

ULTRAFAST, ELECTRIC FIELD-INDUCED FINGERS IN AN ANTICLINIC LIQUID CRYSTAL

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Abstract

Propagating fingers of synclinic liquid crystalline phase were observed to invade the anticlinic phase for applied electric fields E larger than a characteristic threshold field E_{th} . The front velocity was found to be highly nonlinear in E , with enormous velocities reaching 400 cm s^{-1} for the maximum applied field. These are by far the largest velocities ever observed for a liquid crystal. The results are discussed theoretically, including the possibilities of a field-dependent molecular interaction coefficient and shear thinning.

The physics of anticlinic liquid crystals is rich and diverse [1,2]. In both the anticlinic and synclinic phases the director \hat{n} tilts by polar angle θ with respect to the smectic layer normal. In the synclinic phase the azimuthal angle φ is identical in every layer, aside from a spatially slow layer-to-layer rotation due to the helical nature of the chiral molecules. On the other hand, in the anticlinic phase the azimuthal orientation alternates between $\varphi_i = 0$ and $\varphi_{i+1} \approx \pi$ from odd layer to even layer. If the molecules are chiral, φ_i and φ_{i+2} differ slightly, as there exists a pair of long wavelength commensurate helices, one associated with the odd layers and one with the even layers. Materials having an anticlinic phase exhibit tristable behavior [1], and can switch from anticlinic to synclinic for sufficiently large electric field. This switching, in fact, has been shown to occur *via* finger-like solitary waves of the synclinic phase invading the anticlinic region [3]. The fingers, of order 10 μm in width, tend to nucleate at a defect, and propagate in a direction parallel to the smectic layers. In Ref. 3, hereafter referred to as **I**, our group showed that the threshold field E_{th} for the onset of fingering is approximately independent of cell thickness and that the fingering is reversible by reducing the electric field E below E_{th} . The data showed that the finger velocity v is approximately linear in reduced field $E_r \left[\equiv \frac{E - E_{\text{th}}}{E} \right]$, with v as large as 0.3 cm s^{-1} . A theory also was presented to explain the results. In **I**, however, velocity measurements were limited by the speed of our video equipment — approximately 30 frames per second — as the polarized microscope image was recorded and later viewed frame-by-frame. We have recently circumvented this problem by using a completely different scheme: The solitary wave is now imaged onto a small slit, and the total intensity of polarized light passing through the slit followed by an analyzer is recorded as a function of time. With this new technique we obtained results very similar to those in **I** at the same range of (small) electric fields used in **I**. However, at higher fields we now find velocities *much* larger than before, perhaps as high as 400 cm s^{-1} , which is some two to three orders

of magnitude faster than ever observed for a nematic or a ferroelectric liquid crystal. Additionally, the velocity v_s vs. E_r deviates considerably from linearity.

Cells were constructed of electrically-conducting indium-tin-oxide coated glass plates, which were first spin coated with the polyimide CU-2012 (Merck), baked, and rubbed unidirectionally using a dedicated rubbing machine and cotton cloth. The slides were then placed together (with the rubbing directions parallel) separated by a pair of mylar spacers of nominal thickness $d = 5 \mu\text{m}$, and cemented. The cells were filled with the liquid crystal TFMHPOBC [4-(1-trifluoromethylhexyloxycarbonyl) phenyl 4'-octyloxybiphenyl-4-carboxylate [4] in the isotropic phase, placed into a temperature controlled oven, and allowed to cool through the Smectic A – Smectic C_A^* ($\text{Sm } C_A^*$) transition temperature $115.3 \text{ }^\circ\text{C}$, and into the anticlinic $\text{Sm } C_A^*$ phase. Microscope observations revealed a nearly texture-free sample with planar orientation.

The cell was then placed in the optical apparatus shown in Fig. 1. Light from a 35-mW He-Ne laser passed through a polarizer and was then focused onto the sample using a 7.3 cm focal length lens L_1 . The rubbing direction, corresponding to the smectic layer normal, was oriented parallel to the polarizer direction. A second lens L_2 of focal length 6.5 cm was used to form a real image of the liquid crystal sample on a small slit, approximately $w = 10 \mu\text{m}$ wide and $l = 150 \mu\text{m}$ long. The long axis of the slit was oriented parallel to the smectic layers, and the narrow $10 \mu\text{m}$ width ensured that only one, or at most two, fingers would be observed. The slit was placed directly in front of an analyzer oriented at 90° with respect to the polarizer, followed by a photodiode detector having a response time $< 1\mu\text{s}$. The detector output was fed into a fast digitizing storage oscilloscope. In the anticlinic phase $\varphi_i = 0$ and $\varphi_{i+1} \approx \pi$; thus the average projection of the director resulted in a layer averaged polar tilt angle $\langle\theta\rangle = 0$ projected onto the plane of the slit. In consequence, in the absence of an electric field the intensity at the detector was zero. For $E > E_{th}$ a finger of synclonic phase invading the anticlinic region resulted in $\langle\theta\rangle \neq 0$ in

the field-induced synclinic region, and therefore the intensity of light passing through the slit for that region was nonzero. Thus, a finger travelling at constant velocity in principle would result in an intensity profile rising linearly in time to some maximum value, at which point only the synclinic phase would be imaged onto the entire slit. The velocity v of the finger would therefore correspond to l / τ , where τ is the rise time of the detector intensity.

A d.c.-biased square wave voltage of period 0.1 s and having rise and fall times $< 5 \mu\text{s}$ was applied to the liquid crystal cell. The bias was adjusted so that $|E| > E_{\text{th}}$ during only the positive half of the cycle; during the negative half $|E|$ was nearly zero. During both the positive and negative halves of the cycle while $|E|$ was less than the threshold field E_{th} , only a small optical response was observed. This was due partially to an electroclinic effect in the $\text{Sm } C_A^*$ phase [5] and partially to quenching of the optic-like and acoustic-like Goldstone modes [6,7,8,9] through the negative dielectric anisotropy $\Delta\epsilon$ of the material. The electric field also tended to unwind any remnant helix. When the pulse height was set to be larger than E_{th} , however, there was a sharp rise of the intensity with time, as observed on the oscilloscope. Because the single-shot trace tended to be very noisy, it was necessary to average the response over many (hundreds to thousands) of pulses. In order to determine the velocity, the averaged intensity vs. time trace was numerically differentiated. For an ideal solitary wave the intensity is expected to be flat until the threshold field is achieved, after which the signal would increase linearly with time until the entire length of the $150 \mu\text{m}$ long slit is sampling only a synclinic image. Thus the time derivative of the signal would be a square wave whose amplitude corresponds to the finger velocity. In reality, however, there was rounding of the time derivative of the intensity. We believe that this was due to the shot-to-shot variation of the nucleation time of the finger relative to the reference signal from the square wave generator. A smaller contribution to the rounding came from the nonzero rise time of the square wave, and the response time of the detector. In consequence, we associate the maximum

slope of the intensity, corresponding to the maximum value of its time derivative, with the velocity. This, in fact, actually corresponds to a lower limit for the velocity, as the effects discussed above would tend to reduce the apparent velocity.

Fig. 2 shows the velocity v vs. E_r at three temperatures in the Sm C_A^* phase. [For this experiment, E_{th} was found to be $2.44 \text{ statv cm}^{-1}$ at $T = 114 \text{ }^\circ\text{C}$, with similar values at the two other temperatures]. For $E_r < 0.1$ the velocity is relatively small, although as pointed out in **I** the finger velocity is nevertheless larger than any previously measured velocity in a liquid crystalline system. Additionally, when the ordinate is expanded, we find velocities nearly identical to the values previously obtained using a videographic technique and reported in **I**. In fact, data in **I** show a slight positive curvature for $E > E_{th}$, a result that had not been appreciated. For larger E_r Fig. 2 shows a strong increase in the apparent velocity, rising to values greater than 400 cm s^{-1} , or 1000 times larger than the previously measured velocities. It's clear that the data cannot be fitted over the entire range to a single power law — the velocity is initially linear in E_r but rises more rapidly for larger E_r . Instead, we find that a much better fit is obtained at high fields with two other *ad hoc* forms for the velocity, *viz.*, $v \propto \exp(aE)$, where a is a constant, or $v \propto (E_r^* - E_r)^{-x}$, where E_r^* is the reduced field toward which the velocity may be diverging and x is a critical exponent.

Nevertheless, at present there is no theoretical basis for either of these functional forms.

Before continuing, several caveats need to be mentioned. For the lower range of velocities ($v < 5$ to 10 cm s^{-1}), we are clearly able to discern propagating fingers. These velocities are more than an order of magnitude larger than previous measurements [3], and are well into the nonlinear regime v vs. E_r . At higher velocities, however, neither our own visual response nor available imaging equipment is sufficiently fast to discern propagating fingers. Instead, one may imagine that at large E_r the transformation from the anticlinic to the synclinic phase is driven by homogeneous nucleation and growth [10,11]. If this were the case, reported velocities would

correspond to the time associated with such a transition, rather than a real finger velocity.

However, we judge this to be improbable, as the data do not seem to show any critical field where either the velocity or its derivative with respect to E_r changes abruptly, a change that would be expected if the transition mechanism were to undergo a sudden modification.

A second concern is that we *occasionally* observed an apparent slowing down of the solitary wave with time. To see this we measured the delay of the onset of nonzero intensity relative to the synchronous reference signal. The slit was then translated by 25 μm parallel to its long axis, and the delay was measured again. This process was repeated several times, and an example of the delay *vs.* slit position is shown in Fig.3. At later times the velocity is clearly slower than at earlier times. The existence of a change of slope with time depends on the region of the cell being imaged, and may be due to interactions with defects in the sample. Nevertheless, over many experimental runs at different sample positions, we obtained good reproducibility in our velocity measurements using the intensity *vs.* time technique described earlier.

Let us now review the theory in **I**. The free energy $F = \sum_i \int f_i dx$, where $f_i =$

$f_i^{\text{elastic}} + f_i^{\text{electric}} + f_i^{\text{layer-layer}}$, is given by:

$$f_i = \frac{1}{2} K \sin^2 \theta \left(\frac{\partial \varphi_i}{\partial x} \right)^2 - P_o E \cos \varphi_i - \frac{\Delta \epsilon \sin^2 \theta}{8\pi} E^2 \sin^2 \varphi_i + \frac{U}{2} [\cos(\varphi_{i-1} - \varphi_i) + \cos(\varphi_i - \varphi_{i+1})] \quad (1)$$

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 along the \hat{x} - axis (within a smectic layer); P_o is the local polarization; and $\Delta \epsilon$ is the dielectric anisotropy. The coupling between layers is expressed in terms of the coupling coefficient U , 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 plays the role of the spatially-uniform free energy of the system, where it is reasonable to assume that the polarization component of U scales as P_o^2 . [12] The resulting solitary wave velocity v in the Fisher regime [13] is given by

$$v = \left(\frac{P_o - \frac{2U}{E}}{\gamma} \right) \frac{2\sqrt{\pi K}}{\sqrt{-\Delta\epsilon}} \equiv v_o \frac{E - E_{th}}{E}, \quad (2)$$

with $E_{th} = \frac{2U}{P_o}$ and $v_o = \frac{2P_o\sqrt{pK}}{g\sqrt{-\Delta\epsilon}}$, where γ is a rotational viscosity. (For very large fields, a

Huxley-type solution may obtain [14]). Although the results of Fig. 2 are consistent with this model at small E_r and therefore at low velocity, they deviate significantly at larger reduced field.

The theory in **I**, in fact, predicts *downward* curvature of v vs. E_r , whereas the data in both **I** and in Fig. 2 show upward curvature. Wang and Taylor included the additional effects of surface anchoring on the propagation velocity [15], but found that anchoring tended to reduce the velocity. In a more recent paper describing a synclinic to anticlinic phase transition *via* solitary waves on cooling [12], our group introduced an additional symmetry-allowed term into the free energy, *viz.*, $\frac{1}{2}\Lambda\sin^2\phi$, where Λ is a positive constant. This term has the effect of favoring the odd layer tilt plane being parallel to the even layer tilt plane, but disfavoring nonparallel tilt planes. Inclusion of this term, however, does not change the basic nature of the theoretical solution, at least in the Fisher regime [13], and seems to leaves the theory at odds with the experimental results.

Faced with an apparent deviation between experiment and extant theory, we now wish to speculate about two other mechanisms that could produce an upward curvature in $v(E)$. The first

possibility is that the spontaneous polarization of the smectic layers is field-dependent due to a biasing of the molecular rotations by E . In fact, the quantity pE can be of order $0.1k_B T$ for the large fields used in our experiment, where p is a molecular dipole moment. This could have the effect of reducing the effective interlayer coupling parameter U as the field is increased. This would lead to some upward curvature in $v(E)$, but not to a sufficient extent to explain the experimental results.

A second possible mechanism for the upward curvature involves shear thinning. In **I** we assumed not only a constant U , but also a rotational viscosity γ that is independent of the rate of rotation of the molecule. It is well known that the phenomenon of shear thinning reduces the effective viscosity of polyethylene at shear rates $\dot{\tau}$ greater than $\sim 1 \text{ s}^{-1}$ [16]. In our experiments the alkane tails of the molecules move distances of order a molecular length l in times of order $0.1 \mu\text{s}$, which is deduced by dividing the characteristic width of the solitary wave front (typically $\sim 0.1 \mu\text{m}$, *cf.* $\sqrt{K/U}$) by its velocity of order 100 cm s^{-1} . Since the thickness of the layer in which the relative motion occurs was also of order l , the shear rate at the boundary layer was $\sim 10^7 \text{ s}^{-1}$. It thus seems plausible that, despite the shortness of the alkane tails in comparison to those in polyethylene, some considerable shear thinning may occur, leading to an increased velocity. For example, in polymeric liquid crystals it has been found that in a certain range of $\dot{\tau}$ the viscosity coefficient scales as $\dot{\tau}^{-1/2}$, and accordingly the viscous force scales as $\dot{\tau}^{1/2}$ [17]. The tail-tail interactions in anticlinic liquid crystals have some characteristics of a polymer-like linkage [18] that may have similar dynamic consequences. Our preliminary numerical calculations show that a shear rate – dependent viscosity coefficient $\gamma \propto (\partial\phi/\partial t)^{-1/2}$ results in a field-dependent velocity with an increasing upward curvature. Work in this direction is underway.

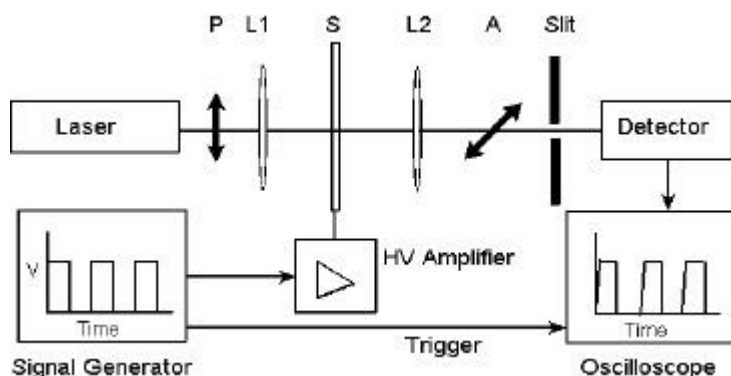
To summarize, we have extended our measurements of synclinc finger velocity invading an anticlinic liquid crystal phase to larger applied electric field. We found that the velocity increases

sharply with applied field, and is by far the largest ever observed for a liquid crystal. This behavior at large fields is apparently inconsistent with a previously published model that adequately describes the (Fisher-type) fingering at low fields. For sufficiently large field ($\sim E_{th}$), however, a Huxley-type solution may obtain [3,14]. This possibility needs further investigation. Nevertheless, we have suggested two possible modifications of the previous model, *viz.*, a field-dependent interaction parameter U and shear thinning, that may help explain the observed behavior. Both experimental and theoretical work are now underway to understand the mechanism responsible.

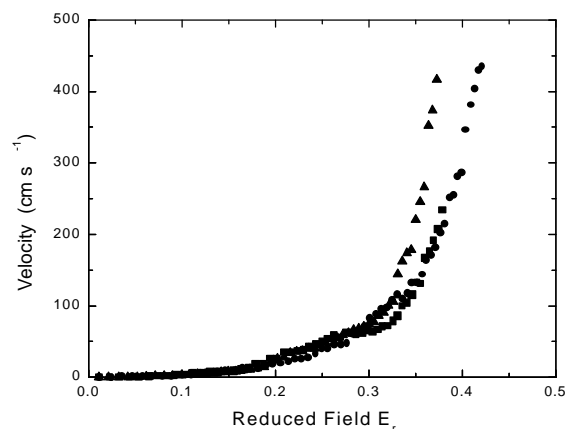
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Figures

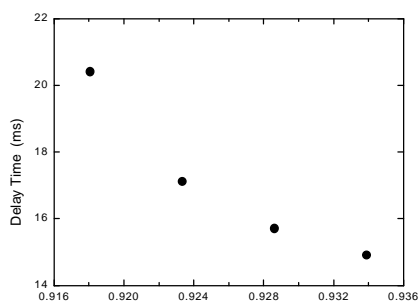
1. Schematic representation of experimental arrangement. **P** and **A** correspond to polarizer and analyzer, **L1** and **L2** are focusing and collimation lenses, and **S** is the sample cell.



2. Measurements of velocity vs. reduced field E_r . \blacktriangle corresponds to $T = 112^\circ\text{C}$, \blacksquare corresponds to 113°C , and \bullet 114.0°C .



3. Delay time between trigger pulse and the onset of an intensity change at the detector vs. the slit position along the smectic layer. The absolute position is determined by the micrometer setting, and does not correspond the distance from the nucleation site of the fingers.



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References

1. A.D.L. Chandani, T. Hagiwara, Y. Suzuki, Y. Ouchi, H. Takezoe, and A. Fukuda, *Jpn. J. Appl. Phys.* **27**, L729 (1988)
2. A. Fukuda, Y. Takanishi, T. Isozaki, K. ishikawa, and H. Takezoe, *J. Mater. Chem.* **4**, 997 (1994)
3. J.-F. Li, X.-Y. Wang, E. Kangas, P.L. Taylor, C. Rosenblatt, Y. Suzuki, and P.E. Cladis, *Phys. Rev. B* **52**, R13075 (1995)
4. Y. Suzuki, H. Hagiwara, I. Kawamura, N. Okamura, T. Kitazume, M. Kakimoto, Y. Imai, Y. Ouchi, H. Takezoe, and A. Fukuda, *Liq. Cryst.* **6**, 167 (1989)
5. S. Garoff and R.B. Meyer, *Phys. Rev. Lett.* **38**, 848 (1977)
6. I. Musevic, A. Rastegar, M. Cepic, B. Zeks, M. Copic, D. Moro, and G. Heppke, *Phys. Rev. Lett.* **77**, 1769 (1996)
7. R. Blinc and I. Musevic, *Mol. Cryst. Liq. Cryst.* **292**, 311 (1997)
8. K. Hiraoka, H. Takezoe, and A. Fukuda, *Ferroelectrics* **147**, 13 (1993)
9. Y.P. Panarin, O. Kalinovskaya, and J.K. Vij, *Appl. Phys. Lett.* **72**, 1667 (1988)
10. P.E. Cladis, W. van Saarloos, D.A. Huse, J.S. Patel, J.W. Goodby, and P.L. Finn, *Phys. Rev. Lett.* **62**, 1764 (1989)
11. P.E. Cladis and W. van Saarloos, in **Solitons in Liquid Crystals**, ed. by L. Lam and J. Prost, Springer-Verlag, N.Y. (1992)
12. X.Y. Wang, J.-F. Li, E. Gurarie, S. Fan, T. Kyu, M.E. Neubert, S.S. Keast, and C. Rosenblatt, *Phys. Rev. Lett.* **80**, 4478 (1998)

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13. D.G. Aronson and H.F. Weinberger, *Adv. Math* **30**, 33 (1978)
 14. P. Fife, in **Mathematical Aspects of Reacting and Diffusing Systems**, ed. by S. Levin, Springer, N.Y. (1979)
 15. X.Y. Wang and P.L. Taylor, *Phys. Rev. Lett.* **76**, 640 (1996)
 16. D. Abraham, K.E. George, and D.J. Francis, *Polymer* **39**, 117 (1998)
 17. Y. Yamakazi, A. Holz, and S.F. Edwards, *Phys. Rev. A* **43**, 5463 (1991)
 18. Y.I. Suzuki, T. Isozaki, S. Hashimoto, T. Kusumoto, T. Hiyama, Y. Takanishi, H. Takezoe, and A. Fukuda, *J. Mater. Chem.* **6**, 753 (1996)