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Electrohydrodynamic convection under a nematic-isotropic interface

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We report experimental results on electrohydrodynamic convection of nematic liquid crystals having a free surface at the nematic-isotropic interface. The applied electric field is orthogonal to the free surface. In this configuration, the thickness of the nematic layer is linearly proportional to the reduced temperature. We observe that the threshold voltage for convective rolls varies significantly as the thickness is decreased, while the dimensionless wave vector remains constant. When convection occurs, the nematic-isotropic interface undergoes a periodic distortion, and we argue that this distortion is largely responsible for the relatively large variation of threshold voltage with layer thickness. [S1063-651X(96)08211-6]

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I. INTRODUCTION

Pattern formation in nonequilibrium systems is not only very intriguing but also currently the subject of intense investigation [1]. One system exhibiting many exciting pattern-forming instabilities is electrohydrodynamic convection (EHC) in nematic liquid crystals [2,3]. This is a popular system for experimental investigation for many reasons, one being that it allows reproducible measurements with well defined boundary conditions. There has been a large amount of both theoretical and experimental work investigating the effect of varying the amplitude and/or frequency of the applied electric field, using different nematic compounds, and, significantly, different models for charge transport in the liquid crystal [4]. While there have been reports published on different types of orienting boundary conditions [5], this work represents a qualitatively different approach to varying experimental conditions. We report the effects of allowing *free* boundary conditions at one surface of a nematic liquid crystal undergoing EHC. The full meaning of the statement ''free'' is discussed subsequently. We obtain this boundary condition at thermal equilibrium by inducing EHC in a nematic liquid crystal in contact with its isotropic phase.

Many experiments have been done in which a temperature gradient was imposed across a nematic substance to obtain a stable nematic-isotropic (NI) interface [6]; there the goal was to observe morphological instabilities of the interface itself, not of the underlying nematic phase. Yokoyama *et al.* [7] reported a NI interface obtained in a conventional sandwich type cell under thermal-equilibrium conditions. In this case, the interface, in the absence of an electric field, is both planar and stable. The aim of that work was to study electric field induced, equilibrium, morphological changes of the nematic-isotropic interface using a nematic having positive dielectric anisotropy.

Our aim is to study the nonequilibrium dynamics of a nematic liquid crystal having a free surface at the nematic-isotropic interface. A liquid crystal having negative dielectric anisotropy was used, in which the instabilities described in Refs. [7,8] should not occur. An electric field was applied orthogonal to the NI interface. We examined electrohydrodynamic convection in the nematic layer underneath the NI interface. In this configuration, we can continuously change the thickness of the nematic layer simply by changing the temperature. The geometry of our system is shown schematically in Fig. 1.

II. BACKGROUND

The standard theory of EHC is based on the electrical conductivity driven, Carr-Helfrich instability [9,10]. These

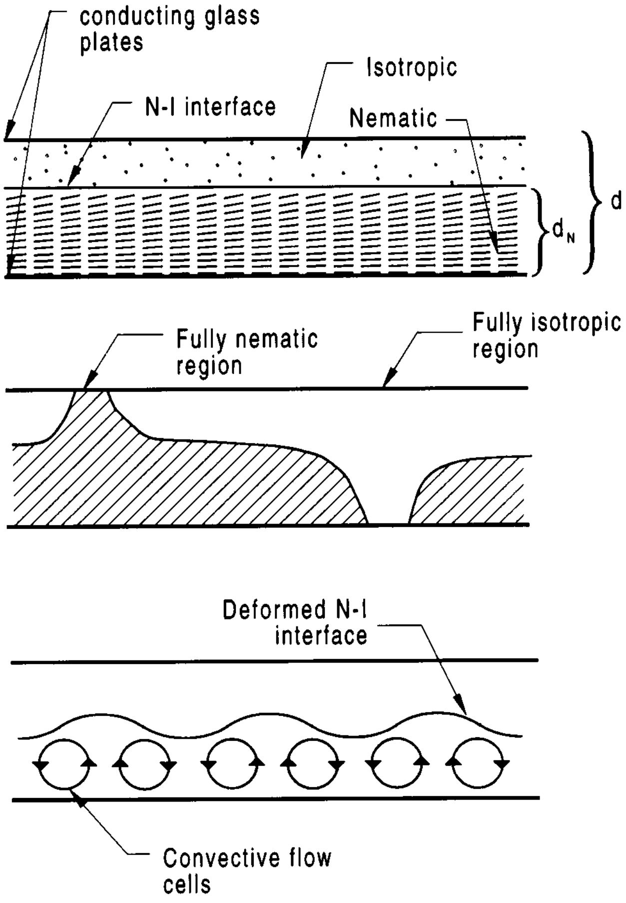

FIG. 1. Top: Schematic cross section of the sandwich type cell with a stable nematic-isotropic interface. Middle: Representation of fully nematic and fully isotropic regions. Bottom: proposed structure of periodic distortion of NI interface in the presence of EHC in the nematic phase.

ideas were the basis of the far more comprehensive study of Bodenschatz *et al.* [11]. This study investigated the threshold and near threshold behavior of electrically driven pattern-forming instabilities in a nematic liquid crystal. Most importantly for our purposes, a variety of different types of boundary conditions were used; two are particularly relevant to the present experiment. The first, called ''fully'' free boundary conditions, assume that at the boundaries, the vertical fluid velocity and the tilt angle are zero; other quantities have vanishing derivatives at the boundaries. The second, ''fully rigid'' boundary conditions, assume that all quantities are zero at the boundaries. In all cases, the same boundary conditions are applied at both boundaries, the planes $z=0$ and $z=d_N$. Also in all cases, the distance between these boundaries is always fixed. The present experiment contains features of both of these situations, especially because we expect different boundary conditions at each boundary. The director angle at the NI interface is usually modeled as being inclined at some angle to the interface normal, but degenerate around that direction, so that the director lies on the surface of a cone [12]. Since in the present experiments no degeneracy is observed, it seems likely that the degeneracy is broken by the homogeneous alignment at the other boundary.

III. EXPERIMENTAL SETUP

The stable nematic-isotropic interface was obtained at thermal equilibrium by exploiting both the ''wettability difference'' and miscibility gap, following Ref. [7]. The different miscibility of impurities in the nematic and isotropic phases means that a lightly doped nematic compound will exhibit coexistence of the nematic and isotropic phases over a range of temperature. We define T_I as the highest temperature at which the nematic phase is observed, and T_N as the lowest temperature at which the isotropic phase is observed. Between T_N and T_I, both phases coexist. We define the reduced temperature t as $(T-T_N)/(T_I-T_N)$; by the lever rule, this quantity is also the fraction of the compound in the isotropic phase. The wettability gap is exploited by preparing a sandwich cell with *hybrid* alignment, that is, planar aligning treatment on both substrates, but one treatment is wetted by the nematic and the other by the isotropic. This type of cell, when filled with a slightly impure nematic, can exhibit a stable nematic-isotropic interface parallel to the plates when the temperature is between T_N and T_I. The surface energy and density difference between the nematic and isotropic phases, together with the characteristic size of the sample, are such that the influence of gravity can be safely ignored.

One of the plates bounding the liquid crystal is prepared such that its surface treatment preferentially wets the isotropic phase, and the other prepared so that it preferentially wets the nematic phase. Tangentially evaporated SiO [13] produces homogeneous alignment, but is known [14] to decrease the nematic scalar order parameter within its vicinity; this was chosen as one surface treatment. Rubbed polymer layers also produce homogeneous alignment, but are known [15] to promote nematic order and so preferentially wet the nematic over the isotropic.

For the experiments reported here, one of the substrates (indium-tin-oxide coated float glass plates) was spin coated with a 1 wt % aqueous solution of poly (vinyl alchohol) (PVA), [16] dried at 80 °C overnight, and then rubbed lightly with a cotton cloth using a total rubbing distance of about 10 m. The other substrate has 600 Å SiO evaporated onto its surface, using an angle of 60° between the substrate normal and the line of sight to the evaporation boat. Both substrates are then clamped together with spacers in between to give a plate separation $d=50\mu$m. The plates are placed together so that their preferred alignment directions are parallel. The liquid crystal methoxy butyl methylanaline (MBBA) is introduced between the plates via capillary action. The MBBA, used as obtained [17], had a sufficiently wide coexistence region, probably due to absorbed water, that further doping was unnecessary. After the sample is filled with liquid crystal compound and glued together at the edges, it is placed in a temperature controlled housing on the stage of a polarizing microscope. It is useful to use monochromatic light for illumination. The hot stage is a Mettler FP-82 which, in addition to controlling the temperature, can precisely control either the heating or cooling rate, which is essential for obtaining a uniform NI interface. Thin wires were attached to each plate to make electrical contact and a sinusoidal electric field with constant frequency (50 Hz) and variable amplitude was applied to the sample via the conductive coating. A charge-coupled device (CCD) video camera was mounted on the microscope to record the images.

There are two critical factors that must be precisely controlled in order to obtain a stable, planar nematic-isotropic interface: rubbing conditions and the cooling and/or heating rate [18]. Reproducible results can only be obtained with the very long rubbing distance referred to earlier. A typical preparatory procedure was to use a rather large heating or cooling rate ($\sim$0.3 °C/min), until a uniform layer formed (usually at $t\sim\frac{1}{2}$). The temperature was then held steady for an hour. Once a planar interface was reached in this manner, it was stable for days. Occasionally, this procedure fails if a fully nematic or fully isotropic region forms. By fully isotropic or fully nematic we mean any area inside which either phase is in contact with both substrates — see Fig. 1. If such an area forms, it is impossible to eliminate it without either heating the sample above T_I or cooling it below T_N, which essentially means beginning the preparatory procedure again. Indeed, if such regions remain for more than a short while, the liquid crystal sample must be ''annealed'' by leaving it well above T_I for several hours, which is long enough for any impurity concentration gradients in the direction parallel to the substrates to diffuse away.

Once the stable interface is formed, the thickness of the nematic layer is continuously varied by slowly changing the temperature ($\pm$0.005 °C/min). As the temperature is lowered, the appearance of the sample changes abruptly when the nematic phase touches the SiO treated substrates; at this point, T_N, the isotropic phase has disappeared altogether. If the temperature is raised instead of lowered, the sample appears completely dark at T_I as the nematic phase disappears altogether and all birefringence is lost. For all experiments reported here, both T_I and T_N varied by approximately 0.5 °C over the course of six months, but T_I-T_N remained constant at 1.06 ± 0.02 °C. Because of this, only the reduced temperature t, defined above, will be used from this point on.

In order to directly measure d_N, optical transmission measurements with the sample placed between crossed po-

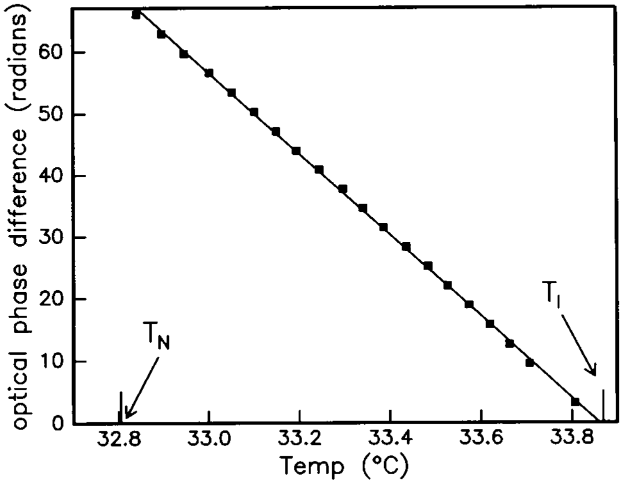

FIG. 2. Phase difference between ordinary and extraordinary rays traversing the sample cell vs temperature. The linear dependence is a manifestation of the lever rule for two-phase coexistence.

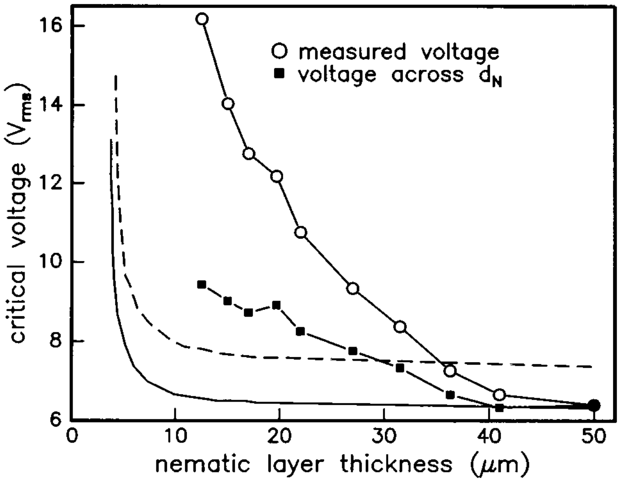

FIG. 3. Open circles: Measured critical cell voltage necessary to observe EHC vs nematic layer thickness. Closed squares: critical potential difference across only the nematic layer necessary to induced EHC calculated from the voltage divider relationship, vs nematic layer thickness. The solid and dashed lines are the calculated results from Ref. [11] for ''free'' and ''approximately rigid'' boundary conditions, respectively. Both these results have been extrapolated to $d_N = 50$ μm.

larizers were also performed. The transmitted light intensity was measured as a function of temperature, in order to quantitatively evaluate the phase difference between the ordinary and extraordinary rays, δ. When the nematic director is everywhere at 45° to the polarizer axis, $\delta = 2\pi \Delta n d_N / \lambda$. When the finite tilt angle (θ_A) at the nematic-isotropic interface ($\sim 10°-30°$ [19,20]) is taken into account, the phase difference is approximately

$$\delta = \frac{2\pi \Delta n d_N}{\lambda} \left[1 - \frac{n_e(n_e + n_o)}{6 n_o^2} \theta_A^2 \right], \tag{1}$$

from which we estimate the error in the original, simpler expression above to be about 7%. Moreover, the error is independent of d_N. Because this error is not significant, we have chosen to use the zero tilt-angle assumption for simplicity. As the temperature changes from T_N to T_I, the birefringence Δn remains constant, so $\delta \propto d_N$. In Fig. 2 we plot δ vs T. As in Ref. [21], we find $d_N = d(1-t)$ where t is the reduced temperature. This result is used in the EHC experiments to find d_N.

IV. EXPERIMENTAL RESULTS

After a stable, planar NI interface was obtained, the applied electric field was slowly increased and the onset of EHC monitored visually. This was performed for different values of d_N; the results are shown in Fig. 3. In this figure one can plainly see that the critical voltage decreases with an increase in the thickness of the nematic layer. These data can be misleading, however, as the measured voltage between the plates is not the quantity of interest. Knowing that the nematic and the isotropic phases have different electrical conductivity, we can find the potential difference across just the nematic layer by modeling the whole sandwich cell as a resistive voltage divider [22]. Within that context, if the potential difference across both layers is V, the potential difference across only the nematic (before the onset of EHC) is

$$V_N = \frac{V}{[(\rho_I/\rho_\perp)(d/d_N - 1) + 1]}. \tag{2}$$

ρ_I and $\rho_\perp$ are the resistivities of the isotropic and the nematic (measured with the director perpendicular to the applied electric field), respectively. They were measured independently for this experiment. The ratio $\rho_I/\rho_\perp$ was found to be 0.24. Although the resistivities are sensitive to the level of impurities, their ratio should be much less so. However, since the existence of the two-phase region is solely due to the different miscibility of impurities in the two phases, the impurity concentration of one phase in equilibrium with the other will be different than that of a single-phase sample, in which the conductivity measurements were made. However, since the width of the two-phase region is only about 1/10 of the temperature difference between the measured clearing point and the clearing point for pure MBBA, and with the reasonable, first-order approximation that the conductivities are proportional to impurity concentration, we can estimate the error made in using the single-phase measurements $\rho_I/\rho_\perp$ to be about 10%, independent of t. Figure 3 also shows the critical voltage needed across the nematic layer to induce electrohydrodynamic convection underneath the nematic-isotropic interface, plotted as a function of thickness of nematic layer. We point out that voltage decreases by more than 50% over our range of d_N. Note that d_N in Fig. 3 is never less than 10 μm, and that it jumps from just over to 40 μm to 50 μm, at which point the sample is fully nematic, and the interface is no longer present. The reason why d_N is limited to this range is discussed subsequently. Also of interest is the wave vector of the roll pattern, λ_c, just above onset. In Fig. 4 the periodicity of the roll pattern is shown. Note that it varies by a factor of more than 3.

In order to make comparison with theoretical calculations, it is necessary to cast our measured quantities in the units used in the calculations. The standard practice is to measure lengths in units of d_N/π. Using the data in Fig. 4 for this rescaling we can plot the dimensionless wave vector q_c,

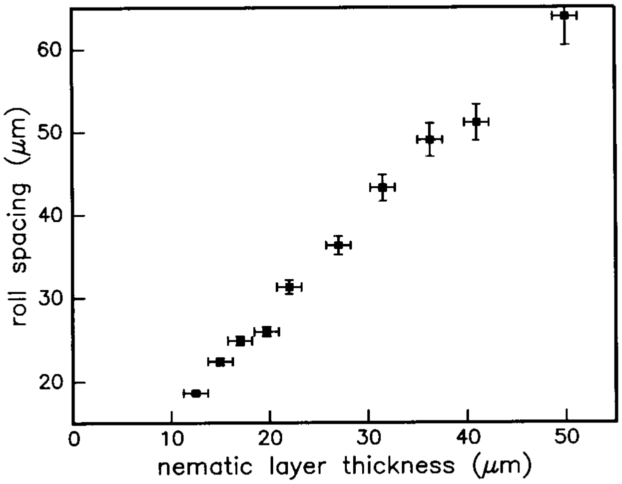

FIG. 4. Observed wavelength λ_c vs nematic layer thickness.

which is the quantity calculated in Ref. [11]. q_c vs d_N is shown in Fig. 5. Note that the error bars reflect the uncertainties in determining both λ_c and d_N.

V. DISCUSSION

If, in the theoretical calculations, all lengths have been rescaled, then why, after rescaling, should any measured quantity depend on d_N? Various quantities having units of time are considered in Ref. [11]: the charge relaxation time τ_0, which depends only on material properties, the period of the sinusoidal applied electric field, $1/f$, where f is the frequency, and the characteristic time for director relaxation, $\tau_d = K_{11} d_N^2 / \gamma_1$, where K_{11} is the splay elastic constant and γ_1 is the rotational viscosity. The argument is made that all calculated results should be independent of d_N if τ_d is substantially larger than both τ_0 and $1/f$. In order for this condition to be violated in our experiments, d_N would have to be significantly less than 1 μm.

The prediction that the dimensionless wave vector q_c should not depend on d_N is apparently on firm ground. The experimental results, within error bars, are consistent with q_c being constant. The critical voltage across the nematic layer to observe convection is more problematic. The calculated V_c for both sets of boundary conditions used in Ref. [11] is also plotted in Fig. 3 for comparison. The calculated results predict that V_c should not vary with d_N for $d_N > 10$ μm, as in the experiment, yet V_c varies by over 50%.

One immediately suspects several factors that might account for the discrepancy with existing theory. Almost all can be traced to differences in the boundary conditions chosen for the theory and those present in the experiment described above. Most conspicuous is that in Ref. [11], the chosen boundary conditions apply at *both* boundaries in every case; in the experiment, one boundary, the NI interface, is clearly very different from the other, nematic in contact with a rubbed polymer surface treatment known to produce ''strong'' anchoring [23]. The ''fully free'' conditions chosen in Ref. [11] are not in fact fully free. The director is still constrained to lie in the x-z plane at the boundaries, and the fluid velocity in the z direction must vanish at this boundary.

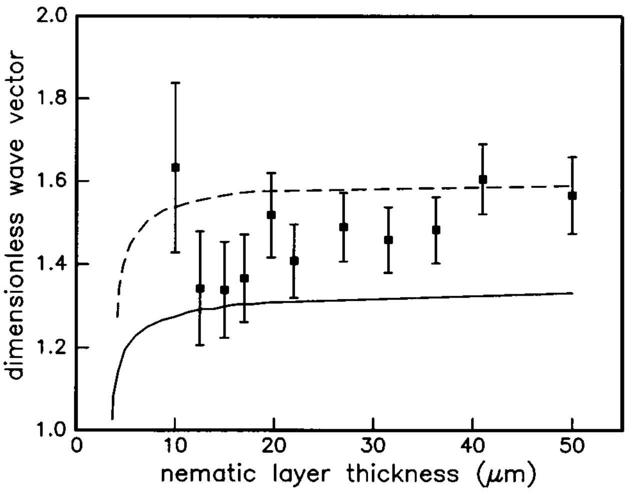

FIG. 5. Dimensionless wave vector $q_c \equiv 2d_N/\lambda_c$ vs nematic layer thickness. The solid and dashed lines are the calculated results from Ref. [11] for ''free'' and ''approximately rigid'' boundary conditions, respectively. Both these results have been extrapolated to $d_N = 50$ μm.

In our experiment, it is unlikely that there is transport of fluid across the NI interface, driven by EHC, but it may be premature to rule it out. In our opinion, the most significant difference in boundary conditions between present theoretical calculations and this experiment is the actual position of the boundary. Since the capillary length at the NI interface is very much less than 1 μm [6], there is essentially no free energy cost associated with a deformation of the NI interface over the length scale of the observed λ_c, and this is exactly what happens. Although this deformation cannot be directly observed using the present apparatus, we can confirm its presence indirectly. This deformation is also the reason EHC cannot be observed for arbitrary values of d_N between 0 and d. If d_N is within about 8 μm of d when EHC is induced, the NI interface is observed to contact the SiO substrate, and remain in contact there after the electric field is switched off, leaving a fully nematic region. Similarly, if d_N is less than about 8 μm, and EHC is induced, the NI interface contacts the rubbed polymer interface, and a fully isotropic region remains after the electric field is removed. Moreover, these regions inside which the NI interface has contacted one of the substrates have the same periodicity as the EHC rolls. These observations demonstrate that EHC induces a periodic distortion of the NI interface; the amplitude of this distortion is on the order of 8 μm. A proposed structure for this distortion is depicted schematically in Fig. 1. At present, we know of no theory of EHC which allows for a distortion of the nematic-isotropic interface, and which can successfully predict a significant decrease in the onset voltage for EHC as the thickness of a nematic layer having a free interface decreases.

ACKNOWLEDGMENTS

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