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Recommended Citation

Wang, X. Y.; Li, Jian-feng; Gurarie, Eliezer; Fan, S.; Kyu, Thein; Keast, S. S.; and Rosenblatt, Charles, "Kinetics of Phase Transition in An Anticlinic Liquid Crystal Induced by a Uniform Temperature Field: Growth in One Dimension" (1998). *College of Polymer Science and Polymer Engineering*. 66.

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Kinetics of Phase Transition in an Anticlinic Liquid Crystal Induced by a Uniform Temperature Field: Growth in One Dimension

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(Received 27 October 1997)

It is experimentally demonstrated that a transition from a synclinic to an anticlinic liquid crystal phase occurs via stable domain wall propagation after quenching in a uniform temperature field. Such a one-dimensional growth may be explained in terms of a nonlinear diffusion equation. The experiment provides the first example of free, one-dimensional growth in a system subjected to a pure and uniform temperature field. [S0031-9007(98)06141-9]

PACS numbers: 64.70.Md

Liquid crystals are among the most suitable materials to mimic the dynamic characteristics of pattern formation and a selection mechanism. Because of their strong interaction anisotropy, dynamic growth processes may be limited to one or two dimensions. Many fascinating phenomena in liquid crystals have been investigated in the past decade [1–4], including oscillating and chaotic patterns of nematics during directional solidification [5], spiral wave growth in quenching of cholesterics [6], and dendrite formation of discotic liquid crystals [7]. Clearly, use of these materials has fostered considerable progress in understanding many nonlinear phenomena.

Compared with directional solidification [8] subjected to a temperature gradient, free growth is a more natural process of pattern formation. Free growth patterns usually show complex dendrites in three dimensions because of competition between growth effects and thermal diffusion. Unfortunately, this makes a quantitative analytical description extremely difficult. A particularly interesting problem is whether free growth patterns in a specific liquid crystalline phase could be sufficiently simple to facilitate an exact description. If yes, such a system could provide an opportunity to investigate pattern formation and test selection mechanisms. The anticlinic liquid crystalline (ALC) phase (the Sm- C_A phase) is a prime candidate for such a study. One may imagine that ALCs consist of smectic- C (Sm- C) layers in which the azimuthal orientation of the director varies by π from layer to layer [9]. Recently it was demonstrated experimentally and theoretically [10,11] that ALCs exhibit fascinating kinetic phase behavior in an electric field. The purpose of this Letter is to present the first experimental evidence of one-dimensional pattern growth subject to uniform temperature field following a rapid temperature quench. The experiment reveals several novel features: (i) The growth pattern is one dimensional; (ii) this is an example in which the kinetics of growth are described by domain wall propagation in a uniform temperature field; and (iii) the kinetics represent an example of a type of nonlinear diffusion process which shows either un-

stable or metastable behavior depending upon the material parameters.

Cells were constructed from two microscope slides, which were cleaned, spin coated with the polyimide CU-2012 (Merck), and baked. The slides were then rubbed unidirectionally with a cotton cloth using a dedicated rubbing machine. A pair of treated slides was separated by Mylar spacers of nominal thickness $d = 3$ mm, and cemented together with the rubbing directions parallel to each other. Two different enantiomeric mixtures of the liquid crystal TFMHPOBC [4-(1-trifluoromethylhexyloxy-carbonyl) phenyl 4'-octyloxybiphenyl 4-carboxylate] were used: a racemic mixture with enantiomeric excess $X = 0$, and a chiral mixture of R - and S -TFMHPOBC, with $X = 0.3$ of S -TFMHPOBC. [We note that for $X \approx 0.4$ the synclinic Sm- C phase is not present. This limits the experimental range of X .] Each of the two cells was filled in the isotropic phase and placed into an oven which was temperature controlled to 25 mK.

The oven was brought into equilibrium in the Sm- C phase just above the Sm- C –Sm- C_A phase transition temperature; for the $X = 0$ sample this corresponded to $T_{\text{initial}} = 100$ °C, and for the $X = 0.3$ sample this corresponded to $T_{\text{initial}} = 106$ °C. Resting nearby on a polarizing microscope stage was another oven, which was equilibrated at some final temperature T_{final} . In order to rapidly quench the sample temperature from T_{initial} to T_{final} , the cell was quickly transferred from the higher temperature to the lower temperature hot stage on the microscope; this process generally took ~ 2 s. Very shortly (a few seconds) thereafter, fingers were observed to nucleate and travel parallel to the layers at constant velocity (Fig. 1). These fingers appear to be similar to photographs of stripes reported earlier [12]. The finger widths w were typically 5 to 8 μm , and no correlation was observed between w and enantiomeric excess X . By rotating the cell on the polarizing microscope stage, we ascertained that the optic axis of the fingers was parallel to the rubbing direction \hat{z} , as opposed to tilted with respect to \hat{z} as in the higher

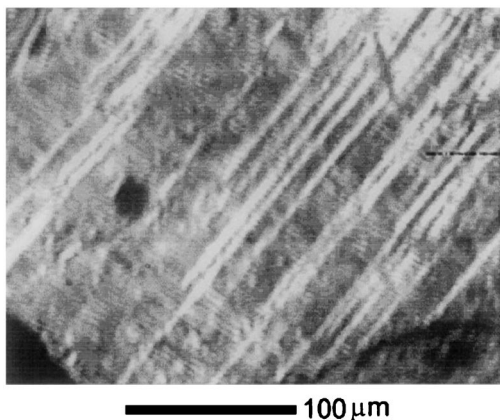


FIG. 1. VCR image showing the one-dimensional nature of fingers.

temperature Sm-C phase. Moreover, the entire cell was transformed to the Sm- C_A phase, over several hours.

To measure the velocity v of the anticlinic fingers, the microscope image was sent to a video cassette recorder from a charge-coupled device camera. The recording, with a spatial resolution of $\sim 2 \mu\text{m}$, was played back frame by frame; the temporal resolution was 0.033 s. The position finger tip, which moved with constant velocity and shape, was measured on the screen, thereby yielding the velocity. Data for velocity vs quench depth $\delta T [= T_{\text{initial}} - T_{\text{final}}]$ are shown in Fig. 2. The data and error bars correspond to an average over approximately ten fingers for each quench depth. Note that due to the quenching technique and noise (see below) we were unable to obtain reliable data for shallow quenches, i.e., $\delta T < 3^\circ\text{C}$.

We also examined the latent heat of the transition by differential scanning calorimetry. For the $X = 0.3$ sample, the latent heat L at the isotropic-smectic-A (I-Sm-A) transition is $(5.84 \times 10^7) \text{ erg g}^{-1}$, and at the Sm-C-Sm- C_A transition it is $(3.9 \times 10^5) \text{ erg g}^{-1}$. Thus,

$$f_i = \frac{1}{2} K \sin^2 \theta \left(\frac{\partial \varphi_i}{\partial x} \right)^2 + \frac{U}{2} [\cos(\varphi_{i-1} - \varphi_i) + \cos(\varphi_i - \varphi_{i+1})] + \frac{[\Lambda + W(\delta(z - \frac{1}{2}d) + \delta(z + \frac{1}{2}d))]}{2} \sin^2 \varphi_i.$$

Here, f_i is the free energy density of the i th smectic layer, $K \sin^2 \theta$ is the effective elastic constant associated with a change in azimuthal orientation φ within a smectic layer, and W is the effective anchoring strength coefficient. The coupling between layers is expressed in terms of the coefficient $U(T)$, which has dimensions of energy per volume, and represents both entropy and a coarsening average of local interactions between layers involving molecular dipoles and steric effects. $U(T)$ plays the role of the spatially uniform free energy of the system. For the

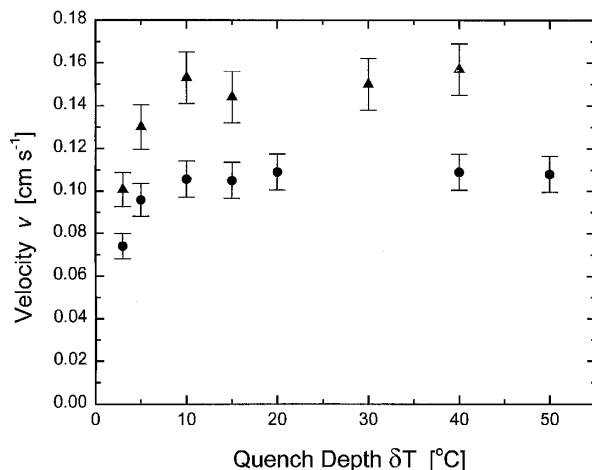


FIG. 2. Finger velocity v vs quench depth δT for the $X = 0$ sample (●) and the $X = 0.3$ sample (▲).

$L_{\text{Sm-C-Sm-}C_A}/L_{\text{I-Sm-A}} \sim 0.0067$. For the $X = 0$ sample, the ratio is even smaller. These results indicate that the Sm-C-Sm- C_A transition is *extremely* weakly first order.

We now discuss a simple phenomenological model for the observed behavior. There are several issues to consider. Because of the tiny latent heat and moderate finger propagation velocity [1], thermal diffusion can safely be neglected; the growth kinetics should therefore be based on a free energy functional, but not on a thermal equation. Additionally, if layer-by-layer enantiomeric segregation were to occur, the time scale of mutual diffusion between layers would definitely be much faster than that of domain growth, and concentration gradients would therefore not affect the finger velocity. Finally, in our sample small chemical impurities would act as a random force, and affect only shallow quenches (see below), not those studied herein. Neglecting any helical structure, we begin with a free energy $F = \sum \int f_i dx$, where $f_i = f^{\text{elastic}} + f^{\text{layer-layer}} + f^{\text{anchoring}}$:

anticlinic phase, $T < T_c$ and $U(T) > 0$; in this case, the most stable configuration is when $|\varphi_i - \varphi_{i+1}| = \pi$, i.e., anticlinic. The term $\frac{1}{2}\Lambda \sin^2 \varphi_i$ is a symmetry-permitted term which involves steric and dispersive interactions and favors both anticlinic and synclonic configurations, but not $\varphi_i = \frac{1}{2}\pi$.

We now take the equations of motion found from f_i and introduce a viscosity γ associated with azimuthal rotations of the director. On integrating over d , we find, in the overdamped limit,

$$\gamma \frac{\partial \varphi_i}{\partial t} = K \sin^2 \theta \frac{\partial^2 \varphi_i}{\partial x^2} - U [\sin(\varphi_{i-1} - \varphi_i) - \sin(\varphi_i - \varphi_{i+1})] - \left(\frac{\Lambda}{2} + \frac{W}{d} \right) \sin 2\varphi_i.$$

We assume the simplest model for this situation, viz., a structure in which all layers have azimuthal angle $\varphi_i = 0$ at

time $t = 0$; this corresponds to the Sm-C phase. As the Sm- C_A phase invades the Sm-C phase, alternate layers have orientation $\varphi_i = 0$ and $0 \leq \varphi_{i+1} \leq \pi$. Long after the finger passes $\varphi_{i+1} \rightarrow \pi$, corresponding to the usual Sm- C_A phase. We accordingly make the approximation that $\varphi_i = 0$ for all odd i , and $\varphi_i = \varphi$ for even i . We then obtain the overdamped double sine-Gordon equation

$$\gamma \frac{\partial \varphi}{\partial t} = K \sin^2 \theta \frac{\partial^2 \varphi}{\partial x^2} + 2U \sin \varphi - \left(\frac{\Lambda}{2} + \frac{W}{d} \right) \sin 2\varphi.$$

We should distinguish two cases: (i) $\Lambda + 2W/d > \frac{1}{2}U$, and (ii) $\Lambda + 2W/d < \frac{1}{2}U$. The first case corresponds to a stable anticlinic phase invading the metastable synclinc phase, for which we have a Huxley-type solution [13] with velocity $v = 2U[K \sin^2 \theta / \gamma^2 (\Lambda + 2W/d)]^{1/2}$. In the second case, we have a Fisher-type solution [14], which will be considered below. For the Huxley case, we need to examine the coefficients U and Λ , where U is based on dipole-dipole interactions associated with anticlinic ordering, a topic which has been controversial. In the classical picture [9,15], the polarizations P_0 lie within the layers, perpendicular to the tilt plane, and alternate sign from layer to layer (Fig. 3). In a more recent picture [16,17], supported by infrared absorption measurements [18], the polarizations P_1 lie in the boundary between layers, in the tilt plane, and again alternate in sign from layer edge to layer edge. On symmetry grounds, both polarizations may exist concomitantly, although a nonzero P_0 requires the system to be chiral. Thus, in a racemic mixture, the layer polarizations P_0 vanish and the P_1 polarizations are largely unaffected [16].

For an *upper limit* of U , we assume dipolar interactions spaced by a dielectric smectic layer. For the pure enantiomer *R*-TFMHPOBC, the bulk polarization $P_0 = 225 \text{ esu cm}^{-2}$ [19]. Although this value may not be quite the same as P_1 , it serves as a reasonable esti-

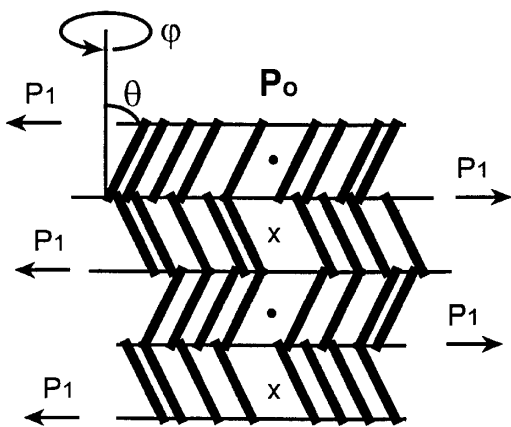


FIG. 3. Schematic representation of the anticlinic Sm- C_A phase. θ and φ correspond to the polar and azimuthal molecular angles. P_0 corresponds to the classical polarizations which are perpendicular to the tilt plane; P_1 corresponds to polarizations which lie in the tilt plane.

mate. Assuming a layer spacing of 25 \AA and a cross-sectional area per molecule of 25 \AA^2 , this corresponds to a dipole moment of $\sim 1.4 \times 10^{-19} \text{ esu cm}$; thus, an upper limit for U is of order $100\text{--}500 \text{ erg cm}^{-3}$. With an experimental velocity $v \sim 0.1 \text{ cm s}^{-1}$, and taking $\theta \sim 20^\circ$, $K \sim 10^{-6} \text{ dyn}$, $\gamma \sim 0.25 \text{ poise}$ [10], we find an upper limit $\Lambda + 2W/d \sim 5\text{--}200 \text{ erg cm}^{-3}$ for the Huxley solution. This is consistent with typical values for W [20]. However, based on our estimates for the physical parameters above, $\Lambda + 2W/d [\propto (U/v)^2]$ is apparently less than $\frac{1}{2}U$, which would seem to be *inconsistent with the requirements of a Huxley-type solution*.

With $\Lambda + 2W/d < \frac{1}{2}U$, the Fisher case holds [10,11,14]. With small latent heats and deep quenches, the system corresponds to a stable Sm- C_A phase invading the unstable Sm-C phase. For $\Lambda + 2W/d = 0$ [21], the exact velocity is $v = (2/\gamma)\sqrt{2UK \sin^2 \theta}$. For $\Lambda + 2W/d > 0$, we have numerically investigated the behavior of v and find that it is quite insensitive to both Λ and W/d as long as $\Lambda + 2W/d \ll \frac{1}{2}U$ [22]. Although this condition is not rigorously satisfied, we may nevertheless take $v \approx (2/\gamma)\sqrt{2UK \sin^2 \theta}$ as a reasonable approximation for the velocity. We therefore find $v \sim 0.04$ to 0.1 cm s^{-1} for the estimated values of U above. As seen in Fig. 2, this is of the same order as observed experimentally. Additionally, we see that the velocity is smaller for smaller quench depths. This is not surprising, as $U(T)$ would grow on decreasing the temperature deeper into the Sm- C_A phase. The apparent plateauing of v for deep quenches is due to a number of factors, including the strong temperature dependencies of K and especially γ . Finally, for Fisher-type behavior, the selection mechanism plays an important role. According to results based on exact solutions of a class of nonlinear diffusion equations [23], the selection mechanism involves the competition between nonlinear eigenmodes. When the system is driven to an unstable state, an infinite number of nonlinear modes, each with a different decay rate, is excited. They interact with each other in a dissipative process. Finally, only the mode with the smallest decay rate survives, and thus determines the selected velocity. Our computer simulations indicate that thermal noise also may significantly affect the selected velocity. This was apparent experimentally, as the finger velocity associated with shallow quenches ($\delta T < 3^\circ \text{C}$) was susceptible to noise and varied with time. The physics of shallow quenching may also involve metastability of the higher temperature phase, and is qualitatively different from the nearly noise-free deep quench results reported herein. Our shallow quench results will be reported elsewhere in the context of nucleation [22].

The seeming similarity between the $X = 0$ and the $X = 0.3$ data requires comment. If only the classical polarization P_0 mechanism were operative, P_0 would be zero for the $X = 0$ sample and no solitary wave behavior would occur. On the other hand, the P_1

polarizations which lie *in* the anticlinic tilt plane are largely unaffected by chirality [16]. Therefore, if the parameter U were indeed dominated by dipole-dipole interactions, the chirality-independent P_1 polarizations would drive the transition and dominate U in the anticlinic phase. This would apply to both the racemate and the $X = 0.3$ samples. The small differences between the two velocity profiles (Fig. 2) may be due to several factors, including a nonzero P_0 polarization component in the anticlinic and synclinc phases of the chiral $X = 0.3$ sample, and chirality-related differences in steric interactions.

In summary, we have observed and studied a Sm-C to Sm- C_A phase transition by growth of a one-dimensional solitary wave. Although the data indicate that the system is in the Fisher regime of our model equation, we cannot completely rule out Huxley-type behavior. Finally, the interaction seems to be dominated by polarizations which lie in the tilt plane of the anticlinic phase.

We thank Dr. Helen Gleeson for critically reading the manuscript. This work was supported by NSF's ALCOM center under Grant No. DMR-8920147 and by NSF's Solid State Chemistry program under Grant No. DMR-9505473.

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