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Thinning transitions in free-standing liquid-crystal films as the successive formation of dislocation loops

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We describe a model for the layer-thinning transition in free-standing liquid-crystal films based on the successive, spontaneous formation of dislocation loops. As the film temperature increases and the smectic order and layer compressional modulus decrease, the condition for creating a dislocation loop of critical radius is met and a thinning is nucleated. The resulting equation for *N*, the number of smectic layers, as a function of temperature yields good fitting results to the thinning transitions obtained from several fluorinated compounds. [S1063-651X(99)50909-4]

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It is well known that in some complex fluids a free surface has an ordering effect. This surface enhanced order in liquid crystals is responsible for the observed growth of smectic order at a vapor-bulk isotropic interface [1]. In a free-standing smectic liquid crystal film, the surface ordering can allow the film to be superheated well into the bulk isotropic temperature window before it loses its smectic structure and ruptures. These superheated films exist in a unique thermodynamic state with a number of interesting features. The highly ordered smectic phase of the overheated film coexists with and is supported by a disordered isotropic meniscus and bulk reservoir, with the thin [almost one-dimensional (1D)] perimeter of the film acting as the interface. A free-standing film is metastable because rupturing the film lowers the free energy of the meniscus-film system. At a given temperature, each integer film thickness of an overheated film represents a different metastable free energy state. Empirically, several compounds show a highly reproducible series of transitions between these metastable states [2–7]. Free-standing films of these compounds spontaneously decrease in thickness by a single smectic layer at a reproducible thinning temperature. This thinning temperature increases with decreasing film thickness. In this Rapid Communication we model the layer-thinning transition as a nucleation process. Our model considers the effect of free surfaces and the phase coexistence of the smectic film and meniscus to describe the thermodynamics of the layer-thinning transition.

Since our first report of the layer-by-layer–thinning transition above the bulk smectic-*A* (Sm-*A*)–isotropic transition temperature (T_{AI}) in a fluorinated compound [2], the existence of the transition has been confirmed in several other fluorinated compounds [3,7]. Unlike free-standing films of most liquid-crystal compounds, a typical thick (>20 layers) film of one of these compounds [2,3] does not rupture when heated above the bulk T_{AI}. In contrast, it undergoes a series of thinning transitions in which the film thickness decreases in a stepwise manner. For example, the thickness, in smectic layers (*N*), might exhibit the following thinning series: $N = 15$, 11, 9, 8, 7, 6, 5, 4, 3, and 2. The two-layer film ruptures at a temperature approximately 30 K above T_{AI}. The thinning transition is thermally driven and irreversible. Moreover, a film of *N* layers or less can be spread and will remain stable at temperatures below the thinning temperature [$T_C(N)$] for the *N*-layer film even though the film plate temperature is above T_{AI}. Recently, in a compound with two fluorinated tails, single layer thinning was observed from 25 down to 2 layers [7].

The film thickness is monitored by measuring the optical reflectivity of the film. The details of our experimental setup have been reported elsewhere [8]. The reflectivity of the film is a sensitive measure of film thickness and changes as small as 1 Å have been resolved [9]. The size of our free-standing films is approximately 1 cm^2, and the sample is typically heated at 75 mK/min in an oven environment of $\frac{1}{2}$ atm. argon.

In the layer-by-layer–thinning regime, where the single layers thin at reproducible temperatures, the thinning series has previously been characterized by the power law expression $N(t)=l_0 t^{-\nu}$, where *N* is the film thickness as a function of the reduced temperature $t\ (=[T_C(N)-T_0]/T_0)$. Fitting to our experimental data for several compounds has yielded an exponent in a rather wide range $0.61<\nu<0.74$ and $T_0 \approx T_{AI}$, while others have found values outside this range [4]. In a thinning transition above the Sm-*A*–nematic transition, the exponent of the power law has been compared to the expected value of the critical exponent of the smectic correlation length [4]. The reasoning is that the center layer of the film will remain stable until the smectic correlation length becomes less than half of the film thickness and the enhanced order at the surface can no longer penetrate to the center.

Considerable experimental [3–7] and theoretical [10–12] effort has been made toward understanding the layer-thinning transition. In some theories, the thinning in an *N*-layer film proceeds by melting the interior layers into either the nematic [11] or ‘‘quasismectic’’ [10] phase, after which material is squeezed out of the film and it is restabilized at $(N-1)$ smectic layers. In both cases the layer structure is destroyed in the middle of the film prior to the expulsion of material and thinning. Our visual observations and optical reflectivity studies suggest instead that a dislocation loop spontaneously forms at the thinning temperature and its

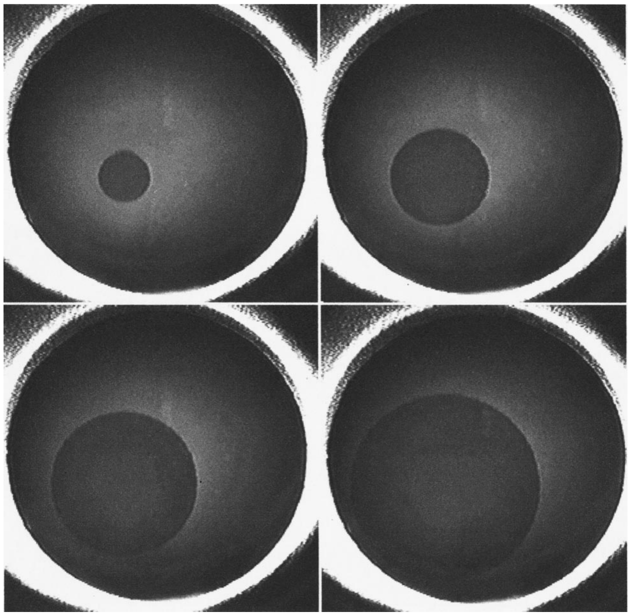

FIG. 1. Photographs showing a growing, single-layer dislocation loop that spontaneously nucleated in a four-layer film as the temperature was raised above $T_C(4)$. Note the circular shape and sharp loop boundary. The time between pictures is 150 ms.

immediate growth causes the film to thin. Figure 1 is a photograph of white light reflected off a free-standing film, and the sequence shows a single-layer, growing dislocation loop that spontaneously nucleated in a four-layer film as the temperature of the film was raised above $T_C(N=4)$. Note that the loop is circular, characteristic of a dislocation loop and its associated line tension, and that the optical thickness changes sharply at the boundary. In addition to visual observations, a laser was used to probe the optical reflectivity of a small area of the film. During a thinning, the reflectivity of the probing area was found to remain constant to within our resolution until the thinning front passed through it, and then it decreased by a value corresponding to an integer number of smectic layers. Furthermore, by using a small, pulsed wire heater similar to that used by Géminard *et al.* [13], we have nucleated thinnings in N-layer films above T_{AI}, but well below $T_C(N)$ (up to several degrees). The reflectivity signals behave the same as for the natural thinning. If in either case the entire layer melted prior to being squeezed out, it is unlikely that a constant optical thickness at a given point would be maintained before decreasing in the observed steplike manner.

We propose instead that the thinning transitions proceed via the successive nucleation of dislocation loops. Unlike an ordinary liquid, a liquid-crystal film in the Sm-A phase can support a pressure difference across a flat interface due to the compressional elasticity of its layers. The formation of a dislocation loop inside a smectic film depends on the competition between the pressure difference across the film-vapor interface and the line tension of the dislocation. Such a pressure difference is necessary in superheated films to maintain the film-meniscus interface as we shall show below. The free energy change of a dislocation loop is $\Delta F = -\pi r^2 d\Delta p + 2\pi r E$, where the first term is the work done against the pressure difference, and the second is the dislocation line energy. From this expression, the critical radius is seen to be $r_c = E/d\Delta p$, in which E depends on the elastic constants (K, bend and B, compression) of the smectic material $E \approx \sqrt{KB}d$. If the dislocation loop is smaller than the critical radius, it will decrease in size, and if it is larger it will grow. The energy of activation is then $\Delta F = E^2\pi/d\Delta p = KBd\pi/\Delta p$ [13,14]. The frequency of formation, per unit area, of a dislocation with $r \geqslant r_c$ is $f = f_0 \exp(-\Delta F/k_b T)$, where $f_0 \approx 10^{26}/\mathrm{cm}^2\,\mathrm{s}$ has been estimated by Prost [15]. Thus the average time needed to nucleate one growing loop in a system of total area S is $t \approx S/f$. The condition for a layer thinning to nucleate in 0.1 s ($t=0.1$) in a 1 cm^2 film is then

$$\pi KBd/\Delta p \approx 60 k_B T. \tag{1}$$

This expression can be evaluated further by looking at the dependence of B on the smectic order parameter $\psi = |\psi| e^{i\phi}$, where ϕ is the phase of the smectic ordering. In a theory for the Sm-A–nematic transition, this dependence is estimated simply as $B = B_0|\Psi|^2$ [16]. In the compounds we have used in studying the layer-thinning transition, there is no bulk nematic phase. However, in the overheated Sm-A films, we believe the nematic order parameter should be saturated as in the nematic phase, and thus a decay in the smectic order should occur analogously to a weakly first order Sm-A–nematic transition. In such a case, presmectic effects, such as a diverging correlation length ξ, will be strong despite the fact that the bulk transition is strongly first order. As previously stated, the optical reflectivity results indicate an ordered layer structure during thinning. In a thin film with such a layered structure, a significant decrease in the nematic order upon approaching a thinning temperature should change the film reflectivity, contrary to our observations. Therefore, we believe the smectic order decays smoothly to the point at which the condition of Eq. (1) is met, while the nematic order remains saturated, and this simple dependence of B on Ψ is justified.

To determine B requires knowledge of the profile of ψ. A model has been proposed by de Gennes [17] for the presmectic ordering between two walls, in which

$$F[\Psi] = \int_{-D}^{D} dz \left[\alpha|\Psi|^2 + L\left(\frac{d\Psi}{dz}\right)^2 \right] - h_s[\Psi(-D) + \Psi(D)],$$

where $\alpha = \alpha_0 t$, $t = T/T_C - 1$, and T_C is close to the bulk transition temperature. In our system the pressure difference between the film and its environment is always less than $\frac{1}{2}$ atm and may lead to some film compression, but it should not strongly affect the density profile. Hence the smectic order parameter phase difference between the two walls is assumed to be small in our approximation. Minimization of the free energy gives $\Psi - \xi^2 d^2\Psi/dz^2 = 0$, where $\xi = (L/\alpha)^{1/2}$ is the penetration length. Applying the boundary conditions at the free surfaces yields the expression for the profile of ψ, which at the center of the film ($z=0$) has the form $|\Psi|^2 = h_s^2\xi^2/\sinh^2(Nd/2\xi)$. If this result is inserted into the simple model for the compressional constant, we have for the center layer $B = B_0 h_s^2 \xi^2/\sinh^2(Nd/2\xi)$. The condition [Eq. (1)] for the formation of a dislocation loop becomes

$$N \approx (2\xi/d)\operatorname{arcsinh}([\pi K B_0 h_s^2 d/(\Delta p) 60 k_B T]^{1/2}\xi) \qquad (2)$$

where d is the layer spacing and $\xi=\xi_0 t^{-1/2}$. We have now related B to the smectic order parameter, but the value of Δp is still undetermined. This value has been determined for thin films in the bulk Sm-A phase temperature window by obtaining the circular profile of the meniscus and measuring its radius of curvature [13]. It is also known that such a meniscus will, over a period of days, relax and retreat toward the edge of the film. Thus it is clear that the film is stressed and is able to sustain this stress for a long period of time. In contrast, upon heating through the bulk Sm-A–isotropic transition, the meniscus of the overheated smectic film quickly contracts as the smectic layers of its interior are melted. There remains a pressure difference Δp between the meniscus-film and the bulk isotropic reservoir. The surrounding bulk reservoir on the film plate has a macroscopically flat isotropic-air interface such that it must be at or near the air pressure. Therefore, Δp for film-bulk and film-air are assumed to be the same. Since the Sm-A film and the isotropic bulk coexist, the difference in the total Gibbs potential per unit volume between the film and bulk must be zero: $\Delta G=-f_{I\rightarrow A}(T)+\Delta p=0$. The first term is the contribution due to the phase change from the Sm-A–isotropic phase, and it will grow as the overheat $T-T_C$ increases. Because the exact form of $f_{I\rightarrow A}(T)$ cannot be determined [18], we will use a linear function as a first approximation. The second term is the work necessary to move molecules from the film to the surrounding bulk against the pressure difference Δp. From the equilibrium condition and our approximation, Δp increases linearly with temperature and we write $\Delta p = p_0 t$. We also see that, unlike films in the Sm-A temperature range, the overheated films at the same temperature have the same Δp, independent of how the films are prepared. Our experimental results support this finding as the thinning temperatures of independently prepared films are reproducible to within a fraction of 1 deg for all but the final rupture of the two-layer film. This fact, together with the thinning condition of Eq. (1), shows that Δp must be the same for all films at a given $T>T_{AI}$. We can now rewrite Eq. (2) as

$$N=a_0 t^{-1/2}\operatorname{arcsinh}[a_1 t^{-1}], \qquad (3)$$

where we have introduced the dimensionless constants $a_0 = 2\xi_0/d$ and

$$a_1=(\pi K B_0 d h_s^2 \xi_0^2/60 k_B T_C p_0)^{1/2}.$$

A thinning run on the compound F3MOCPF6H5OB ($T_{AI}=105\,°\mathrm{C}$) [7], which has two fluorinated tails, yielded the thinning temperatures shown in Fig. 2. The least-squares fit of N vs $T_C(N)$, using Eq. (3), yielded $T_C=105.2$, $a_0=0.12$, and $a_1=0.024$. Eight experimental runs on this compound yielded an average value for a_0 of 0.13 ± 0.013. Similar to the simple power law fitting, three fitting parameters are required. Equation (3) was also fitted to data from the compound H8F(4,2,1)MOPP ($T_{AI}=71\,°\mathrm{C}$), which contains one fluorinated tail. Figure 3 shows the fit to the thinning temperatures for one run. Note that the layer-by-layer–thinning regime only extends to eight or nine layers in thickness for this compound. Seven runs were performed with an average for a_0 of 0.12 ± 0.011.

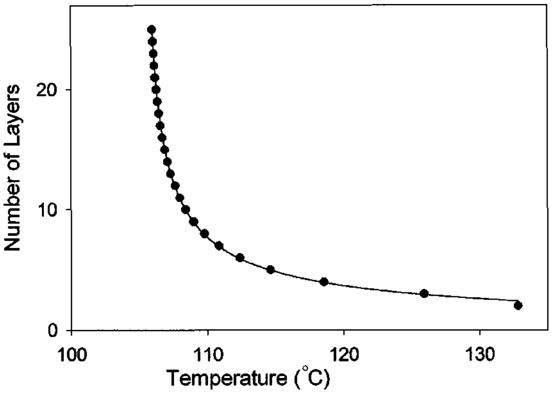

FIG. 2. N vs $T_C(N)$ for the doubly fluorinated compound F3MOCPF6H5OB. The solid line is the fitted result [Eq. (3)] with $T_C=105.2\pm0.02$ and $a_0=0.12\pm0.01$.

Using the simple model for B given above, we can predict the stability time of the film after a single-layer thinning. If it is short, there is a high probability that the dynamics of the initial thinning will immediately create a second dislocation loop and lead to a multilayer thinning. In our experiments, a thin film that has thinned by a layer will remain stable at that thickness for long periods of time if the temperature is constant. Taking 1 h as a very conservative time of stability, 0.1 seconds as the time to nucleate a single thinning (N to $N-1$), and ΔB as $B_{N-1}-B_N$, we can write the condition $0.1 e^{\pi K \Delta B d/\Delta p k_B T}\approx 3600$, or $\pi K \Delta B d/\Delta p \approx 10 k_B T$. Comparing with the original condition necessary to thin the N-layer film, $\Delta F \approx 60 k_B T$, shows that B must be roughly 20% larger at the center of the $(N-1)$-layer film than the N-layer film for the $(N-1)$-layer film to be stable for 1 h after thinning. This estimate is approximate, as the stability time depends very sensitively on ΔB (a 50% reduction of ΔB changes the time to 15 s and a 25% increase changes it to 12 h). Thus a crossover from a stable $(N-1)$-layer film to an unstable one occurs rapidly as a function of decreasing ΔB, equivalent to stating that the probability of multilayer thinnings increases with decreasing ΔB. Since removing one layer from a thick film changes B by a lesser degree than for a thin film, we expect multilayer thinnings to occur primarily in thicker

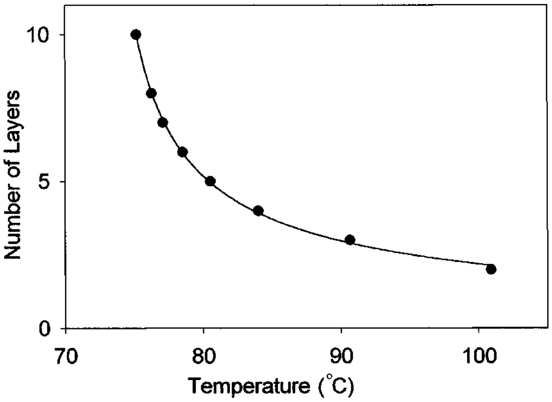

FIG. 3. N vs $T_C(N)$ for the singly fluorinated compound H8F(4,2,1)MOPP. The fitting result (solid line) using Eq. (3) yielded $T_C=72.5\pm0.23$ and $a_0=0.11\pm0.01$.

films. This is the observed behavior.

For comparison, many attempts have also been made to observe layer-thinning behavior in nonfluorinated compounds, with little success. For example, we conducted 19 experimental runs on the nonfluorinated compounds nAB (p,p'-di-alkylazoxybenzene, $n=7$ and 8), which exhibit a Sm-A–nematic–isotropic phase sequence. Similar to the results of almost all other nonfluorinated compounds we have tested, none of these showed what could be classified as a layer-thinning transition. X-ray scattering measurements on a fluorinated compound in the Sm-A phase have yielded a value for B up to two orders of magnitude larger than for nonfluorinated ones [19], indicating a more ordered layer structure. Thus for a fluorinated compound, as T is raised above T_{AI}, the correlation length is large enough and decays sufficiently slowly to allow for the successive loss of interior layers. For a nonfluorinated material the decay of ξ from its much lower value in the Sm-A temperature range may quickly reduce it below the value necessary to stabilize the film.

In summary, we have presented a model for the layer-thinning transition based on the spontaneous nucleation of dislocation loops. The model fits the data as well as the power law, and has the advantage of being derived from a physical description. Similar to the power law, the thinning transitions in our model proceed based on the critical decay of the smectic correlation length. However, the thinning in the interior layer is initiated by the formation of a dislocation loop, while the smectic order is still finite, rather than by reaching the condition for melting. With no theoretical justification available for the power law and a rather wide range of the critical exponent ν being obtained, we believe that our theoretical advance presented here provides a physical insight into the nature of layer-thinning transitions. More fitting results from other compounds are necessary to ascertain whether different thinning behavior yields different physical quantities in the model.

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$$f(T)=\int_{T_{AI}}^{T} dT\left[\frac{\partial G_{Iso}}{\partial T}-\frac{\partial G_{\mathrm{Sm}A}}{\partial T}\right]=\int_{T_{AI}}^{T} dt[S_I(T)-S_A(T)],$$

but $S_A(T)$ is not an accessible quantity above the bulk transition temperature. At T_{AI}, (S_I-S_A) is equal to $\Delta H/T$, but this equality does not hold as the Sm-A phase is overheated. Since $f(T)$ is not known, Δp is approximated as $p_0 t$ in Eq. (3).

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