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Regular Dendritic Patterns in Liquid Crystals Induced by Non-Local Time-Periodic Forcing

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Abstract. We explore both experimentally and numerically (by phase-field model) the possibility of controlling the side-branching process by a homogeneous time-periodic forcing on dendrites observed at the nematic-smectic B liquid crystal (LC) interface. We apply either pressure oscillations or a modulated AC voltage. The pressure oscillations generate a periodic change of the phase transition temperature via the Clausius-Clapeyron relation. The modulated electric current causes a temperature oscillation in the sample. We show that both methods can be used for controlling the side-branching process in a range of the relevant parameters. Our experiments performed on viscous fingering demonstrate that dendritic side-branching can be also induced and/or regularized at the nematic—air interface in a radial Hele-Shaw cell by modulated electric field that influences the surface free energy, and the effective viscosity of the nematic LC in the plane of observation.

1. Introduction

Side-branching process in dendritic solidification observed in metals, alloys and also in transparent organic substances (HURLE, 1993) has besides of the academical aspects expressed practical importance too. Namely, it plays a crucial role in the formation of the microstructure of the solid phase and by that influences its mechanical, chemical, thermal, electrical, and other properties.

The selective amplification of thermal noise has been discussed in the literature as a probable source of the dendritic side-branching during solidification (PIETERS and LANGER, 1986). Series of recent experiments have shown that a localized thermal perturbation applied to the tip of a growing dendrite (LOSERT *et al.*, 1998) or spatially inhomogeneous oscillatory flow (BOUISSOU *et al.*, 1990) can drastically alter the sidebranch structure. However, from the viewpoint of possible applications a spatially homogeneous perturbation would be more advantageous.

We explore both experimentally and numerically (by phase-field model) the possibility of controlling the side-branching process by a spatially homogeneous time-periodic forcing on dendrites observed at the nematic (N)—smectic-B (SmB) LC interface, known as a suitable model system (BUKA *et al.*, 1995; TÓTH-KATONA *et al.*, 1996; BÖRZSÖNYI *et al.*, 1998). We apply either pressure oscillations or a modulated AC voltage. The pressure oscillations generate an instantaneous periodic change of the phase transition temperature according to the Clausius-Clapeyron relation:

$$\frac{dT_{\mathrm{N}\to\mathrm{SmB}}}{dp} = \frac{T^{\mathrm{o}}_{\mathrm{N}\to\mathrm{SmB}}\Delta V_{\mathrm{N}\to\mathrm{SmB}}}{\Delta H} \tag{1}$$

where $T^{\mathrm{o}}_{\mathrm{N}\to\mathrm{SmB}}$, $\Delta V_{\mathrm{N}\to\mathrm{SmB}}$ and ΔH are the phase transition temperature at atmospheric pressure p_0, the molar volume change on phase transition and the molar heat of fusion, respectively.

On the other hand, the modulated electric current causes a temperature oscillation in the sample via volumetric heat release. We point out here that the two methods drive the system in different directions: the excess pressure $p_e > p_0$ increases $T_{\mathrm{N}\to\mathrm{SmB}}$ (increases the undercooling ΔT), while the electric current heats the nematic phase (i.e. lowers ΔT).

To identify the range of conditions under which periodic external perturbations dominate the pattern formation, the parameter space defined by the frequency, the amplitude and the wave-form of the modulations, as well as by the undercooling and by the anisotropy of the system has been mapped.

Using localized perturbation or periodic forcing (pressure oscillations) in viscous fingering, the destabilization of the lateral front of anomalous Saffmann-Taylor fingers can be regularized as it has been shown previously (RABAUD *et al.*, 1988). It has been also shown—see e.g. (BUKA, 1996)—that the inherent anisotropy of LC can stabilize the tip (prevent the tip splitting) and can produce stable dendritic growth with side-branches.

The aim of our experimental work in the Saffmann-Taylor problem presented here was to regularize the side-branching process at the air—nematic LC interface by modulated AC voltage. Namely, using nematic LC with positive dielectric anisotropy $\varepsilon_a = \varepsilon_{||} - \varepsilon_{\perp} > 0$ ($\varepsilon_{||}$ and $\varepsilon_{\perp}$ are components of the uniaxial dielectric tensor parallel and perpendicular to the director **n** that describes the orientation of the nematic phase), and applying an appropriate electric field E perpendicular to the plane of the sample, the effective viscosity μ_{eff} and the surface free energy σ—two important parameters in viscous fingering— change depending on p_e and E. When the shear torque—see e.g. (DUBOIS-VIOLETTE and MANNEVILLE, 1996)—exerted on the director is much larger than the electric torque (high p_e and low E, elastic torques are negligible in our case) one has $\mu_{\mathrm{eff}} \approx \eta_1$ and $\sigma \approx \sigma_{\perp}$ (if one assumes 'flow alignment' so that the molecules are aligned perpendicular to the interface). In the opposite case, when the electric torque is much larger than the shear torque, we have $\mu_{\mathrm{eff}} \approx \eta_2$ and $\sigma \approx \sigma_{||}$ (here η_1 and η_2 are the corresponding Miezowicz viscosity coefficients (DUBOIS-VIOLETTE and MANNEVILLE, 1996), and $\sigma_{||}$ and $\sigma_{\perp}$ are the surface free energies of an interface parallel and perpendicular to **n**). Accordingly, in the experiments μ_{eff} and σ should change in the range of:

$$\eta_1 \le \mu_{\mathrm{eff}} \le \eta_2 \tag{2}$$

and

$$\sigma_{\perp} \le \sigma \le \sigma_{||}. \tag{3}$$

2. Experimental Setup and Simulation Procedure

In the phase transition experiments ready-made sandwich cells of E.H.C. Co. (Japan) of thickness $d = 10$ μm and 2 μm have been filled with CCH3 (Merck, Darmstadt) with $T_{N \to SmB} = 56.3°C$. The surface treatment of the bounding glass plates assured planar alignment of both N and SmB phases (**n** parallel to the glass plates) and conducting layers on the plates were used as electrodes.

For maintaining the pressure oscillations the cell was placed into a brass box surrounded by a hot stage of accuracy ±3 mK. The gas pressure in the brass box has been regulated by a PC controlled valve system that switches on and off the excess pressure preset between 0 to 2 bar with an accuracy of ±0.03 bar. This setup assured square-wave pressure modulations up to the frequency $\nu = 2$ Hz. For the modulated heat injection in the bulk a high frequency (600 kHz) electric current has been transmitted through the LC layer periodically (square-wave modulation) with a frequency in the range of $\nu = (0 - 2)$Hz.

The growth patterns were observed in transmitted light in a polarizing microscope equipped with a CCD camera. The images were stored and processed by a PC with a spatial and time resolution 512×512 pixels and 0.04 s, respectively. The calibration of the system gave scale factors of 1.35 ± 0.01 μm/pixel in x direction and 0.95 ± 0.01 μm/pixel in y direction.

For numerical simulations we used the phase-field model that represents a dynamic extension of the Cahn-Hilliard theory of first-order transformation. The model couples the evolution of the order-parameter distribution (that defines the two phases) to thermal transport (HURLE, 1993; WHEELER *et al*., 1993). The model described by WHEELER *et al*. (1993) has been modified in order to avoid the difficulties when introducing an oscillatory melting point, and time dependent terms have been introduced for periodic external perturbations—for details see (BÖRZSÖNYI *et al*., 1999, 2000). Other details of the numerical method are given in (BÖRZSÖNYI *et al*., 1998). Due to the known limitations of the phase-field model—see e.g. (HURLE, 1993)—the experimental and numerical results should be compared on the qualitative level only.

In the viscous fingering experiments a commercial LC mixture RO-TN-430 (La Roche) has been used with positive dielectric anisotropy $\varepsilon_a = 17.6$ and a broad temperature range of the N phase (from $T_m = -10°C$ up to $T_{N \to I} = 70°C$). The LC mixture has been doped with dichroic blue dye D16 (BDH) in order to enhance the contrast at the air—N interface. The experiments were performed at room temperature $T = 23°C$.

The radial Hele-Shaw cell has been assembled from two glass plates, both coated with a conducting SnO_2 layer used as electrodes. The bottom plate of dimensions (160×160) mm^2 and of thickness of 5.5 mm in the center had a hole of 1 mm in diameter as an inlet for the air. On the upper plate of dimensions (140×140) mm^2 and of thickness of 3.1 mm we made a groove running along its diagonal. This groove assured the dendrite to grow always in the same direction. The glass plates were separated by $d = 0.32$ mm or $d = 0.19$ mm thick spacers. The different cell thicknesses impose different external anisotropies to the system due to the presence of the groove (smaller d means higher anisotropy).

After filtration, the air pressure p_e has been regulated by ported precision regulator (Norgren 11-818-100) with an accuracy of ±0.03 bar. We used a unit for pressure reduction also that decreased further the pressure and enhanced its stability. The path of the air has been regulated by two 3-path solenoid valves. p_e has been measured by precision pressure meter (Watson and Smith) with an accuracy of ±1 mbar. The same accuracy of ±1 mbar could be determined for p_e with this setup. For the regularization of the side-branching process an AC electric field of frequency 1 kHz has been applied, modulated (switched on/off) by a frequency ν. The recorded images of the growth processes were fed into a PC for digital analysis, with spatial resolution of 512 × 512 pixel and 256 gray scaling for each pixel. With the magnification used in the experiments a spatial resolution of (0.241 × 0.166) mm^2/pixel has been determined.

3. Results

3.1. Nematic—smectic-B phase transition

We have measured the pressure dependence of the phase transition temperature and we found a value of $dT_{N\rightarrow SmB}/dp = (0.032 \pm 0.003)$ K/bar for the Clapeyron coefficient. Similar value of $dT_{N\rightarrow SmB}/dp = 0.033$ K/bar has been calculated from the material parameters of CCH3. It means that pressure oscillations of amplitude of 2 bar lead to oscillations of the phase transition temperature of an amplitude of about (0.06 – 0.07)K. Similar temperature oscillations of ~0.1 K were realized by a period averaged heating power of $\overline{P} \sim 10^{-5}$ W/cm^2. In the experiments presented here an undercooling of $\Delta T = 1.0$°C has been used i.e., the temperature variations due to the external forcing were about 10% of ΔT.

Experimentally square-wave oscillations of the pressure (or electric current) have been applied, with different filling coefficient

$$\xi = t_{on}\nu \tag{4}$$

where t_{on} denotes the time while the pressure (el. current) is applied within a period. Phase-field simulations have been performed both with square-wave and sine-wave oscillations.

Let us consider first the effect of the *pressure oscillations*. Without pressure oscillations an uncorrelated side-branching was observed both in experiments and in simulations—see Figs. 1(a) and 1(c). The width change in time of the main dendrite arm measured at a constant distance behind the tip could be decomposed into a Fourier spectrum of oscillations that covers a relatively broad frequency range centered around a characteristic frequency f_0 depending on ΔT (BÖRZSÖNYI *et al*., 2000). Pressure oscillations of frequency ν led to a highly correlated side-branching process as shown in Figs. 1(b) and 1(d) up to $\nu \approx f_0$. At higher forcing frequencies $\nu > f_0$ the uncorrelated side-branching similar to Figs. 1(a) and 1(c) reappeared— the interface could not follow the high forcing frequency.

We note here that in the Fourier spectra of the width oscillations besides of the forcing frequency ν, higher harmonics (2ν, 3ν, ...) were also observed with considerable amplitudes even in the case of sine-wave pressure modulations. Fairly similar patterns were observed for sine-wave and square-wave oscillations with $\xi = 0.5$. However, the relative amplitudes of the higher harmonics were found different when square-wave oscillations of $\xi \neq 0.5$ have been applied.

As one can expect, the regularity of the patterns increases with the amplitude of forcing, but the phenomenon shows saturation at high forcing amplitudes.

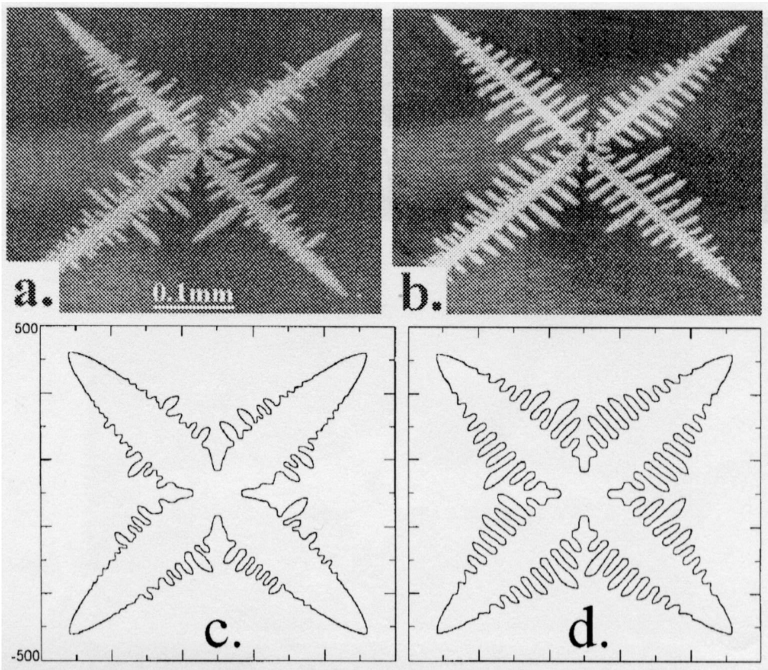

Fig. 1. The effect of oscillatory pressure on the dendrite growing into undercooled melt. (a) Experiment, $d = 2$ μm, $\Delta T = 1.0°$C, without pressure oscillations; (b) experiment, $\Delta T = 1.0°$C, with square-wave pressure modulations of parameters $p_e = 2$ bar, $\xi = 0.2$, and $\nu = 1.18$ Hz; (c) simulation, without pressure oscillations; (d) simulation, with square-wave pressure modulations of parameters $\xi = 0.3$, $\tilde{\nu} = 60$.

Numerical simulations have shown that by increasing the undercooling the effect of the regularization becomes stronger, because the formation of the side-branches becomes more intensive (both with and without periodic forcing), while at lower ΔT free growth produces essentially no side-branches and periodic forcing is needed to trigger them. By further increase of ΔT the tendency is reversed, because the spontaneous (irregular) side-branching overcomes the effect of regularization. This maximum type of behaviour is in accordance with fact that the frequency at which the dendrite can be excited the most easily is increasing with the undercooling.

Phase-field model simulations have also shown that the regularizing effect of external forcing decreases drastically with vanishing anisotropy of the system (BÖRZSÖNYI *et al.*, 2000).

We also found by numerical simulations that *alternating heating and cooling* oscillations lead to essentially the same type of resonance patterns as pressure oscillations. The *oscillatory heating* has, however a somewhat different effect on the growth patterns: in order to prevent the melting of the crystal for the heating amplitudes needed to generate regular patterns, the introduction of a local off-plane thermal transport (always present in the experiments) was necessary in numerical calculations (BÖRZSÖNYI *et al.*, 2000). In the experiments, a period averaged heating power of the order of $\overline{P} \sim 10^{-5}$ W/cm^2 assured

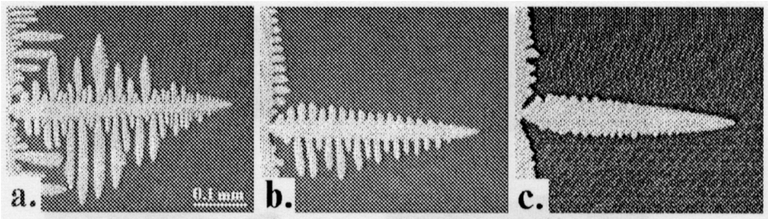

Fig. 2. The effect of the oscillatory heating on smectic-B dendrite growing into undercooled nematic phase ($\Delta T = 1.0°C$, $d = 10\ \mu m$). (a) No oscillatory heating; (b) $\nu = 0.46$ Hz, $\xi = 0.16$, $\overline{P} = 6 \times 10^{-5}$ W/cm^2; (c) $\nu = 0.81$ Hz, $\xi = 0.61$, $\overline{P} = 1.1 \times 10^{-4}$ W/cm^2.

heating amplitudes large enough for regularization of the side-branching process —see Fig. 2(b). With the increase of the heating amplitude up to $\overline{P} \approx 10^{-4}$ W/cm^2, the formation of the side-branches is suppressed (and the tip's growth velocity is lowered)—Fig. 2(c). Further increase of the heating amplitude (i.e., $\overline{P}$) melts the dendrite back.

An oscillation of the dendrite tip velocity correlating with the periodic forcing has been observed both in simulations and experiments for pressure oscillations as well as for periodic heating. However, the amplitude of these oscillations in the experiments were just above the resolution of the present experimental setup.

3.2. *Viscous fingering at air—nematic interface*

At low excess pressures p_e (low driving forces) the two stable viscous fingers running in the direction determined by the groove do not show any side-branching with E off or E on—Figs. 3(a) and 3(b), respectively. The only difference between the morphologies presented in Figs. 3(a) and 3(b) is that with E on the tips become narrower compared to the case with E off. Moreover, the velocity of the tip is smaller with E on due to the increase of the effective viscosity—compare the times indicated in the figure caption. However, in case of E modulated by frequency ν the tip goes through a successive width change that *induces* formation of side-branches in a strong correlation with the forcing frequency ν as shown in Fig. 3(c). Oscillations in the tip velocity have been also detected in case of periodic forcing (TÓTH-KATONA and BUKA, 2000).

With a cell thickness of $d = 190\ \mu m$, qualitatively the same results have been obtained as shown in Fig. 3, but the width of the tip became smaller due to the increased anisotropy imposed by the groove.

At higher p_e the main tips show a weak, uncorrelated side-branching both with E off and E on (Figs. 4(a) and 4(b), respectively), presumably as a consequence of the presence of 'frozen noise' at the groove. Modulation of E with a frequency ν here leads again to a successive width change of the tip that *regularizes* the side-branching process in a strong correlation with ν—see Fig. 4(c).

Similarly to the dendritic growth during 1st order phase transition described in the previous subsection, an upper frequency ν_c of the side-branching regularization has been observed for a given p_e, above which (at low p_e) the main dendrite does not show any side-branches or (at high p_e) the weak uncorrelated side-branches (as in Figs. 4(a) and 4(b)) reappear.

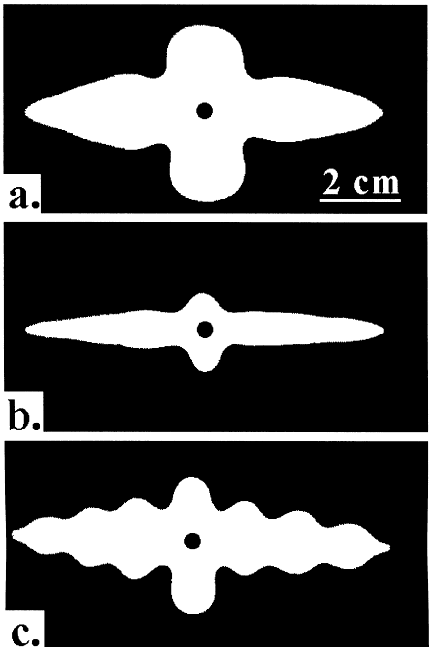

Fig. 3.

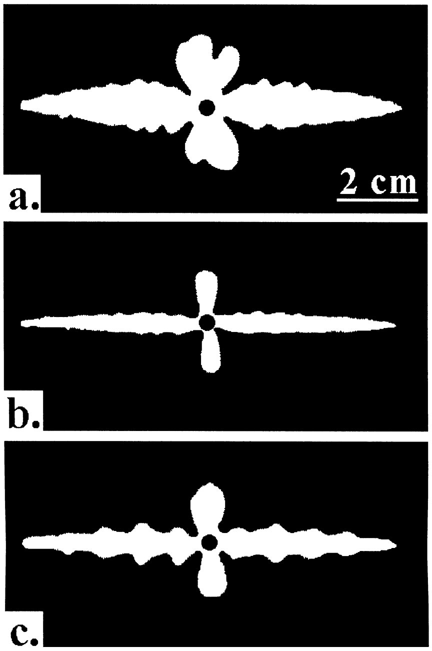

Fig. 4.

Fig. 3. Viscous fingers at the air—nematic interface, $d = 320\ \mu$m, $p_e = 5$ mbar. (a) E off, $t = 1.32$ s; (b) $E = 0.32$ V/μm on, $t = 4.44$ s; (c) $E = 0.32$ V/μm modulated (gated) by square-wave oscillations of frequency $\nu = 1.4$ Hz and $\xi = 0.68$, $t = 2.88$s.

Fig. 4. Viscous fingers at the air—nematic interface, $d = 190\ \mu$m, $p_e = 22$ mbar. (a) E off, $t = 0.24$ s; (b) $E = 0.55$ V/μm on, $t = 0.36$ s; (c) $E = 0.55$ V/μm modulated (gated) by square-wave oscillations of frequency $\nu = 13.81$ Hz and $\xi = 0.68$, $t = 0.32$ s.

Finally, one should mention that the mechanism of the change in the width of the tip when one switches E off/on, is not completely understood yet, but preliminary numerical simulations based on the phase-field model that incorporate both the changes in the viscosity and surface free energy, qualitatively reproduce the experimental results (FOLCH *et al.*, 2000).

4. Summary

We have shown both in solidification and in viscous fingering process that the dendritic side-branching can be regularized by spatially homogeneous (non-local) time-periodic forcing.

In both systems an upper frequency of regularization has been found, above which the dendrite tip can not follow the external forcing and the correlation between the forcing and the side-branch generation disappears.

A parameter space consisting of the frequency, amplitude, and wave-form of the oscillations, the undercooling and the anisotropy of the system determines the range of the conditions under which periodic external perturbations dominate the pattern formation in solidification process, while in viscous fingering problem the change of the viscosity and of the surface free energy seem to play decisive role in the regularization of the side-branching process.

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