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Role of elastic effects in the secondary instabilities of the nematic-isotropic interface

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Résumé. — Nous montrons expérimentalement que certaines instabilités secondaires du front nénmatique-isotrope dépendent de la topologie de la ligne de disclinaison qui est accrochée au ménisque et de l’anisotrope élastique du matériau choisi.

Abstract. — We show experimentally that certain secondary instabilities of the nematic-isotropic interface depend both on the topology of the disclination line which is pinned to the meniscus and on the elastic anisotropy of the material chosen.

1. Introduction.

In recent years, many observations of the Mullins-Sekerka instability of the nematic-isotropic interface of the liquid crystal 8CB (4,4'-n-octylcyanobiphenyl) have been reported [1-6]. An advantage of this compound is that its physical constants (diffusivities, partition coefficient, . . .) allow the study of the full marginal stability curve in the velocity-gradient parameter space. On the other hand, this front undergoes many secondary instabilities in the cellular regime [2, 6]. Some are observed in all samples, whatever their thickness. One of them is a « solitary-mode » solution, where domains of long-wavelength, tilted cells propagate along the macroscopic interface. Another is a drop instability that always occurs at larger velocities than the solitary modes. Here the interface is so distorted that droplets of isotropic liquid break off and are left behind the moving interface. In very thin samples, other secondary instabilities have been reported [6], such as travelling waves near the onset of instability and an optical mode where the width of neighbouring cells oscillates periodically in phase opposition along the interface. This last mode has not yet been studied in detail.

An important question is to know whether these instabilities are universal, or generic and can be described by a general theory of secondary instabilities of one-dimensional cellular patterns [7]. Although similar observations were done recently in a directional viscous fingering experiment [8] and in eutectic growth [9], certain phenomena observed in 8CB do not seem universal for two reasons:

— first, some instabilities (travelling waves and optical modes) are only observed in very thin samples. That means, as pointed out by Simon and Libchaber [6], that the sample
thickness and the meniscus effects play a critical role in the physics of the nematic-isotropic interface.

— second, there exists a non-planar, wedge disclination line, pinned to the top of the meniscus «Non-planar» means that the molecules tend to go out of a plane perpendicular to the line axis, so that the reflection symmetry is spontaneously broken along the interface. As a consequence point defects exist on the line separating regions of opposite molecular orientations. Thus, one might wonder whether these «nematic» effects are not partly responsible for the propagating modes which are observed experimentally.

In order to test their importance, we have done similar experiments with another compound whose meniscus is symmetrical, and released from point defects. We observed that this liquid crystal does not always behave like 8CB. Our results are reported in section 4 where we show the complete bifurcation diagram of this liquid crystal, as well as an oscillatory mode that was previously observed [3] but not studied in detail. The differences with 8CB are emphasized. In section 2, the origin of the symmetry breaking of the director field is discussed. In section 3, we briefly describe the experimental procedure.

2. Role of elastic anisotropy on the nature of the wedge disclination pinned to the meniscus.

The experiments on 8CB have shown that the nematic-isotropic front is curved in a plane perpendicular to the interface. The result is a meniscus whose shape depends on the surface treatment of the glass. With a silane, that orients the molecules perpendicular to the glass plates, one observes a meniscus of nematic phase extending into the isotropic liquid. This is because the nematic phase wets the silane. The shape of the meniscus changes with the pulling velocity and results from a subtle competition between the buildup of impurities in front of the interface, the wetting on the glass that fixes the contact angles, the Gibbs-Thomson curvature effects and the attachment kinetics. On the other hand, previous experiments on 8CB have shown that there exists a wedge disclination line of strength \( S = -1/2 \) pinned to the top of the meniscus. This line can detach from the interface, leaving between itself and the interface a nematic region of planar orientation in the bulk (see Fig. 9) (for further details concerning this nematic effect, see [1]). This line exists because there is a preferential tilt angle \( \theta_1 \) of the molecule at the nematic-isotropic interface (for 8CB, \( \theta_1 = 50^\circ \)). Thus, the line is the result of a competition between the anchoring energy gained on the surface of the meniscus and the curvature elastic energy lost in the bulk of the sample (including splay, twist and bend contributions). The molecular arrangement around the line is more subtle but we might expect that it strongly depends on the elastic anisotropy of the material. Suppose, indeed, that the twist constant \( K_2 \) is much larger than both the splay constant \( K_1 \) and the bend constant \( K_3 \). In this case, the planar configuration (no twist deformation) is obviously more favourable (Fig. 1a). If all the elastic constants are of the same order of magnitude, one expects that the director escapes along the line axis, because both the splay and the bend energies decrease. The counterpart of this is that the twist energy is no longer equal to zero. Thus, a complete calculation must be performed to know which configuration will be energetically more favourable. This calculation was performed by Anisimov and Dzyaloshinskii [10]. They showed that a planar \( S = -1/2 \) line is stable if

\[
K_2 > 1/2(K_1 + K_3) .
\] (1)

In 8CB, \( K_1 \approx 10^{-6} \) dyn, \( K_2 \approx 5 \times 10^{-7} \) dyn and \( K_3 \approx 10^{-6} \) dyn [11] so that this condition is not fulfilled. The line escapes in the third dimension and possesses point defects as observed experimentally. The same phenomenon was described in nematics contained in capillary tubes too [12].
Fig 1 — a) Planar disclination line pinned to the top of the meniscus (from Ref [1]) b) In order to minimize its elastic energy, a line can escape into the third dimension and break the reflection symmetry along the interface. A nail represents the director making an angle $\alpha$ with the plane of the figure. Its length is proportional to $\cos \alpha$, the head of the nail is below the plane of the figure and its point is directed towards the observer.

A convenient way to fulfill condition (1) is to approach a nematic-smectic A phase transition. Close to a smectic phase, the constants $K_2$ and $K_3$ often diverge in the same way [11], while $K_1$ remains approximately constant. So one expects that the inequality (1) is satisfied in the vicinity of a smectic phase. For this reason we have chosen a material whose nematic temperature range is very narrow. The cyanobiphenyl mixture 9CB-10CB (75% and 25% in weight respectively), for which we measured $T_{\text{Nem-Sm A}} \approx 49.3^\circ C$ and $T_{\text{Nem-Is}} \approx 50.2^\circ C$, fulfills this condition. With this mixture, we have indeed observed that the disclination line pinned to the meniscus is planar (see Sect 4) and consequently does not break the mirror symmetry along the interface.


The liquid crystals 9CB and 10CB are used as received from the manufacturer (Merck Corp), without further purification. Here, the absorbed water is the main impurity. We measured the freezing range at the nematic-isotropic interface $\Delta T \approx 0.05^\circ C$.

The glass plates are treated with a silane (Merck ZLI 3124) in order to align the molecules perpendicularly to the glass plates (homeotropic anchoring). The thickness of the sample is controlled by placing two thin wires between the glass plates and putting a few drops of epoxy on each wire. The angle between the two plates is controlled by minimizing the amount of interference fringes. It ranges between 1 and $2 \times 10^{-4}$ rd.

Our directional solidification apparatus is standard and little different from the one used in reference [5]. It will be described in detail elsewhere. In brief, the experiment consists of placing the sample between two ovens. Because their temperatures are different and chosen in order that the front sits in between, there is a temperature gradient along the sample. The sample is then set in motion at a velocity $V$, the nematic phase growing into the isotropic.
liquid. The interface is observed through a Leitz polarizing microscope. The temperature gradient was measured, to about 5%, using a dummy sample with a Copper-Constantan thermocouple inside, as a function of the pulling velocity.

4. Bifurcation diagram of the 9CB-10CB mixture.

Contrary to 8CB, the sequence of secondary instabilities does not depend on the sample thickness, which we varied from a few μm up to 50 μm. In the following, we describe the behavior of a 10 μm-thick-sample in detail. This thickness is the same as that used recently by Simon and Libchaber [6], so that a direct comparison between their experiment and ours is possible.

We now describe what we observed experimentally at increasing velocity, for a temperature gradient $G = 4.8 \degree C/cm$ (Fig. 2).

At small velocity, the front is flat. As in 8CB, a meniscus occurs in front of the interface, but its optical contrast is different. By rotating the crossed polarizers in parallel light, it is possible to extinguish it completely when one of the polarizer is parallel or perpendicular to the front (Fig. 2a). That means that the director (unit vector parallel to the molecule) lies in a plane perpendicular to the interface. By contrast, the optical contrast is maximum when the polarizers make an angle of 45° with respect to the interface. In this case, the disclination line pinned to the top of the meniscus is visible as a thin bright thread (Fig. 2b). As in 8CB, this line can detach from the meniscus at large enough velocity (see Fig. 11). Finally, the meniscus width saturates towards a value corresponding to a temperature span of about 0.013 \degree C smaller than the freezing range.

At a critical velocity $V_{c1} = 20 \mu m/s$, the interface destabilizes. A very small amplitude sinusoidal undulation occurs, compatible with a supercritical bifurcation (Fig. 2c).

Above the onset velocity $V_{c1}$ and up to a velocity $V_{c2} = 65 \mu m/s$, the undulation is stationary and does not drift along the interface. Its amplitude increases with the velocity, then saturates at $V/V_{c1} = 1.7$. Before saturation, the interface has a rather sinusoidal shape (Fig. 2d), whereas above, it has a squared-off shape (Fig. 2e). Above saturation, there is a typical 10% scatter in the cell wavelength and the interface dynamics is local, the wavelength decreasing via tip-splitting instability as one increases the velocity (Fig. 3). One must also emphasize that there are no travelling waves in this large range of velocities, contrary to what is observed in thin samples of 8CB [6]. Finally, one sometimes observes stable pairs of asymmetrical cells (Fig. 4) which are a little wider than the others. These stationary localized defects in the cellular pattern occur near $V_{c2}$ and are certainly the precursors of the solitary modes that we describe below. Similar associations of asymmetrical cells have also been observed very recently in eutectics [13].

Above $V_{c2}$, a new regime appears, with solitary modes propagating in both directions along the interface. These solitons behave exactly like in 8CB, so we refer to reference [2] for their detailed description. A side-effect of this instability is, for a wide range of initial conditions, to drive the interface to a constant wavelength periodic pattern (Fig. 2f). One also notes that the length of a distorted propagating cell corresponds to about twice the basic wavelength of the cellular pattern (Fig. 5). The solitons disappear when the velocity is larger than $V_{c3} = 100 \mu m/s$.

$V_{c3}$ is the velocity beyond which the cells are so distorted that the grooves of the walls touch (Figs. 2g-1). This pinching-off causes the formation of droplets of isotropic liquid which are left behind the front. This instability, also common in 8CB, first occurs in the grooves of the tilted cells of the solitary domains, then rapidly extends over the whole interface. It is surprising to see that the solitary modes completely disappear while, at the same time, the droplet formation becomes self-sustained and periodic in time: in one step of the process,
Fig 2 — The nematic-isotropic interface photographed between crossed polarizers. The pulling velocities in μm/s are marked on the right-hand side of each picture. The nematic phase is below the interface, which is moving upwards into the isotropic phase. In (a) the polarizer is parallel to the front; in (b)-(i) the polarizer make an 45° angle with respect to the interface in order to enhance the contrast $G = 4.8 \, ^\circ C/cm$, $d = 10 \, \mu m$. 
every odd numbered groove sheds a droplet whereas in the second step, the even grooves shed their droplets (Fig. 6). In 8CB, this mode occurs occasionally over two and three periods [3] so that it was impossible to study it. By contrast, it is very insensitive to noise in our experiment, and it exists over a large range of velocity. We measured the drop emission frequency versus the pulling velocity: it scales like $V^{15}$ (Fig. 7). At large velocity, typically $V > V_{c4} \approx 180 \mu m/s$, the droplet emission becomes irregular or chaotic (Figs. 2l and 11b). For technical reasons (too short run time), we have not yet studied, in detail, this transition towards the chaos.

For the sake of completeness, we have determined the full bifurcation diagram as a function of pulling velocity and temperature gradient (Fig. 8). The critical velocities that separate each growth regime increase systematically with the temperature gradient and with the sample thickness. Conversely, the restabilization velocity above which the front is stable again, decreases with the temperature gradient down to complete dispartion of the Mullins-Sekerka instability. This classical phenomenon, also observed in 8CB [3, 4, 6], appears when the temperature gradient is larger than $G_{Max} \approx 20 °C/cm$ for a sample thickness $d = 10 \mu m$. This value is very close to that observed by Simon and Libchaber in 8CB [6]. Just below $G_{Max}$, the amplitude of the modulation remains small whatever the velocity (Fig. 9) so that solitons and other non linear phenomena disappear (region 2 in Fig. 8). In figure 10, we reported the average wavelength $\lambda$ of the cellular pattern versus the pulling velocity, for different temperature gradients. One sees that all the experimental points lie on the same curve, whatever the temperature gradient which means that the mean wavelength is mainly determined by the velocity whereas the temperature gradient sets the cell amplitude. The best fit to the experimental data of figure 10 gives $\lambda (\mu m) = 206 V^{-0.46} (\mu m/s)$. We also observed that, in planar regions, the droplet emission is more regular than in homeotropic ones.
Furthermore, the cell wavelength in these regions is systematically larger than in homeotropic ones with, on average, $\lambda_{\text{planar}} \approx 1.1 \lambda_{\text{homeo}}$ (Fig 11). Finally we observed that the restabilization velocity is slightly lower in planar regions than in others (Fig. 9). So far, we have not been able to explain these differences but we suggest that elastic effects are responsible.
Fig. 7 — Droplet emission frequency $f$ vs. velocity $V$ at $G = 47{\degree}C/cm$ and $d = 10{\mu}m$.

Fig. 8 — Bifurcation diagram ($d = 10{\mu}m$). Points are experimental data and the lines are guides for the eye. The solid line indicates the marginal stability curve. In (1), the front is stable, in (2), the front is cellular and its dynamics is local (tip-splitting and cellular death), in (3), solitary modes propagate along the interface, in (4), one observes a periodic emission of droplets with a wavelength doubling, in (5), the droplet emission becomes irregular.

5. Conclusion.

We have observed the behaviour in directional growth of the nematic-isotropic interface of the 9CB-10CB liquid crystal mixture and have compared our results with those obtained previously in 8CB.

Although these compounds are chemically very similar, yet they do not have the same physical behaviour. In particular we do not observe with the 9CB-10CB mixture the travelling
waves that Simon and Libchaber reported in thin samples of 8CB. We believe that this mode is due to a nematic effect, namely the spontaneous breaking of symmetry of the director field in the nematic phase of 8CB. This broken symmetry results from a three-dimensional escape of the director along the meniscus axis and is related to the elastic anisotropy of the material chosen.

Despite this important difference, two secondary instabilities are always present, whatever the liquid crystal chosen and the sample thickness. The first one corresponds to the appearance of soliton defects in the cellular interface pattern. This mode is common and has been observed in many other experiments [8, 9]. The second is the formation of droplets which occur at velocities slightly larger than those needed to form solitons. We observed that in the 9CB-10CB mixture, this mode is periodic in time and occurs with a wavelength twice that of the primary cell spacing; by contrast, it is much less regular in 8CB, probably because of the underlying molecular symmetry breaking which makes the cells drift.
Fig. 10 — Average cell spacing $\lambda$ vs. pulling velocity $V$ measured at various temperature gradients $d = 10 \, \mu m$.

Fig. 11. — Pictures showing the differences between planar and homeotropic regions. The velocities in $\mu m/s$ are indicated beside each picture. $G = 4.8 \, ^\circ C/cm$ and $d = 10 \, \mu m$. In the planar regions, the cell spacing is slightly larger than in the homeotropic ones (a). As one increases the velocity, the droplet emission becomes chaotic in the homeotropic regions (a) whereas it is still regular in the planar regions (c).

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