A Shear-Induced Instability in Freely Suspended Smectic-*A* Liquid-Crystal Films

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(Received 3 April 1997)

This experiment examines the stability of a smectic-*A* liquid-crystal film subject to a uniform shear flow with velocity and velocity gradient in the plane of the smectic layers. The experiment is made possible by virtue of a freely suspended liquid-crystal film which is sheared at its edge by a Couette apparatus. It was found that while there was no shear-induced phase transition, line defects were nucleated in the film when the shear rate $\dot{\gamma}$ attained a certain threshold. The critical shear rate $\dot{\gamma}_c$ was measured as a function of temperature and film thickness. [S0031-9007(97)03898-2]

PACS numbers: 61.30.Gd, 47.20.Hw, 61.30.Jf, 64.70.Md

Elongated molecules are capable of forming various mesophases with different translation and rotation symmetries. Smectic-*A* (Sm-*A*) is unique among these phases in that it has a layered structure with molecules aligned parallel to the surface normal. Since there is no translational order, molecules within the layers behave like a two-dimensional liquid. The purpose of this investigation is to explore the effects of shear on this simply structured fluid, with emphasis on defect generation and evolution of these defects in the presence and absence of the flow field.

That Sm-*A* is a strongly anisotropic fluid raises interesting questions concerning stability of layer orientations, characterized by their surface normal, with respect to an imposing velocity field. This question was addressed experimentally by Safinya *et al.* for a sheared thermotropic liquid crystal (LC) using synchrotron x-ray scattering [1]. Specifically, they examined how molecular orientations, which were well known in the nematic phase under shear flow [2], transformed when the smectic phase appeared. It was found that while the average orientation of the molecules, called the director $\hat{n}$, was shear aligned along the velocity direction deep in the nematic phase, it switched to a new configuration with $\hat{n}$ parallel to the vorticity direction in the vicinity of the nematic to SmA transition. The sudden change took place when the shear rate $\dot{\gamma}$ became comparable to the incipient smectic-order fluctuation time τ_ξ of domain size ξ. More recently simultaneous rheological and structural measurements have been carried out by Panizza *et al.* [3]. These measurements seemed to suggest that smectic layers could also form multilamellar cylinders oriented along the flow at low shear rates, whereas the layer's normal $\hat{n}$ became parallel to the vorticity direction at high-shear rates similar to that found by Safinya *et al.* Though it is intuitively reasonable that this so-called a configuration, i.e., with the velocity and velocity gradient in the plane of smectic layers, has a relatively high stability compared to other configurations due to minimal distortions of the smectic order as well as the director field $\hat{n}$, it gained theoretical support only recently [4,5].

We have observed a striking effect that seems to indicate that even in the a configuration, shear can cause an instability which is not captured by linear theory [4,5]. The a configuration in this experiment was ensured by using a freely suspended LC film [6,7] that was sheared by a Couette-flow apparatus [8,9]. Specifically, it was found that defect lines with strong transverse striation were created in the film when the shear rate $\dot{\gamma}$ reached some critical value $\dot{\gamma}_c$. Persistent shear caused these defect lines to coagulate into large domains that drastically altered the mechanical and optical properties of the film. Though the defect lines have the appearance of "oily streaks" which are commonly seen in quiescent layered LCs, they were here found to be transient and relaxed shortly after switching off the shear. It can be argued that because of this similarity in structure, the defect lines in our films are a result of a binding transition of dislocation lines [10–12] which will be discussed in detail later in this paper.

The freely suspended films in this experiment were made of 4-cyano-4′-octylbiphenyl (8CB). Studies showed that in bulk form this LC has a SmA phase spanning a temperature range between 22 and 33 °C [13]. However, it was found here that in free-standing films the SmA phase had a wider temperature range, $12 < T_A < 33$ °C.

A Taylor-Couette flow is convenient for imposing linear shear in a freely suspended film [8,9]. The setup consisted of a rotating inner disk and a stationary outer ring, both made of either stainless steel or Delrin. The disk and the ring had sharp edges that made contact with the film. The diameters of the disk ($2R_i$) and the ring ($2R_o$) were, respectively, 2.4 and 3 cm. Rotation of the disk was controlled by a dc motor which could produce a rotation frequency up to $f \simeq 100$ Hz. The entire setup was enclosed in a copper chamber whose temperature was regulated to within ± 0.2 K.

The thickness of the LC film h was determined using two different methods. For thin films, $h < 3000$ Å, h was measured by optical reflectivity. This was done by monitoring the reflected light intensity as a function of the incident angle. For thick films, $h > 3000$ Å, it was more convenient to measure the ellipticity (or birefringence) of the transmitted light. The details of the latter technique can be found in Ref. [14]. In both cases a HeNe laser with $\lambda = 633$ nm was used.

Newly drawn films were found to be very thin, typically $h \simeq 100-1000$ Å. However, after being subject to shear with a rotation frequency of a few hertz, the films grew in thickness and eventually reached a steady state with h that could be a few microns. Despite the fact that they were thin and large in surface area, the LC films were surprisingly robust under shear. A typical film could be readily spun up to a frequency $f \simeq 40$ Hz without breaking. In some cases f as high as ~ 100 Hz could be reached.

The most dramatic observation, which is the focus of this Letter, was the emergence of a "cloudy state" within the film when the shear rate reached a critical value $\dot{\gamma}_c$. Below $\dot{\gamma}_c$ the LC film was transparent with optical transmission being more than 90% at normal incidence. Above $\dot{\gamma}_c$ the optical transmission dropped precipitously to well below a few percent with a significant amount of multiple scattering. Empirically we defined $\dot{\gamma}_c$ to be the shear rate at which the transmission dropped to 20% of that of a quiescent film. The effect is rather remarkable considering the film was only a few microns thick. To better characterize the behavior of the film for $\dot{\gamma} < \dot{\gamma}_c$, systematic birefringence measurements were carried out along radial positions of the film as $\dot{\gamma}$ was increased. It was found that for low shear rates, $0 \leq \dot{\gamma} \leq 200\ \mathrm{s}^{-1}$, the thickness profile was rather uniform and independent of $\dot{\gamma}$. However, for high-shear rates, $\dot{\gamma} > 200\ \mathrm{s}^{-1}$, the birefringence signal showed large spatiotemporal fluctuations that could be associated with either variations in h or orientational fluctuations of LC molecules. In this high-shear regime, a discernible amount of light scattering could be observed in the neighborhood of the reflected laser beam. The intensity of the scattered light increased rapidly and eventually saturated when $\dot{\gamma}_c$ was reached.

The appearance of the cloudy state was found to be a sensitive function of h. As shown in Fig. 1, $\dot{\gamma}_c$ increases markedly as h decreases. The trend of the data could be parametrized in an exponential fashion: $\dot{\gamma}_c = \dot{\gamma}_{c0} \exp \times (-h/h_c)$, with $\dot{\gamma}_{c0} \simeq 2700\ \mathrm{s}^{-1}$ and $h_c \simeq 3.5\ \mu$m. This is delineated by the solid line in Fig. 1 and by the semilogarithmic plot in the inset. Though the functional form suggests a smooth continuation as $h \rightarrow 0$, the possibility cannot be ruled out that the relationship between $\dot{\gamma}_c$ and h is singular in the limit of a molecular scale, i.e., $h \rightarrow R_c$ with R_c being the core radius of a disclination line. Experimentally it was found that for LC films that were less than about a micron in thickness, it became practically impossible to produce a cloudy state as $\dot{\gamma}_c$ was then so large that the film often ruptured before the cloudy point could be achieved. For these data upward arrows were plotted in the graph indicating the unknown upper bound for $\dot{\gamma}_C$. It should be noted that though the cloudy state can be readily observed at small $\dot{\gamma}$ for thick films, the effect has not been previously reported in bulk samples [1,3]. The data in Fig. 1 is shown for several temperatures, and was taken with many different films and over many days. As can be seen the temperature dependence was so weak it was clearly shadowed by sample-to-sample variations in the measurements. A careful study, using a single film over a span of a few hours, was able to reveal the weak temperature dependence of $\dot{\gamma}_c$, which is shown in Fig. 2. For two different thicknesses, $h = 3.9$ and $4.8\ \mu$m, $\dot{\gamma}_c$ was found to increase slightly ($\sim$20%–40%) with T from 12 to 27 °C.

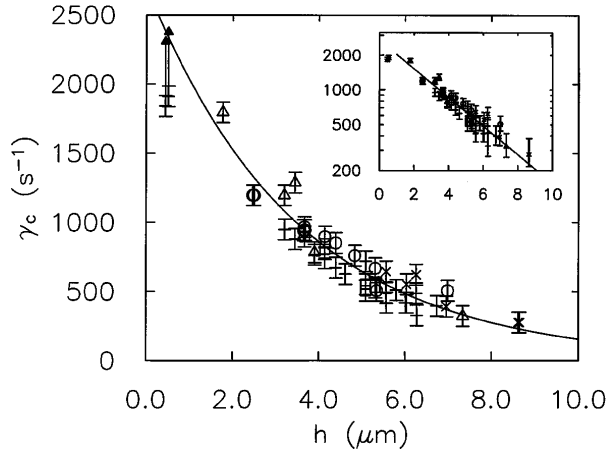

FIG. 1. Critical shear rate $\dot{\gamma}_c$ vs film thickness h. The data were taken over a range of T with squares, circles, triangles, pluses, and crosses corresponding to $T = 12$, 18, 22, 24, and 27 °C, respectively. The effects of temperature on $\dot{\gamma}_c$ were rather weak. For $h < 1\ \mu$m, $\dot{\gamma}_c$ could no longer be measured due to the rupturing of films at high $\dot{\gamma}$. These measurements are shown by upward arrows. The inset is a semilogarithmic plot of the same graph.

Can the observed instability be due to some extraneous effects such as air boundary layers or meniscus instability? The air boundary layers can impose a shear stress $\sigma_{\mathrm{air}} \simeq \sqrt{32\eta_a\rho_a R_i^2 f^3}$ across the smectic layers [15], where η_a and ρ_a are, respectively, the viscosity and the density of air. This is a legitimate concern considering previous experiments and theory that showed a lamellar phase could be unstable under such a shear configuration

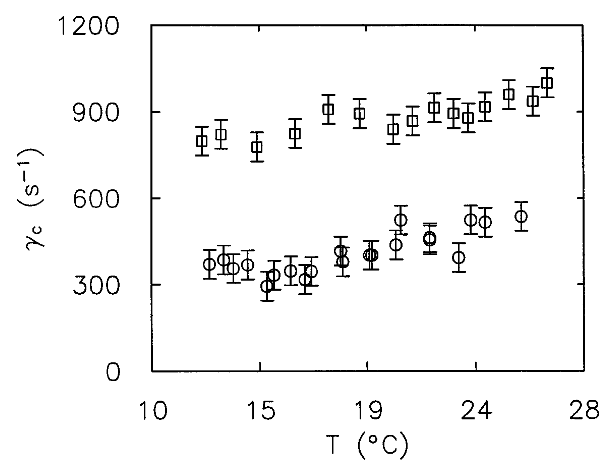

FIG. 2. Critical shear rate $\dot{\gamma}_c$ vs temperature T. For a fixed film thickness $\dot{\gamma}_c$ is a weakly increasing function of T.

[1,4,5]. In light of this our measurements were repeated in a vacuum in which the pressure was reduced to a few torr. At such a pressure the air density was reduced by more than a factor of 100, corresponding to a reduction in air shear stress of about ten. No change either in the appearance of the cloudy state or in $\dot{\gamma}_c$ could be detected in this case. The meniscus instability was also ruled out by examination of the defect generation process under a microscope. Here it was found that the cloudy state set in spontaneously with defects distributed uniformly throughout the film instead of in isolated regions. The above two observations convinced us that the in-plane shear was solely responsible for the cloudy instability observed.

Next the structure and transient relaxation behavior of the cloudy state were studied. Video microscopy showed that in the neighborhood of $\dot{\gamma}_c$ a swarm of defects was nucleated, and they were shear aligned along the flow direction. Figure 3(a) is a low-magnification (×50) snapshot of defects taken shortly after the shear was stopped. As can be seen the defects consisted of lines of different lengths, and some of them were sufficiently curved to give a wormlike appearance. In addition to open-ended line defects, a significant number of closed-ended (ring) defects can be seen. Inspection of isolated defect lines under a higher magnification (×500) revealed periodic internal structures having a variety of zigzag patterns as shown in Fig. 3(b). The width of the defects varied dramatically, but the maximum width was typically about the thickness of the film. The spatial periodicity in general was slightly less than the width of the defect. For a layered LC the commonly seen defect structure is focal conic domains as originally proposed by Friedel [16,17]. They appear, under an optical microscope with crossed polarizers, as a periodic line of ellipses, and within each ellipse the light intensity is modulated in a $\pi/2$ fashion [11]. Our defects clearly do not possess the symmetric inner structure required for focal conic domains. Rather the defects shown in Fig. 3(b) have an appearance similar to oily streaks found in the L_α phase of a lyotropic system first discovered by Schneider and Webb [12]. The quiescent zigzag pattern observed by these authors was explained as the transverse undulation of paired $+1/2$ disclination cores. If this explanation is applied to our system, the cloudy point that we have observed could be interpreted as a pairing instability of dislocation lines. For $\dot{\gamma} < \dot{\gamma}_c$ the dislocations are free and straight, whereas for $\dot{\gamma} > \dot{\gamma}_c$ disclination pairs are formed and the cores of disclination lines wiggle in the transverse direction [12]. This causes macroscopic deformations in $\hat{n}$ which give rise to strong light scattering.

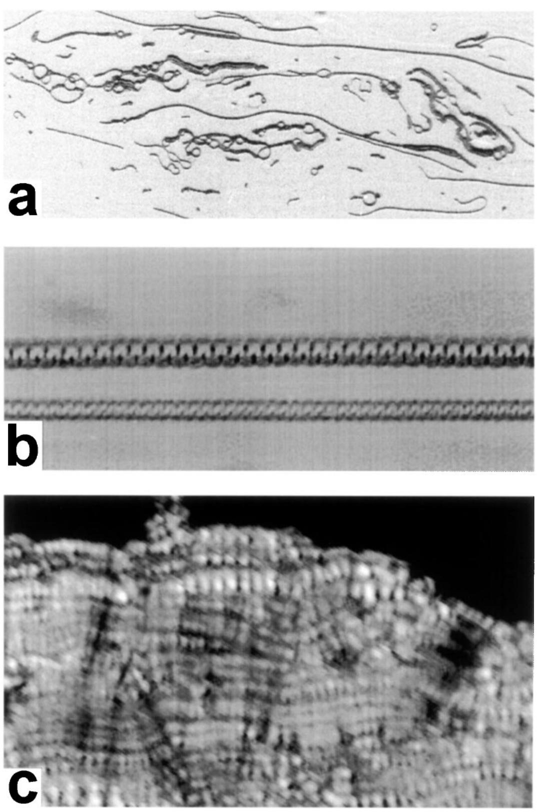

FIG. 3. Defect structures. Above the critical shear rate $\dot{\gamma}_c$ the LC film turned cloudy. Examination under a microscope at ×50 magnification revealed line defects as shown in (a). Though the picture was taken after cessation of shear, the long line defects were still preferentially aligned along the flow direction. The structure within isolated defects, as shown in (b) with ×500 magnification, are periodic with periodicity less than the defect width. Persistent shear above $\dot{\gamma}_c$ causes line defects to aggregate forming large domains as shown in (c).

If the LC film was sheared continuously, the number of defects proliferated rapidly. Observations showed that the defects were attractive and had a tendency to stick together whenever they came into contact with one another. Continued shearing for $\dot{\gamma} > \dot{\gamma}_c$ thus produced domains of defects that would quickly fill large areas of the film as shown in Fig. 3(c). The presence of large domains dramatically changed the flow properties of the film. The velocity profile became independent of radial position r, except near the solid boundaries, and the domains were convected as a whole like a solid body. The flow behavior was therefore strongly non-Newtonian in the presence of a large number of defects.

The relaxation kinetics of the cloudy state were also interesting. It was found that defects could persist even when the $\dot{\gamma}$ was reduced to a value of about $\dot{\gamma}_c/10$. Such a hysteresis is suggestive that nucleation of the defects is like a "first-order" transition with a significant energy barrier. However, under sufficiently small $\dot{\gamma}$ the defects could anneal with their contour length $s(t)$ shrinking in time. Figure 4 shows the contraction velocity $v = |ds(t)/dt|$ averaged over more than a hundred open-ended defect lines that were repeatedly generated in a single film with $h \simeq 3$ μm. The measurements were taken immediately after cessation of shear. As can be seen, there is a clear dependence of v on s, and the general trend is that as s increases the velocity increases. Phenomenologically the data can be fitted by a power law, $v \sim s^\alpha$ with

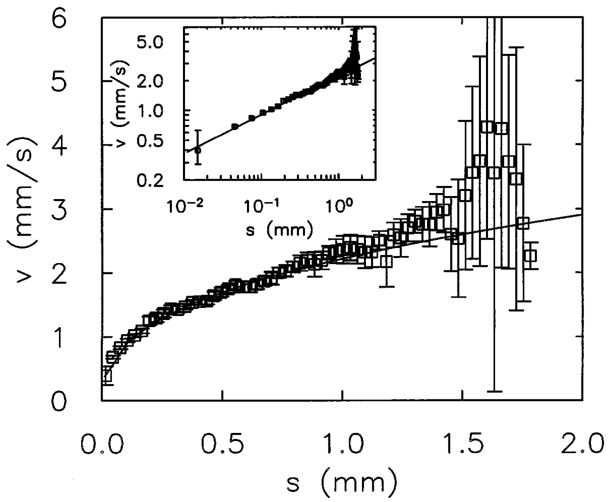

FIG. 4. Relaxation kinetics of open-ended defect lines. Upon switching off shear flow the length of defect lines s contract with time t. The inset is a log-log plot of the same data.

$\alpha \simeq 0.39 \pm 0.04$. A straightforward integration then gives the scaling relation between the contour length s as a function of time t with the result $s \sim (T - t)^{1.6}$, where T is the instance when s shrinks to a point. The diminishing velocity for shorter defects is qualitatively different from coarsening of type-$1/2$ disclination lines seen in a nematic phase when the LC was thermally quenched from the isotropic phase [18]. In the quenched nematic phase v was found to be *inversely* proportional to the contour length s, and hence the rate of collapse of the line defects increased as s decreases. Different contraction rates of line defects may not be surprising considering very different defect structures in the nematic and the smectic phases. However, at present there is no theory that can account for the scaling behavior we have observed.

In summary, we have found a novel instability in a freely suspended SmA LC film under shear flow. The instability produces a swarm of line defects that show periodic transverse undulations. Under persistent shear, with $\dot{\gamma} > \dot{\gamma}_c$, the defect lines aggregate and form large domains, and flow becomes strongly non-Newtonian. Though the instability is hysteretic, the critical shear rate $\dot{\gamma}_c$ nonetheless could be measured reliably as a function of the film thickness with the result that $\dot{\gamma}_c$ increases rapidly as h approaches zero. We have also studied the transient relaxation of defects upon cessation of shear. Here a scaling relation $v \sim s^{0.39}$ was found for s spanning more than two decades in length scales. Though the instability was observed for a single LC compound (8CB) we believed that the phenomenon is perhaps more general and may be observable in other layered systems formed by block copolymers and lyotropic liquid crystals. It is noteworthy that though classification of defects in layered systems began over 70 years ago by Friedel [16], questions still remain concerning selection rules for different defects, their relationship with material parameters, such as elastic moduli, and their formation kinetics [11]. The mere fact that defects in our system can be readily created by shear and are transient in nature provides excellent new opportunities to address some of these interesting issues.

We would like to thank H. Y. Chen, D. Jasnow, H. Kellay, T. Lubensky, S. Morris, and T. Ohta for helpful discussions. This research is supported by the NSF under Grant No. DMR 9424355 and by the Petroleum Research Fund under Grant No. PRF 26567-AC9.

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