10^{-7}$ cm, we can verify $\zeta \ll 1$ in both cases, justifying the perturbative approach. Hence, the anchoring corrections to q_m and τ_m are small:

$$\frac{\delta q_m}{q_m} \sim -\zeta, \quad \frac{\delta \tau_m}{\tau_m} \sim \zeta.$$

Finally, in order to check the assumption implicit above that director reorientational dynamics takes place on a faster timescale than the dewetting dynamics, we construct the criterion $\tau_d/\tau_m \ll 1$, where $\tau_d \sim \eta/Kq^2$ characterises director dynamics (see Ref. [8]). Using Eq. (5), we require equivalently $l \gg \gamma a^2/K \sim 10$ nm, which should be reasonably well satisfied in general.

This completes our overview of the role of nonantagonistic anchoring conditions in the spinodal dewetting process. We conclude that nematic corrections of this type are unlikely to be significant experimentally.

There is, nevertheless, a related sense in which a strong anchoring free surface could interfere quite considerably with spinodal wetting. This concerns the well-known roughening of a free surface induced by a *magnetic field* antagonistic to the anchoring. Roughening occurs due to a proliferation of nematic topological defects with their cores pinned to the surface. These ''surface disclinations'' were first predicted by de Gennes [8] using a Hamiltonian similar to Eq. (1), but with an additional term in the integrand $-(K/\xi_B)|\nabla z_s|$, expressing the reduction in director elastic free energy effected by surface deformation. Here $\xi_B = \sqrt{K/\chi_a B^2}$ defines a magnetic coherence length, with χ_s the anisotropic part of the magnetic susceptibility, and B the magnetic field strength.

Let us consider what happens if surface disclinations proliferate during the spinodal dewetting process. For illustration, we retain the homeotropic free surface anchoring conditions considered above. If the magnetic field is oriented along, say, the x direction, the favored topology is then a line disclination along the y axis. The solution of the Euler-Lagrange equations associated with De Gennes's Hamiltonian corresponds to a sinh-like roughness profile with discontinuities at the disclination cores.

On the other hand, when the film is unstable, as for spinodal dewetting, the solution is sinusoidal rather than sinh-like, independently of whether disclinations are present or not. We envisage the situation depicted in Fig. 1. Initially, when the spinodal modes first start growing, there are no line disclinations present. However, as the undulations amplify, spontaneous nucleation of disclination pairs becomes energetically favorable if the amplitude of the fastest mode q_m reaches

$$\tilde{z}_s(q_m,t) \sim \xi_B \frac{\mu}{K}. \tag{10}$$

This expresses a balance between the line tension due to the disclination cores μ, and the reduction in elastic energy they effect elsewhere in the film.

Assuming $\mu \sim K$, we require $\xi_B \sim l$ or less to stabilize disclinations during dewetting, corresponding to a rather high B. We can draw a comparison with the threshold field for the well-known Fredericksz transition, where typically

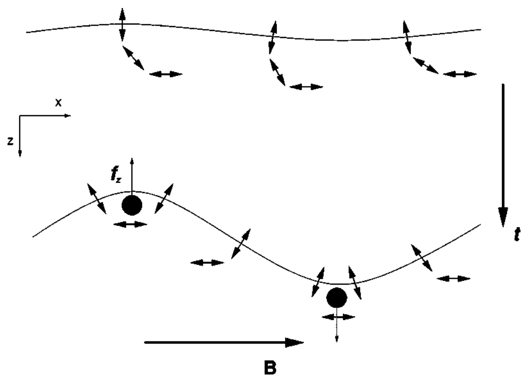

FIG. 1. Time evolution of an unstable undulatory mode of the free surface (thin solid lines) in the presence of an external magnetic field antagonistic to the anchoring. Surface disclinations become energetically favorable when the undulation reaches a critical amplitude. Double-headed arrows represent local director orientation; solid circles represent disclination cores.

$B \sim 1$ kG for 50 μm cell thickness [8]. In our case, with $l \sim 100$ nm, this suggests $B \sim O(100$ kG), which is feasible using a superconducting magnet.

The cores of a stable disclination pair sit respectively in a trough and at an adjacent peak of the undulation. Each experiences a force in the z direction, $f_z \pm K/\xi_B$ per unit length. Since they are pinned to the surface, f_z augments the capillary pressure p_s driving the dewetting hydrodynamics, Eq. (3). In a similar vein to the above, we can quantify the associated deviation from the isotropic case according to the dimensionless parameter

$$\zeta_B = \frac{f_z}{p_s \lambda} \sim \frac{K}{\gamma a} \left(\frac{l}{\xi_B} \right)^2 .$$

Using the values suggested above, it appears feasible that values $\zeta_B \sim 1$ are experimentally accessible, capable of disrupting the dispersion relation, Eq. (4). One would expect then to observe some deviation from the sinusoidal shape of the unstable capillary modes (to triangular).

In summary, we have shown that the anchoring component of curvature elasticity at the free surface of a destabilized nematic film results in at most a fractional increase in the characteristic rupture time. However, the situation changes if an external magnetic field is applied. If the field couples to anchoring conditions at the free surface in such a way as to stabilize surface disclinations, then the character of the spinodal process may be significantly altered.

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