Instabilities of a Moving Nematic-Isotropic Interface

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A moving nematic-isotropic interface is subject to several instabilities. Some are traceable to phenomena typical of liquid crystals; others are tentatively identified with a Mullins-Sekerka instability.

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The transition between the nematic and isotropic phases of a liquid crystal is weakly first order. Although the stationary interface is reasonably well understood, the case of a moving nematic-isotropic interface is yet to be examined.[1] This motion is subject to many instabilities, which, with some care, can be sorted into two classes: those related to the special properties of liquid crystals and those related to more general properties of moving interfaces. Below, we describe what happens as we systematically increase the velocity of the interface.

Our samples consist of two parallel glass plates (bottom plate, 24×28 mm^2; top plate, 22×22 mm^2), separated by spacers with thicknesses of 19, 30, and 50 μm. Into the gap between the two plates we introduced the liquid crystal 4-*n*-octylcyanobiphenyl (8CB), which is chemically stable and has a nematic-isotropic phase transition at 40.5 °C. The inner glass surfaces were treated with silane in order to orient the nematic phase perpendicular to the glass plates, a configuration known as homeotropic.

Our directional solidification apparatus has been described elsewhere.[2,3] Briefly, one end of the sample is placed in a hot oven and the other end in a cold oven. The high conductance of the glass plates relative to the liquid-crystal layer imposes a linear temperature gradient along the sample. In practice, some care must be taken to eliminate temperature gradients normal to the sample and also to calibrate accurately the horizontal gradient. The gradients reported here are accurate to about 3%.

The temperatures are chosen so that the nematic-isotropic interface sits in the gap between the two ovens. The experiment consists of moving the sample at a constant velocity from the hot side to the cold, while holding the ovens fixed. Thus, we "freeze" the liquid, creating the nematic phase at a constant rate.

Figure 1(a) shows a stationary interface, photographed between crossed polarizers. Because the phase transition is first order, the interface is a sharp line. We found this to hold whatever the thickness of the sample.

At small velocities a diffuse, scintillating band appears in front of the interface. The width of the band w was observed and measured under Nomarski differential interference illumination. It increases with velocity before saturating at a value that is inversely proportional to the temperature gradient, corresponding to a temperature span of 0.11 °C. The width at saturation is independent of the sample thickness. (See Fig. 2.) When we stop the interface, the diffuse band relaxes and disappears with a typical relaxation time $\tau\sim w^2$, which suggests a diffusive mechanism. The corresponding diffusion coefficient is about 5×10^{-5} cm^2/sec, which is characteristic of self-diffusion or impurity diffusion in liquids. As we increase the velocity, the diffuse zone divides progressively into two bright strips separated by a narrow black band. [See Fig. 1(b).]

We hypothesize that our silane treatment induces a boundary layer of nematic phase on the glass plates and picture the diffuse band as a meniscus of nematic phase extending slightly into the isotropic phase. [See Fig. 3(a).] The diffuse band in Fig. 1 can be seen because of the layer of nematic phase that wets the glass in front of the bulk interface. The band, however, is caused by the buildup of impurities in front of the interface.[4] The patterns in the diffuse zone would thus be an instability of this meniscus, analogous to the instability of the interface itself discussed below.

At a critical velocity $v_c^{(1)}$, the interface destabilizes. [See Fig. 1(c).] The destabilization velocity increases slightly faster than linearly with the gradient. (Least-squares log-log fits give $v_c^{(1)}=G^b$, with b ranging from 1.2 to 1.6 over different runs.) (See Fig. 4.) $v_c^{(1)}$ depended linearly on the sample thickness.[5] One very important finding, which held for all samples, was that the bifurcation was supercritical; in other words, just above the onset velocity, we observed a sinusoidal interface deformation of arbitrarily small amplitude.[6] We were thus able to study the linear regime of the instability. For example, the wavelength at onset, λ_c, was found to vary as $G^{-0.72\pm0.03}$. (See Fig. 5.) Finally, adding an impurity (hexachloroethane) reduced $v_c^{(1)}$ and increased λ_c but did not affect qualitatively the other features of the instability.

The dependence of the instability threshold and wavelength on impurities and on the temperature gradient suggest that the relevant physical mechanism is the Mullins-Sekerka instability, which is known to describe pattern formation in growing solid-liquid interfaces.[7,8] It predicts that an interface will be unstable when its velocity v exceeds $v_c^{(1)}=DGk/mc_0(1-k)$. Here, G is the

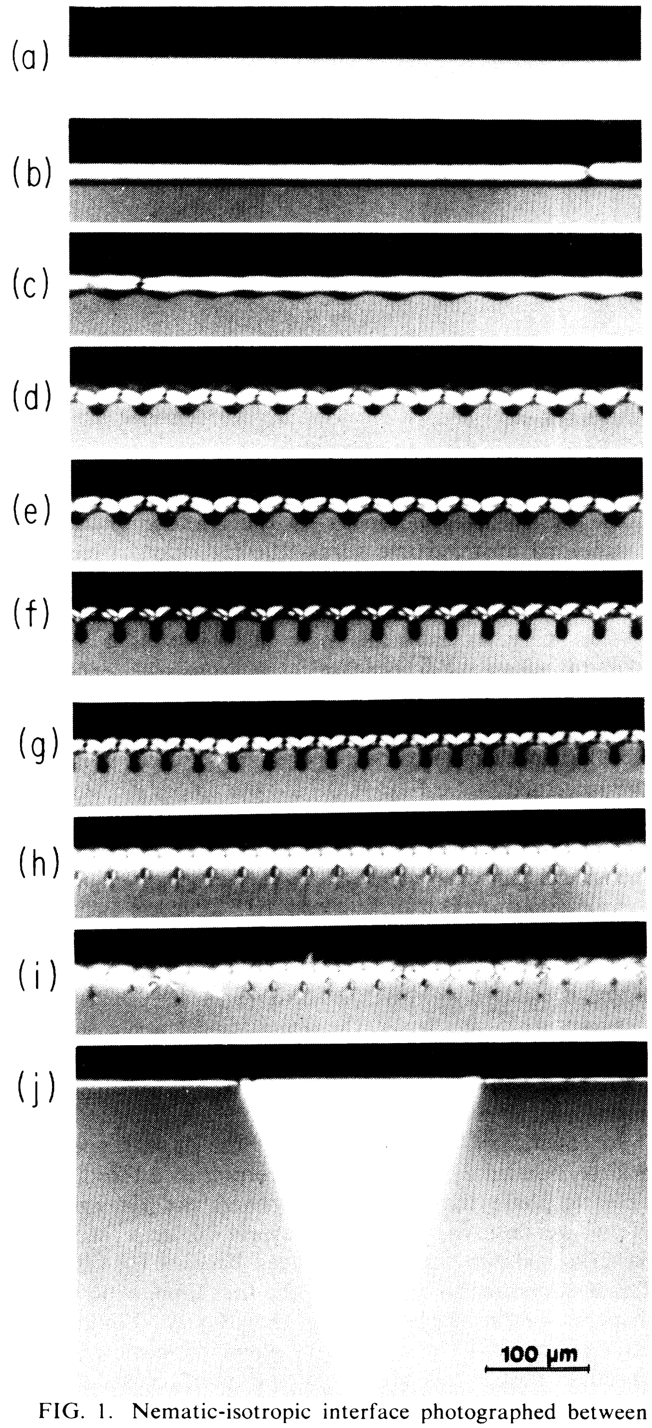

FIG. 1. Nematic-isotropic interface photographed between crossed polarizers. The black regions are isotropic; the gray regions are nematic. Thickness $d=30$ μm, $G=25$ K/cm for (a)-(i). (a) Stationary interface; (b) diffuse zone with band, $v=7$ μm/sec; (c) slightly unstable interface, $v=7.5$ μm/sec; (d)-(h) decorated instability, $v=8$, 9, 10, 18, 32 μm/sec; (i) bubbles, $v=36$ μm/sec; (j) planar region, $v=40$ μm/sec, $G=82$ K/cm, $d=30$ μm. Note that because of the strong gradient, the interface itself is stable, and the diffuse zone is much narrower.

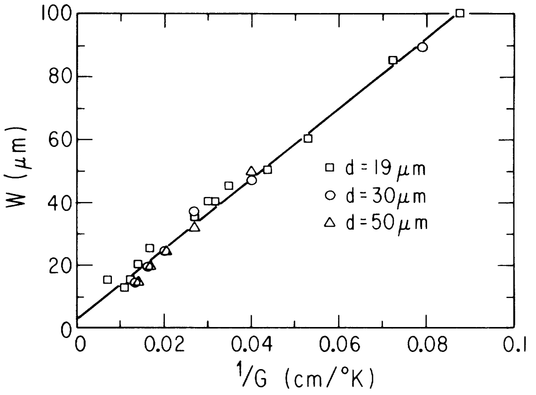

FIG. 2. Width w of the diffuse zone vs G^{-1} (d=thickness of sample).

temperature gradient, D is the diffusion coefficient of impurities in the liquid, c_0 is the average concentration of impurities in the sample, m is the liquidus slope, and k is the partition coefficient, defined as the ratio at equilibrium of the concentration of impurities on the solid (here, nematic) side of the interface to that on the liquid side. Our observations that the destabilization velocity increases with the temperature gradient and decreases with the addition of impurities is consistent with the predictions of Mullins and Sekerka.[9] Another prediction of the Mullins-Sekerka theory is that $\lambda_c \propto c_0^{1/3} G^{-2/3}$, which fits

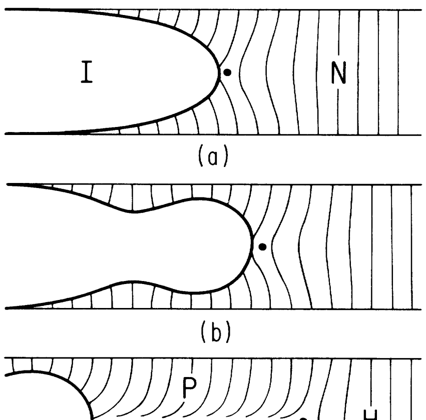

FIG. 3. A model for the diffuse zone. (a) Stable meniscus; N denotes the nematic region, I the isotropic region. The directors follow the solid lines. We assume that the molecules orient themselves approximately perpendicular to the interface. There is a $S=-\frac{1}{2}$ disclination attached to the tip of the meniscus. (b) Unstable meniscus; the buckling of the meniscus can explain the appearance of a dark band in the diffuse zone. (c) Detached $S=-\frac{1}{2}$ line; P denotes a nematic region of planar orientation (in the bulk), H one of homeotropic orientation.

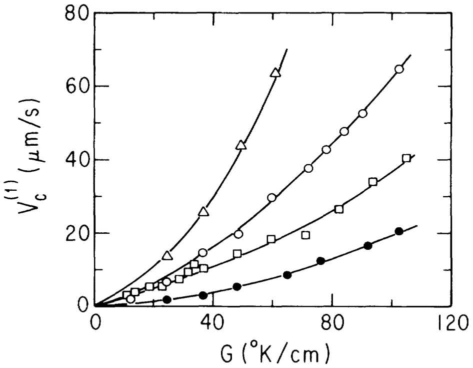

FIG. 4. $v_c^{(1)}$ vs G The open square, open circle, and open triangle represent samples of thickness $d=19$, 30, 50 μm, respectively. The closed circle is a 30-μm-thick sample, to which hexachloroethane was added. The lines through the points are guides only.

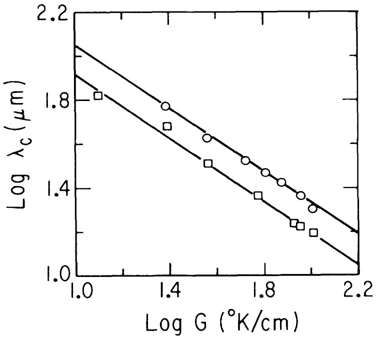

FIG. 5. Logλ_c vs log$G$. $d=30$ μm. Open square means 8CB alone; open circle means 8CB plus a small amount of hexachloroethane.

our data very well.[8] (Fig. 5.) If our identification of the instability as a Mullins-Sekerka mechanism is correct, then this experiment would be the first to observe the predicted supercritical bifurcation and to explore the linear regime. Also, the increase in λ_c in Fig. 5 resulting from the addition of an impurity corresponds in the above law to an increase in concentration of 2.8 ± 0.2 times. This is near the factor of 3 to 4 by which the critical velocity was reduced in the same sample. In other words, our data are consistent with both the gradient and the concentration dependence of λ_c.

Above the onset velocity $v_c^{(1)}$, we observe various nonlinear effects. The amplitude of the oscillation increases, saturating at $v/v_c^{(1)} \approx 1.2$. The saturation amplitude is inversely proportional to the gradient, corresponding to a temperature range of about 0.05 °C, which is equivalent to roughly half the thickness of the diffuse band. The wavelength of the instability decreases with velocity, but the measurement is difficult because of minor imperfections in the sample. The large-amplitude interface deformations that develop are not sinusoidal but have grooves of isotropic fluid that are small in relation to the cell wavelength. [See Figs. 1(d)-1(h).] Eventually, at $v/v_c^{(1)} \approx 3$ to 4, the grooves pinch off, leaving behind an isotropic bubble, which then disappears into the nematic phase. [See Fig. 1(i).] In the nonlinear regime, the diffuse zone organizes itself into one of several kinds of periodic patterns with a period equal to the cell wavelength. These textural defects are perhaps due to variations of the thickness of the meniscus.

We now turn from the Mullins-Sekerka instability to a new instability related to the nematic phase and its orientation. Above a velocity $v_c^{(2)}$, which is independent of the temperature gradient and of $v_c^{(1)}$, we can easily nucleate nematic regions that are oriented in the plane of the sample, and are hence perpendicular to the molecules in the homeotropic orientation. In our experiment, the nucleation is brought about by the passage of a large (≈ 5 μm) dust particle across the interface. [See Fig. 1(j).] For the 30-μm-thick sample, $v_c^{(2)} \approx 15$ μm/sec. $v_c^{(2)}$ decreases for thicker samples.

This suggests that this new instability is a purely nematic effect. For topological reasons, we expect a $-\frac{1}{2}$ defect line to exist at the nematic-isotropic interface. [See Fig. 3(b).] The effect of the passing dust particle would then be to detach this $-\frac{1}{2}$ defect line from the interface. [See Fig. 3(c).] If the velocity of the defect line is less than the velocity of the interface, then the line cannot detach, and planar regions are not seen. Dimensional analysis gives $v_c^{(2)} \sim K/\gamma d$, where K is the Frank curvature constant ($\approx 5 \times 10^{-7}$ dyn), γ is the rotational viscosity (≈ 0.5 P), and d is the sample thickness (30 μm).[10] We then estimate $v_c^{(2)} \approx 30$ μm/sec, which is close to what we measure.

From $v/v_c^{(2)} \approx 5$ to 10, the nematic region is essentially all planar. For larger velocities, the situation becomes more complicated and will be analyzed in a future publication.

In conclusion, we have seen first the appearance of a diffuse, banded zone, which we interpret as a thin film of nematic phase that preferentially wets the glass plates. Next, we observe what we interpret to be a Mullins-Sekerka instability of the interface. Because the bifurcation is supercritical we can, for the first time, explore the dispersion relation predicted by that theory. Finally, we have observed the nucleation of planar nematic regions, an effect that is independent of the interface instability. One caveat: The Mullins-Sekerka instability is a balance between a diffusive instability and a stabilizing force due to surface tension. Here, there may be other stabilizing forces, such as the elastic force associated with the $-\frac{1}{2}$ defect line along the interface.

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[4] As pointed out in the text below, there is, in addition to the diffusion constant D of impurities, a diffusion constant K/γ associated with the relaxation of elastic stresses. Both diffusion constants are of the same order, but we believe that the relaxation is due to diffusion governed by D, not by K/γ. We observe $\tau \sim w^2$ for $w > d$, the sample thickness. If the relaxation were governed by elastic forces, one would expect a single $\tau \sim d^2$.

[5] For samples thicker than 50 μm, we observed nucleation of nematic bubbles in front of the interface.

[6] Caroli *et al.* have noted that if the partition coefficient $k \approx 1$, as it might in a liquid crystal, then one expects a supercritical bifurcation. In typical solid-liquid systems, $k < 0.1$, and a subcritical bifurcation to a finite-amplitude state is both predicted and observed. See B. Caroli, C. Caroli, and B. Roulet, J. Phys. (Paris) **43**, 1767 (1982); S. de Cheveigne, C. Guthmann, and M.-M. Lebrun, J. Crystal. Growth **73**, 242 (1985).

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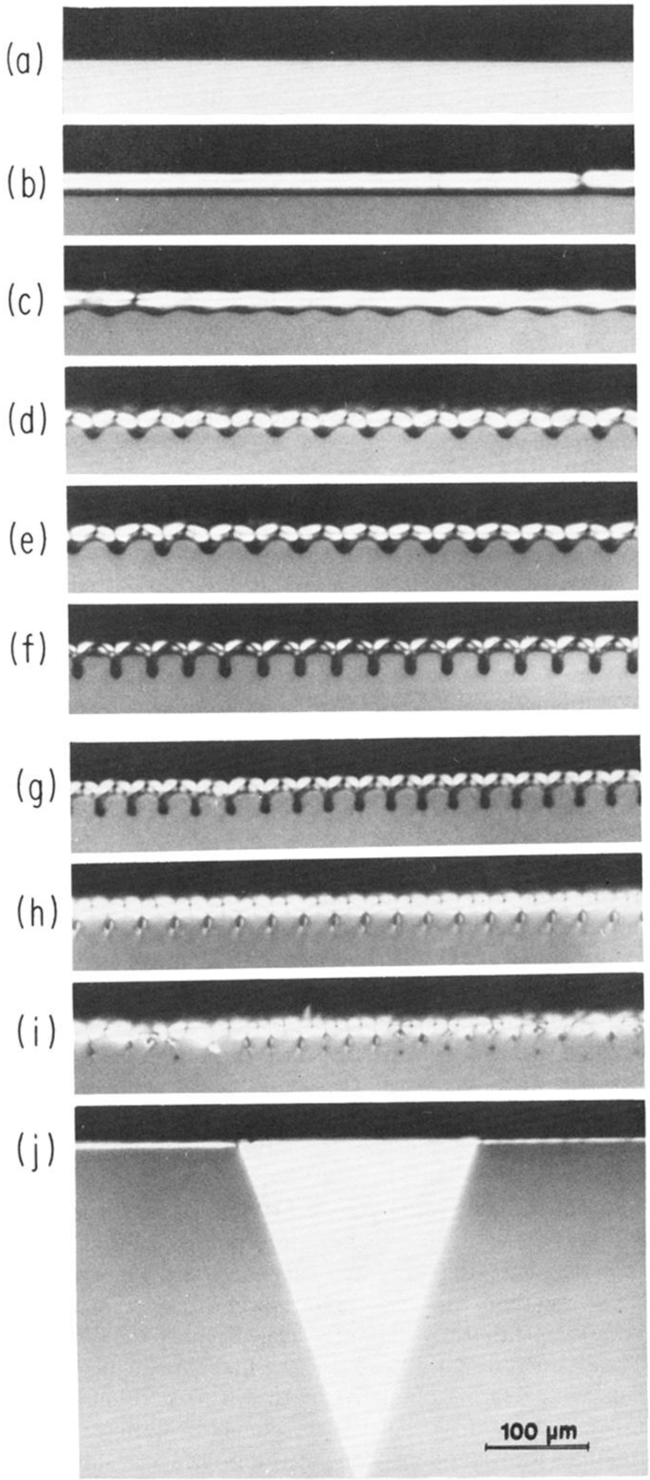
[9] Although the Mullins-Sekerka criteria predict that $v_c^{(1)} \propto G$, that prediction rests on several assumptions that we have been unable to test. For example, the partition coefficient k is assumed to be independent of the concentration c_0.

[10] One needs to balance the elastic force due to the difference in configurational energy between the homeotropic and planar orientations against the force due to the rotational viscosity of the molecules. Setting these equal gives the relation in the text.



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