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Anisotropic Domain Growth in the Bistable Cholesteric Twist Cell

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We describe anisotropic domain shapes which occur in a first order phase transition between two configurations of the bistable cholesteric twist cell. A Wulff plot analysis is described in which equilibrium domain shapes can be constructed from previously reported data on the anisotrophy of the domain wall tension. The predictions for the equilibrium shape are in qualitative agreement with the domain shapes observed growing in the absence of an applied field. The shapes of the experimentally observed growing domains depend on the two operating parameters of the cell: the thickness to pitch ratio and the voltage. We also describe a situation in which we can adjust the voltage to halt the domain growth and thus a true experimental equilibrium shape is obtained. Small differences are observed between the equilibrium shape and the kinetic one, but the main features are preserved.

I. INTRODUCTION

The anisotropic character of the nucleated domain shapes at solid-liquid[1] or solid-gas[2] equilibrium is a well known phenomena. The strong anisotropy of the crystal surface tension is responsible for the often multifaceted equilibrium shapes. If the surface tension is known in detail as a function of crystallographic direction, then the equilibrium shapes can be predicted with the aid of a Wulff plot.[3] In liquid-liquid or liquid-gas equilibria nucleation usually results in spherical domains because of the isotropy of the surface tension in these cases.

For thermotropic liquid crystals the full rotational symmetry of the liquid is no longer present. Attempts have been made to observe the anisotropy of the nematic-isotropic[4] and nematic-air[5] interface tensions where magnetic fields are used to provide the additional symmetry constraint, but the anisotropy is very small. In general no pronounced anisotropy is observed in the nucleated domains of cho-

lesteric or nematic phase growing from the isotropic. An exception to this occurs in the blue phases. Here sharp crystallographic platelets of both blue phase I[6] and blue phase II[7] have been observed growing in isotropic. Anisotropic domains have also been observed between different configurations in the cholesteric phase. Bouligand[8] has described various shapes observed between configurations of different twist in a Cano wedge with planar surface alignment.

In this paper, we wish to describe anisotropic domain shapes which we observe in the bistable cholesteric twist cell (BCTC). The BCTC is an ideal system in which to study nucleation and domain shapes because detailed calculations are available for this system including some calculations on the anisotropy of the domain wall tension. We will discuss how data on the orientation dependence of the wall tension can be interpreted in terms of Wulff's theorem to predict the shape of small domains at equilibrium. We also describe the shapes of domains which are observed growing in experimental cells. The shape of the domains vary with the two system parameters: the thickness to pitch ratio t/P and the voltage V. The qualitative features of some of the shapes of the domains are similar to the calculated equilibrium shape, in spite of the fact that the observed and calculated shapes were not determined at the same conditions. We also show, that by adjusting the voltage, we can compare the shape of the growing domains with the experimental shape obtained at equilibrium.

II. WALL TENSION IN THE BISTABLE CHOLESTERIC TWIST CELL

When a nematic or cholesteric liquid crystal is placed between two surfaces, the directors can be constrained throughout the cell to certain equilibrium configurations. The configuration of the liquid crystal directors throughout the cell are determined by the surface boundary conditions and the material constants. For certain geometries and material parameters, two or more configurations may be found as solutions to the Oseen-Frank equations. In this case a first order phases transition may occur from the state of higher free energy to the configuration of lower free energy.

In such a phase transition between configurations, the interface between the two phases may be highly anisotropic, i.e., the energy of the configuration joining the two states may vary considerably with the direction of the orientation of the boundary between them. This reflects the fact that the symmetry of the configuration being less than the that of the thermotropic bulk state itself.

An example of such a first order transition between two configurations is found in the bistable cholesteric twist cell.[9-14] In this cell bistability can occur between two topologically equivalent states of different twist. Reliable bistable behavior is achieved by introducing an appreciable surface tilt, in addition to adding sufficient chiral dopant to provide an unstrained pitch approximately equal to the thickness of the liquid crystal layer. The thickness to pitch ratio forms a critical parameter of the BCTC. For appropriate values of the surface tilt and the thickness to pitch ratio, two laminar states, described as the UP and DOWN states, may exist either with no field[9,10] or in the presence of a holding field.[11,14] The two states of the BCTC with a holding field are shown in Figure 1, together with the states observed when no field is applied. Note that with no field the "UP"-like state is "nematic".

In the case where no field is applied, a thickness to pitch ratio (t/

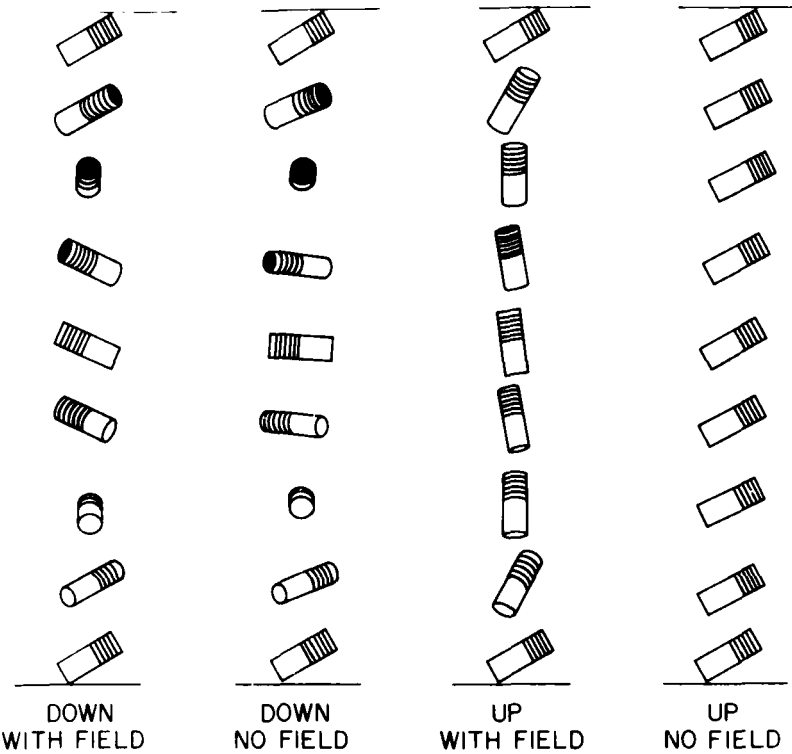

FIGURE 1 The configurations of the BCTC with a holding field. The UP and DOWN configurations are the bistable states. The middle configuration is that obtained when no field is applied.

P) can be found so that the UP and DOWN states have the same free energy. For the holding voltage cell, both t/P and the voltage can be adjusted independently to achieve this condition. In either case, above or below some t/P (or voltage), one state will be of lower free energy and nucleation may occur.

One of the features helpful in studying the BCTC is that detailed calculations have been performed on the configurations and free energies of the states for this system. Recently Berreman[13] has performed calculations simulating the wall between these two states. The free energy density was calculated as a function of position, on passing through straight walls at different orientations. Berreman used the orientation dependence of the excess free energy of the transition region to provide a measure of the anisotropy of the wall tension of the boundary separating the UP and the DOWN states. The calculations were performed for straight walls with no field present because electric fields and wall curvature make the problem more difficult.

The wall tension was reported at nine azimuthal angles, only five of which were independent because of the C2 symmetry of the cell. The wall energy is found to be quite anisotropic. His data is reproduced in Figure 2. The angle β in this figure is referred to the projection of the director at the top surface. The calculations were performed using the elastic and dielectric constants for E7 at 20°C.[15] A surface tilt of 55° and a t/P of 0.58 were chosen. At these conditions, the DOWN state has a free energy slightly below that of the UP state.

The smallest of the computed wall tension values occur at wall orientations of 45° and 135°. Two maxima were found, the largest at $-90°$ and a smaller one at $+90°$. We will show next how this anisotropy of wall tension can be used to describe observed domain shapes.

III. WULFF PLOTS AND SHAPES OF EQUILIBRIUM DOMAINS

When the orientation dependence of the surface tension is known, the Wulff plot[3] provides a convenient method for predicting the shape of the nucleated domains at equilibrium. A Wulff plot is a polar plot of the surface tension (γ) as a function of the orientation angle of the interface. Wulff's theorem, as set out over 80 years ago, describes how to calculate the equilibrium shape which minimizes the free energy from such a γ plot. Herring[16] has given a particularly clear review of the procedure for constructing the equilibrium shape for

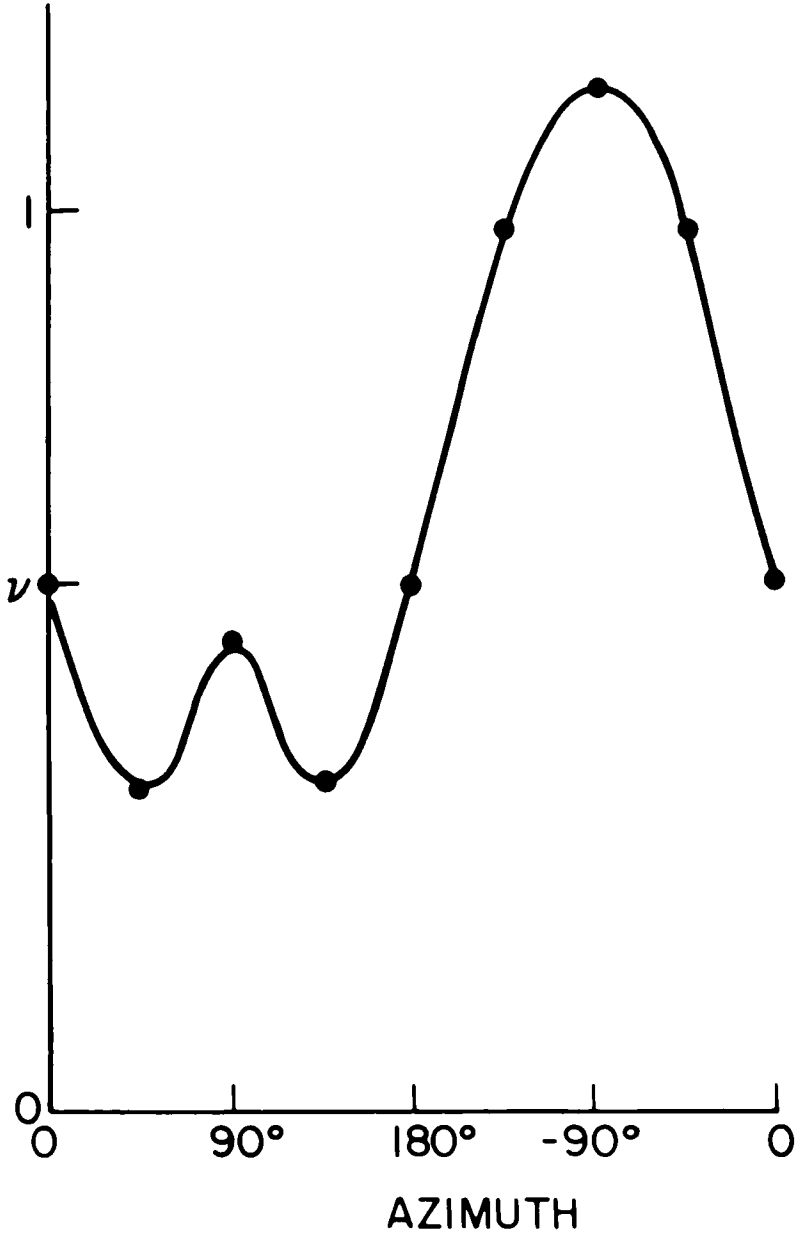

FIGURE 2 Variations with azimuthal angle of the excess free energy of the laminar barrier state separating regions of UP and DOWN. The ordinate is scaled to the product of the cell thickness and the free energy density of the laminar barrier state. This figure is reproduced after reference 13.

crystals in 3-dimensions, and we will briefly describe that method here. We limit our discussion to a 2-dimensional example, which is appropriate for our case where the liquid crystal is confined between two plates.

The procedure is as follows. Let γ be plotted radially as a function of the orientation. At each point on the polar γ plot, construct a line perpendicular to the radius vector at that point. Then the area that can be reached from the origin without crossing any of the perpendicular lines is geometrically similar to the ultimate equilibrium shape of the domains.

The procedure is illustrated in Figure 3 using Berreman's wall tension data which has been least square fit to a cubic polynominal in cos β. Note that the figure exhibits the C_2 symmetry of the cell about $\beta = 90°$. The solid line represents the surface tension while the dotted line represents the resulting equilibrium shape. Because the DOWN state has the lower free energy at these conditions, the shape is that for a domain of DOWN at equilibrium in a region of UP state. The equilibrium shape is a smooth curve whose derivative is continuous everywhere except at a single cusp at $\beta = 90°$. The curvature is nowhere zero on this shape. Herring[16] has proved that, in general, no straight sections are possible in the equilibrium shapes that arise from γ curves whose derivatives are everywhere continuous, as is the case for our liquid crystal example.

It should be emphasized that Wulff's theorem and the domain shapes predicted are rigorously appropriate only when the system is at equilibrium. However, if the growth rates are sufficiently slow we might expect the same shapes to be appropriate for growing domains away from equilibrium. In the next section we will discuss the shape of domains which we observed growing in an experimental cell.

IV. EXPERIMENTAL RESULTS

Effect of t/P under Zero Field

In Figure 4 we show two photographs of nuclei of DOWN state growing in UP state for a mixture of cholesterol nonanoate in E7. The cell had a nominal thickness of 10 μm. For Figure 4(a) the t/P is 0.77 while in the lower photo the t/P is approximately 0.72. Tilted surface alignment was achieved using an oblique (7°) evaporation of SiO. This produces a tilt in the liquid crystal at the surface of about 55°. The cell is initially prepared in the UP state by applying a large electric field (6.5 volts). When the field is removed, the cell returns

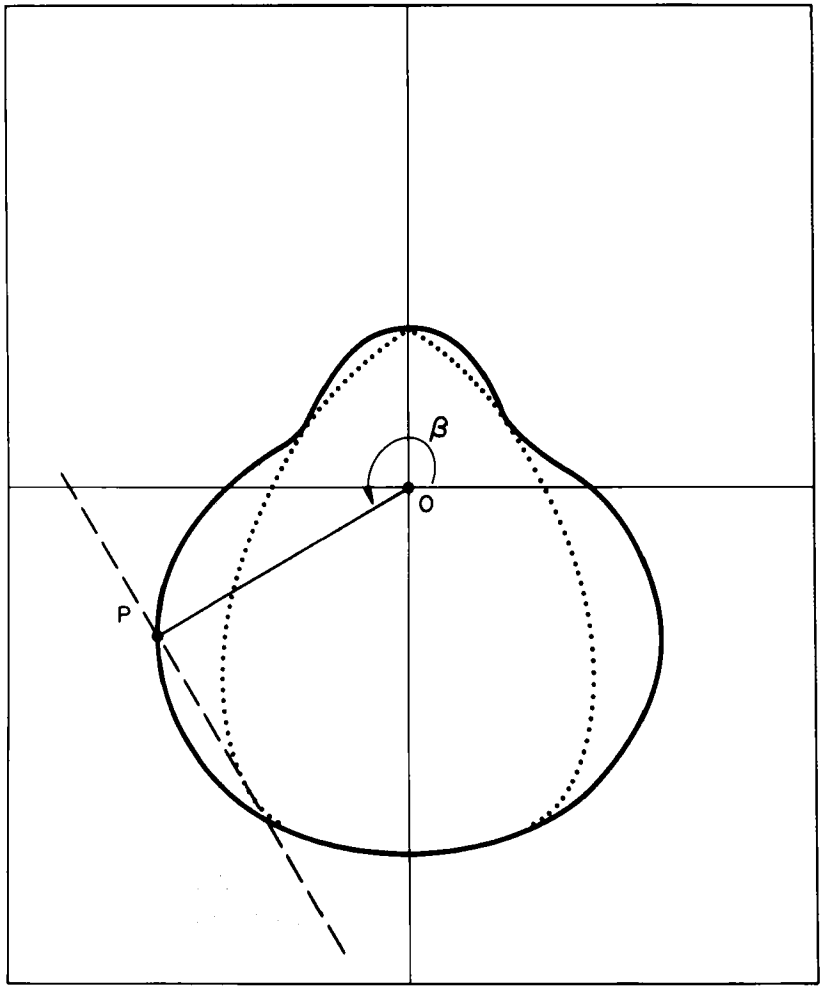

FIGURE 3 Wulff plot for a domain of DOWN nucleated from the UP state. Solid line indicates the γ plot while the dotted line represents the shape of the domain at equilibrium. The dashed line depicts one of the perpendicular lines which circumscribe the equilibrium shape.

to the UP state. Shortly thereafter, the lower energy DOWN state begins to grow on dust particles or other surface inhomogeneities. Note the white spec near the center of the domains, where nucleation occurred. The growth rate increases with increasing t/P (greater separation of the free energies of the UP and DOWN states). The photomicrograph in Figure 4(a) was taken 45 seconds after nucleation,

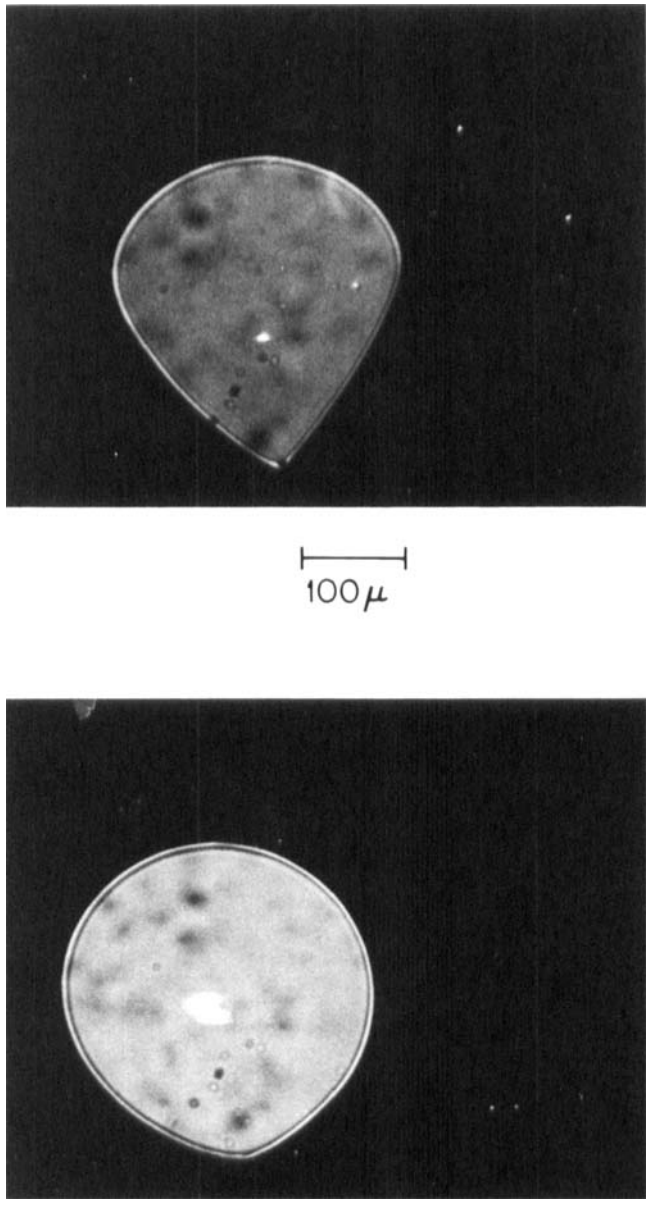

FIGURE 4 Domains of DOWN observed growing in the UP state: (a) t/P = 0.77 taken 20 seconds after nucleation, and (b) t/P = 0.72 taken 45 seconds after nucleation. The photographs are oriented with the alignment direction, at the surface, pointing toward the left.

while that in Figure 4(b) was taken after only 20 seconds. These photographs could also be used to obtain information on wall growth rate as a function of t/P, but these data have already been reported.[14]

Both domains exhibit the qualitative features described by the Wulff plot. The photographs in Figure 4 were taken with the $\beta = 0$ direction pointing toward the left. Thus the cusps occur in the $B = 90°$ direction, as is the case for the equilibrium shape of Figure 3. The angle of the wedge decreases as the t/P ratio increases. The angle at the apex of the thicker sample is approximately 70°, while that of the thinner domain is more rounded and roughly 120°. The apex of the wedge is perpendicular to the evaporation direction ($\beta = 90°$). Nearly circular domains are observed at lower t/P values.

We do not observe domains of DOWN state growing in the UP state at thickness comparable to those of Berreman's calculation. Apparently, the free energy difference between the two states at this t/P (0.58) is insufficient to promote nucleation. Projecting our results at larger t/P values, we might expect nearly circular domains to occur for t/P values equivalent to Berreman's data. It appears that the equilibrium calculations at $t/P = 0.58$ do not agree with our projections for domain growth at the same t/P. This suggests that the shape of the growing domains is probably determined more by anisotropies in the growth rates than by anisotropies in the wall tension. Nonetheless, the general symmetry and the cusp of the calculated equilibrium shape are present in the observed shapes.

Effect of Field on Domain Shape

In Figure 5 we show domains of DOWN growing in the UP state at different voltages. These photographs were taken at $t/P = 0.80$, 20 seconds after the voltage was lowered from 6.5 volts to the given values. In Figure 5(a) growth occurs via the usual wedge shaped domains of DOWN when no voltage is applied. As the voltage is increased, the anisotropy begins to disappear. At 0.50 volts the domain is nearly circular; at $t/P = 0.70$ no anisotropy in shape is observed.

The growth of the domain at 1.05 volts is quite retarded. At 1.10 volts we observed a domain of approximately the same size to occur immediately after the voltage was reduced from 6.5 volts. However, at this voltage, the small domain actually shrank and disappeared. Apparently, the size of the initially nucleated domain was below the critical size required for spontaneous growth to occur at this voltage. The equilibrium voltage at this t/P is 1.18 volts. This was determined

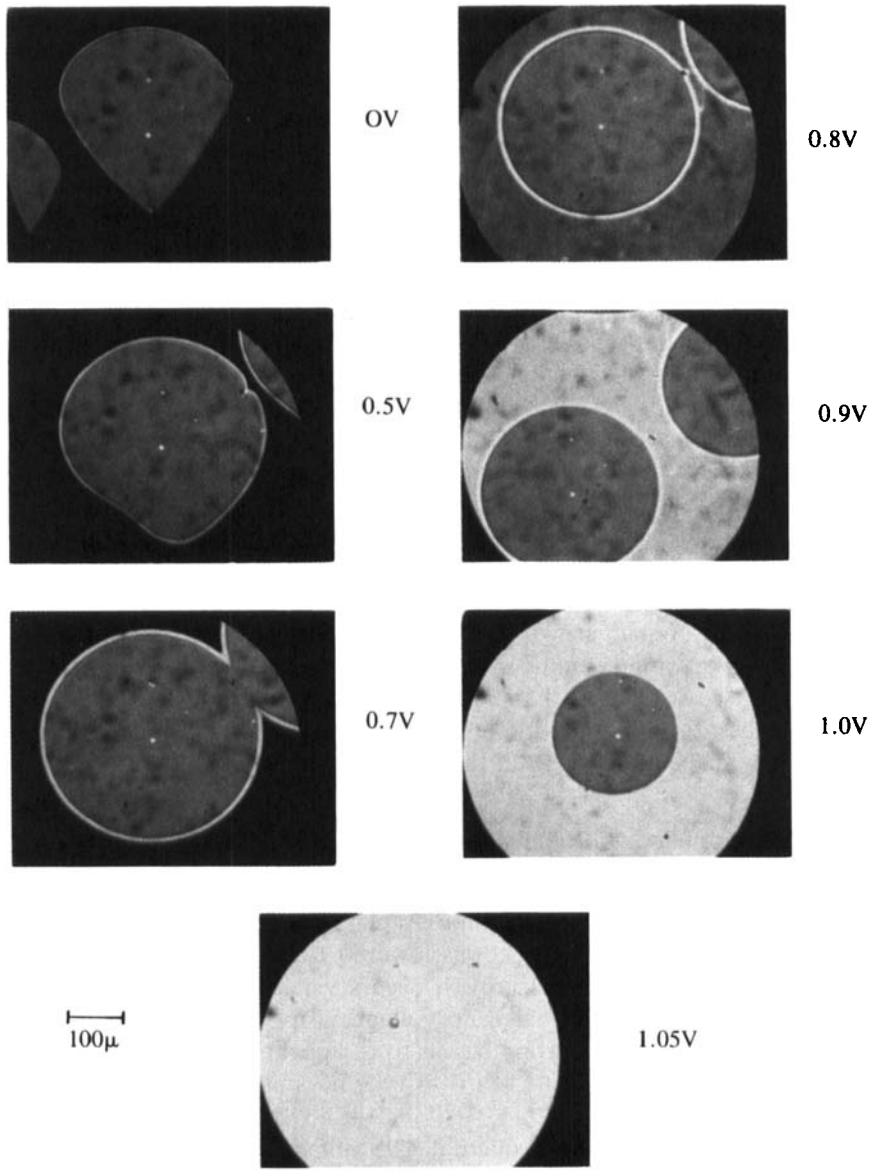

FIGURE 5 Domains of DOWN growing in the UP state at different voltages. Photographs were taken 20 seconds after nucleation began. Orientation in these photographs was the same as in Figure 4.

by observing the voltage at which straight walls between the UP and DOWN state became stationary.

The photograph in Figure 5 can also be used to obtain domain wall growth rates as a function of voltage. The growth rate in the $\beta = -90°$ direction is proportional to the distance between the top edge of the domain wall and the white spec which nucleated the domain. The growth rates in this direction are plotted in Figure 6 as a function of the voltage. For the lower voltages the growth rate is independent

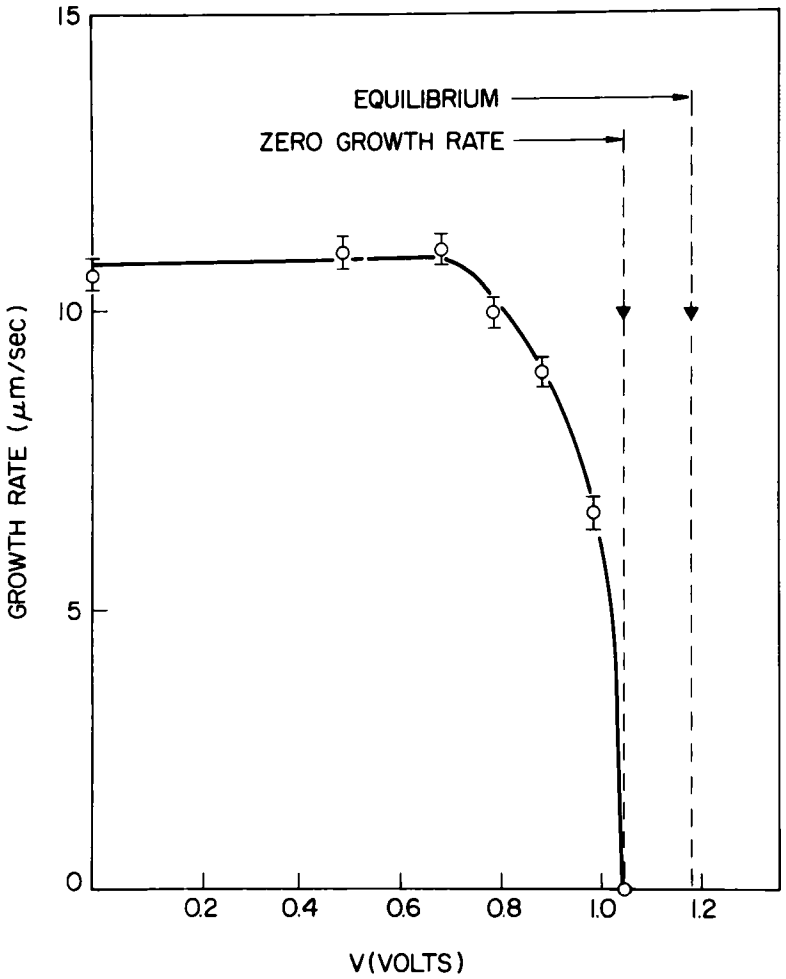

FIGURE 6 UP-DOWN domain wall growth rate in the $\beta = -90°$ direction at t/P = 0.80.

of the voltage, but above approximately 0.70 volts the rate begins to decrease as equilibrium is approached.

It is difficult to ascertain to what extent the shapes described so far are determined by equilibrium or kinetic consideration, i.e., by the anisotropy of the surface tension or the anisotropy of the growth rate. In order to decide between these two mechanisms, we need to adjust some parameter so that the domains can be studied while no growth occurs. The only convenient adjustable parameter is the voltage and that clearly is inadequate for DOWN growing in UP because, as we have seen, the field destroys the anisotropy. We can, however, investigate this question by looking at the growth of the UP state from the DOWN state at voltages above the UP-DOWN equilibrium voltage.

In Figure 7(a) we show a photograph of the UP state growing from the DOWN state at a t/P of approximately 0.98 and a voltage of 1.60 volts. Here, the domains grow as nearly symmetrical ellipses; although, only one end displays a true cusp. Once the domain has grown, we can reduce the voltage so that the growth stops. This is actually a condition of unstable equilibrium rather than a true minimal equilibrium condition. The photo in Figure 7(b) represents the domain two minutes after the voltage has been reduced to 1.50 volts. Notice that, while the shapes are similar, the lower end of the "equilibrated" domain has rounded out appreciably. This indicates that at least some difference exists between the kinetically determined domains and those at equilibrium. It is also of interest that the direction of the apex points in a direction 180° to that observed in the case where the DOWN domains grow from the UP state at lower t/P and with no field. That this is truly the equilibrium shape was confirmed by observing that the same shape was observed when a domain of "square-ish" shape was allowed to equilibrate at 1.5 volts. The square domain of UP was obtained by allowing the DOWN state to grow in from the region exterior to a square pixel in the UP state, initially leaving a square domain of UP with rounded corners in the center of the pixel. This square shape gradually readjusted to one similar to that shown in Figure 7(b).

State Separated by Disclinations

There are other configurations which are possible to achieve in the bistable cell such as the 1/2 TURN state.[9] This state is separated from both the UP and DOWN states by a disclination rather than a wall. It is difficult to obtain any regular domain pattern involving this 1/2

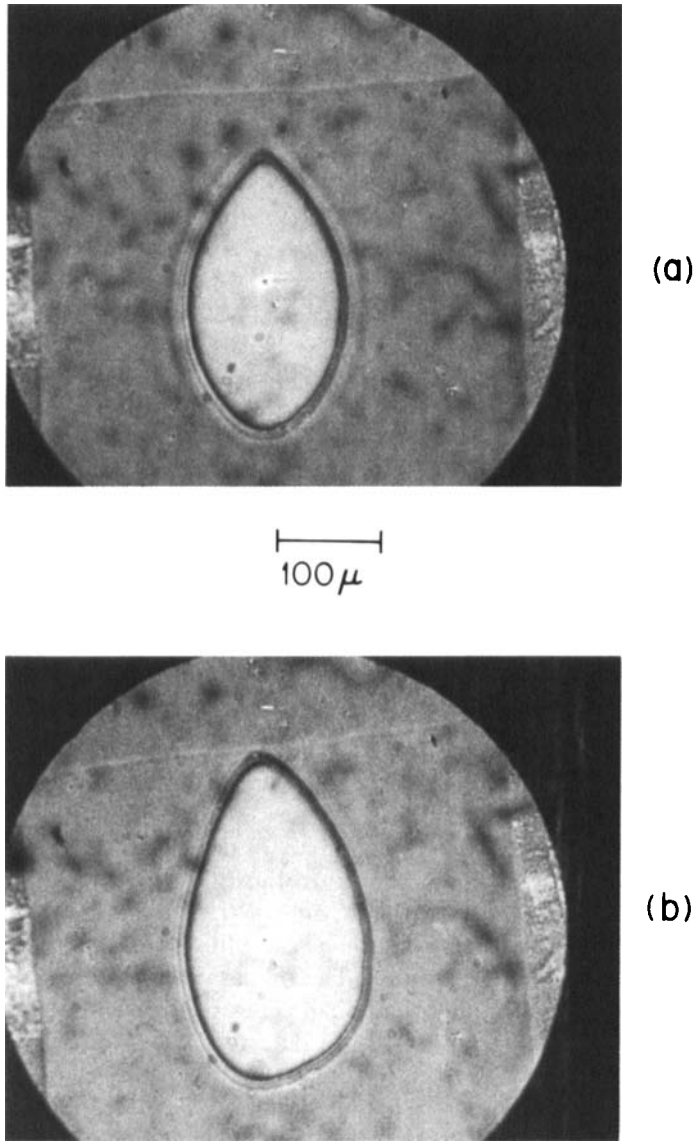

FIGURE 7 Domains of UP state (a) growing in the DOWN state at 1.60 volts, and (b) equilibrated with DOWN by lowering the voltage to 1.5 volts. The lower photomicrograph was taken two minutes after lowering the voltage. Orientation in these photographs was the same as that in Figure 4.

TURN state because the growing disclination is easily pinned by small surface imperfections.

In our cell the 1/2 TURN state is the stable state at zero field in a range of t/P that begins below approximately 0.82. Within this range, the cell may be prepared in this state by turning the voltage off and allowing the exterior 1/2 TURN region to grow into the electrode area. After the active area has become completely converted to the 1/2 TURN state, the field was reapplied and the UP state was observed to grow in the 1/2 TURN region. The growth of the UP state from the 1/2 TURN state results in very irregular domains with little reproducible nature in their patterns. However, when the domain growth is halted by lowering the voltage to its equilibrium value (approximately 1.10 volts for t/P = 0.75), the domains often develop wide angle kinks. The shape and the direction of the kink is the same as that of the apex in the DOWN domains which grew in the UP state. The angle is large and approximately equal to 130°. That the kink is an anisotrophy, and not a pinning site, was verified by observing that the position of the kink moves along with the growing or retarding boundary as the voltage is changed.

V. CONCLUSIONS

We conclude that the anisotropy observed in the growth of unstable domains in the bistable cholesteric twist cell demonstrate many interesting features of the classical theory of nucleation and growth. Because it is possible to calculate many of the thermodynamic properties of liquid crystal configurations, the BCTC provides a unique system in which to study these theories. We have made some comparisons between the observed shapes and those calculated from the anisotropic surface tension data. The shapes observed show some of the features of the equilibrium shape, but differences suggest that the shapes of growing domains are determined by the anisotropies in growth rates as well as anisotropies in wall tension. A more complete picture would be provided if calculations were available at conditions where the experimental anisotropic shapes are observed, and, in particular, if calculations were available which included the effect of the holding field. It would also be useful if calculations could be performed on the anisotropy of the wall growth rates.

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