Critical Pitch in Thin Cholesteric Films with Homeotropic Boundaries

Fred Fischer

Physikalisches Institut der Westf. Wilhelms-Universität Münster

Calculations of the planar cholesteric texture with homeotropic boundary conditions are presented. At a constant film thickness there is a critical twist t_{0c} below which the planar texture has transformed into a homeotropic one. The additional influence of an external field is discussed for positive and negative anisotropy and with field orientations parallel or normal to the film plane. A general solution of the director field has been found for a normal orientation of the field. A properly adjusted twist t_0 obtained by dilution of an optically active material in a nematic matrix opens a possibility to reduce the critical voltage in technical devices.

§ 1. Introduction

The unstrained cholesteric liquid crystal is known to have a uniform helical structure. The director normal to the helical axis is wound around it with the material immanent twist $t_0 = 2\pi/P$, where P is the pitch. External homogeneous magnetic or electric fields parallel or normal to the helical axis can generate various transitions [1]. They have been discussed for thick layers. In the case of a thin layer and by adding special boundary conditions the critical equations have to be modified.

The influence of normal homeotropic boundary conditions on a fingerprint texture in the absence of external fields has been studied experimentally by Brehm, Finkelmann and Stegemeyer [2]. They have found that with decreasing thickness of the film there is a transition of the fingerprint texture into the homeotropic texture known from nematics.

Cladis and Kleman [3] have studied the fingerprint texture and could give approximate solutions for the director field also in the case of homeotropic boundary condition. They conclude that the fingerprint texture is connected with disclinations in the plane of the sample. So the formation of the fingerprint texture out of a planar texture requires some kind of nucleation process, which will need time to develop.

One may expect that the homeotropic texture observed in thin layers of small twist cholesterics, as observed by Brehm et al. [2] should be stabilized to a higher thickness by a field normal to the layer in case of positive anisotropy. Now by switching off

the field there could be some chance that before the fingerprint texture can develop the homeotropic layer will be deformed into a planar texture resp. Grandjean texture. Such a case, where the director $\boldsymbol{n}$ is only a function of z (the direction normal to the layer), hereby simultaneously conserving the homeotropic boundaris, shall be discussed here.

Let us start with a homeotropic nematic layer of thickness d. In this case we have a twist $t_0 = 0$. One might increase t_0 contineously, for instance by the diffusion of chiral molecules into the layer. The homeotropic texture will stay stable until a critical twist t_{0c} is reached where the transformation into the planar texture takes place. Because of the homeotropic boundaries there arises no problem of hysteresis contrary to the case of parallel boundaries [4].

This critical twist t_{0c} can also be influenced by external fields, normal or parallel to the layer. Other directions of the field shall be excluded because they would violate the conditions for obtaining a critical twist.

In Chapt. 2 we present the critical equation and the solution for small amplitudes in n_x and n_y (linear approximation) in presence of a normal or parallel external field. In Chapt. 3 we derive the general solution for any amplitude in n_x and n_y in presence of a field normal to the layer. In Chapt. 4 the results shall be discussed.

§ 2. Approximation for Small $\boldsymbol{n}_x$ and $\boldsymbol{n}_y$

The homeotropic boundary conditions require $n_x = n_y = 0$ at the plane boundaries $z = \pm d/2$. The equilibrium condition is $\boldsymbol{\Gamma} = \boldsymbol{n} \times \boldsymbol{h} = 0$. The molecular field $\boldsymbol{h}$ contains contributions of the elastic splay, twist and bend and of the external field. In the

twist term we have to use $(A + t_0)$ instead of $A = \boldsymbol{n}(\nabla \times \boldsymbol{n})$. By only leaving terms linear in n_x, n_y or the z derivatives of n_x, n_y one gets a system of two linear homogeneous differential equations for n_x and n_y.

a) Field Parallel to the Layer

Without restrictions of the generality all equations are formulated for a magnetic field $\boldsymbol{H} = (H, 0, 0)$. It can easily be replaced or extended by an electric field.

$$\Gamma_x = 2 K_2 t_0 n_x' - K_3 n_y'' = 0 , \qquad (1)$$
$$\Gamma_y = 2 K_2 t_0 n_y' + K_3 n_x'' + \mu_0 \chi_a H^2 n_x = 0 .$$

We are looking for a set of critical values H_c and t_{0c}, which give nontrivial solutions for Equation (1).

We use the abbreviations

$$u = \frac{\mu_0 \chi_a}{K_3} \left(\frac{H d}{2 \pi} \right)^2 , \qquad (2)$$

$$v = (\varkappa_2 t_0 d/\pi)^2 ; \quad \text{where} \quad \varkappa_2 = K_2/K_3 \qquad (3)$$

and

$$k = (2 \pi/d)(u + v) \qquad (4)$$

χ_a (or ε_a in the electric case) can be positive or negative. Therefore we distinguish two cases:

Case $u \leqq 0$: Here the critical equation is

$$u + v = 1 . \qquad (5)$$

The solution for small n_x, n_y is

$$n_x = a \sin k z ,$$
$$n_y = - a \sqrt{v} (\cos k z + 1) \qquad (6)$$

where we have to use a k value for which Eq. (5) is fulfilled, which means $k = 2 \pi/d$.

Case $u \geqq 0$: Here the critical equation is

$$\frac{u}{v} + \frac{\operatorname{tg} \pi(u + v)}{\pi(u + v)} = 0 . \qquad (7)$$

The solution for small n_x, n_y is

$$n_x = a \left[\cos k z - \cos k(d/2) \right] ,$$
$$n_y = a \sqrt{v} \left[\sin k z - (2 z/d) \sin k(d/2) \right] \qquad (8)$$

where Eq. (7) has to be fulfilled for k.

The critical equation of case $u \leqq 0$ could also be extended to $u > 0$. But the solution is no more the stable one and the critical parameters would be larger than those in Equation (7). In Fig. 1 you see a graph of the critical parameters derived from Eqs. (5) and (7) (full curve).
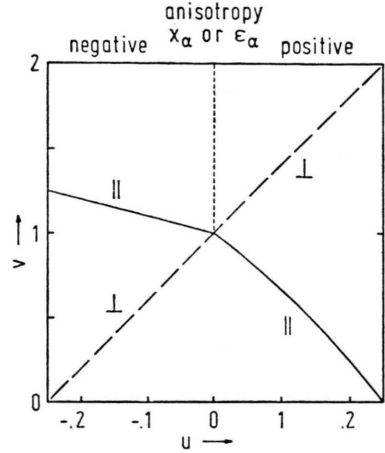

Fig. 1. Graph of the critical equations v ($\sim t_{0c}^2$) versus u ($\sim H_c^2$) for negative and positive anisotropy. *Full curve:* field parallel to the layer. *Dashed curve:* field normal to the layer. The vertical dotted line separates the two regimes of different conformation in case of a field parallel to the layer.

b) Field Normal to the Layer

With the magnetic field $\boldsymbol{H} = (0, 0, H)$ the differential equations are

$$\Gamma_x = 2 K_2 t_0 n_x' - K_3 n_y'' + \mu_0 \chi_a H^2 n_y = 0 ,$$
$$\Gamma_y = 2 K_2 t_0 n_y' + K_3 n_x'' - \mu_0 \chi_a H^2 n_x = 0 . \qquad (9)$$

A solution which satisfies the boundary conditions is

$$n_x = a \cos \frac{\pi z}{d} \cos \varkappa_2 t_0 z ,$$
$$n_y = a \cos \frac{\pi z}{d} \sin \varkappa_2 t_0 z . \qquad (10)$$

In order to fulfill the differential equations simultaneously we obtain the critical equation

$$v - 4 u = 1 . \qquad (11)$$

In Fig. 1 the graph for the normal field yields a straight line (dashed curve), which holds in like manner for positive and negative anisotropy.

§ 3. General Solution

The solutions for n_x, n_y given in § 2 only hold for the critical parameters that means for an infinitesimally small amplitude a. A general solution which also holds beyond the critical u-v graph can be obtained for the case of a field normal to the layer. This time we prefer to introduce polar co-

ordinates

$$n_x = \sin \vartheta \cos \varphi ,$$
$$n_y = \sin \vartheta \sin \varphi , \qquad (12)$$
$$n_z = \cos \vartheta ,$$

and to be short we define

$$f(\vartheta) = 1 + (\varkappa_1 - 1) \sin^2 \vartheta ; \quad \varkappa_1 = K_1/K_3 ,$$
$$g(\vartheta) = 1 + (\varkappa_2 - 1) \sin^2 \vartheta ; \quad \varkappa_2 = K_2/K_3 ,$$
$$M = \mu_0 \chi_a H^2/K_3 . \qquad (13)$$

The equilibrium condition $\boldsymbol{\varGamma} = \boldsymbol{n} \times \boldsymbol{h} = 0$ yields two independent differential equations. The first one we obtain from $\varGamma_z = 0$:

$$\varGamma_z = K_3 \frac{\mathrm{d}}{\mathrm{d}z} \{ \sin^2 \vartheta [g(\vartheta) \varphi' - \varkappa_2 t_0] \} = 0 . \quad (14)$$

The second one we obtain from a suitable combination of $\varGamma_x = 0$ and $\varGamma_y = 0$, namely

$$\varGamma_y n_x - \varGamma_x n_y \qquad (15)$$
$$= K_3 \sin \vartheta \left\{ f(\vartheta) \vartheta'' + \frac{1}{2} \frac{\mathrm{d}f(\vartheta)}{\mathrm{d}\vartheta} \vartheta'^2 + \frac{1}{2} \sin^2 \vartheta \right.$$
$$\left. \times [\varphi'^2 + 2 \varphi' (\varkappa_2 t_0 - g(\vartheta) \varphi') - M] \right\} = 0 .$$

Because of $\boldsymbol{\varGamma} \cdot \boldsymbol{n} = 0$ the other feasible combination $\varGamma_x n_x + \varGamma_y n_y = 0$ is equivalent to $\varGamma_z n_z = 0$. Here $n_z \equiv 0$ can be excluded with regard to the boundary conditions, and $\varGamma_z = 0$ is already used in (14). When we integrate (14) and use one of the boundary conditions

$$\vartheta = 0 \quad \text{at} \quad z = \pm d/2 \qquad (16)$$

we obtain

$$\sin^2 \vartheta [g(\vartheta) \varphi' - \varkappa_2 t_0] = 0 . \qquad (17)$$

Either $\sin^2 \vartheta \equiv 0$, which however means homeotropic texture, or

$$g(\vartheta) \varphi' = \varkappa_2 t_0 . \qquad (18)$$

We see that φ' is only a function of ϑ. For $\vartheta = 0$ we have $\varphi' = \varkappa_2 t_0$, for $\vartheta = \pi/2$ we have $\varphi' = t_0$ which has been known before.

Using (18) we can replace φ' in (15) and obtain

$$\frac{\mathrm{d}}{\mathrm{d}z} [f(\vartheta) \vartheta'^2] + [\varkappa_2^2 t_0^2/g(\vartheta)^2 - M] \frac{\mathrm{d}}{\mathrm{d}z} \sin^2 \vartheta = 0 . \qquad (19)$$

When we set $t_0 = 0$ this equation reduces to the case of pure nematics as already known. Now we integrate (19) choosing $z = 0$ as the lower limit with $\vartheta(0) = \vartheta_2$ and for symmetry reasons $\vartheta(0)' = 0$.

We expect $\vartheta(z)$ to decrease from ϑ_2 to zero, when z runs from 0 to $d/2$. The integral is elementary soluble and we get

$$\vartheta'^2 = [\varkappa_2^2 t_0^2 g(\vartheta_2) - M g(\vartheta)] \cdot \frac{\sin^2 \vartheta_2 - \sin^2 \vartheta}{f(\vartheta) g(\vartheta)} . \qquad (20)$$

Integrating (20) we end up with

$$z(\vartheta) = \pm \frac{d}{2} \left[1 - \frac{I_{\vartheta_2}(\vartheta, M)}{I_{\vartheta_2}(\vartheta_2, M)} \right] ; \quad \text{for} \quad z \gtrless 0 \quad (21)$$

where

$$I_{\vartheta_2}(\vartheta, M) = \int_0^\vartheta \left[\frac{f(\chi) g(\chi)}{\sin^2 \vartheta_2 - \sin^2 \chi} \right]^{1/2} \qquad (22)$$
$$\cdot \left[1 - \frac{g(\vartheta_2)}{\varkappa_2^2 t_0^2} M g(\chi) \right]^{-1/2} \mathrm{d}\chi .$$

The magnitude of ϑ_2 is implicitly determined by

$$t_0(\vartheta_2) = \frac{2}{d} \frac{\sqrt{g(\vartheta_2)}}{\varkappa_2} I_{\vartheta_2}(\vartheta_2, M) . \qquad (23)$$

The critical Eq. (11) derived in § 2.b can also be obtained from (23) by going to the limit of t_0 when ϑ_2 approaches zero.

In order to further simplify this result let us consider the one constant approximation ($f = g = \varkappa_2 = 1$). From Eq. (18) we obtain

$$\varphi = t_0 z . \qquad (24)$$

And Eq. (21) yields an expression which contains elliptical integrals. For $z > 0$ we have

$$(1 - 2 z/d) = F(\theta, \sin \vartheta_2)/K(\sin \vartheta_2) \qquad (25)$$

where

$$\sin \theta = \sin \vartheta/\sin \vartheta_2 . \qquad (26)$$

K and F are the complete elliptic and the Legendre normal integral of the first kind [5].
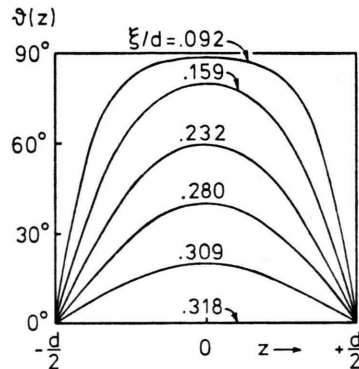

Fig. 2. Graph of ϑ as a function of z in the one constant approximation. Parameter is ξ/d, where $\xi^{-1} = (t_0^2 - M)^{1/2}$.

The external field only contributes via Eq. (23) which becomes

$$2\,\xi/d = 1/K(\sin\vartheta_2)\,. \tag{27}$$

We have introduced here a generalized coherence length

$$\xi = 1/\sqrt{t_0{}^2 - M}\,. \tag{28}$$

In Fig. 2 you find a graph of $\vartheta(z)$ with ξ/d as a parameter. As long as $\xi/d \geqq 0.3183$ the whole film stays in the homeotropic state, which means $\vartheta \equiv 0$.
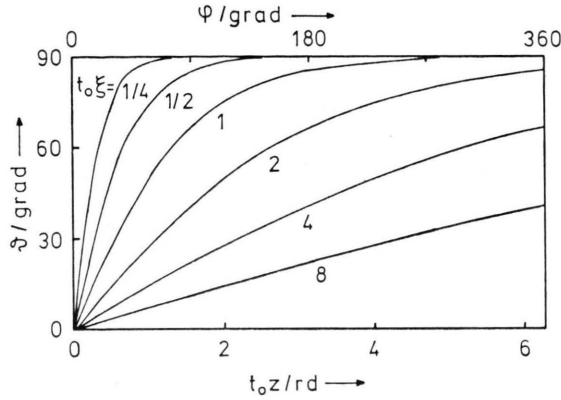

Fig. 3. Graph of ϑ as a function of $t_0 z = \varphi$. One constant approximation for the halfspace. Parameter is $t_0 \xi$, where $\xi^{-1} = (t_0{}^2 - M)^{1/2}$.

With decreasing ξ then the maximum deflection ϑ_2 increases and in the limit $\xi \to 0$ it approaches the value $\pi/2$. $\vartheta(z)$ varies from 0 to $\pi/2$ within a thin surface layer of thickness ξ.

In order to illuminate the situation near the boundary more closely we look for the solution in the case of a halfspace ($\vartheta = 0$ for $z = 0$ and $\vartheta' = 0$, $\vartheta = \pi/2$ for $z = \infty$). From Eq. (25) we obtain

$$\vartheta(z) = \operatorname{arc\,sin\,Tg}(z/\xi) \tag{29}$$

and Eq. (24) remains unchanged.

In Fig. 3 we have plotted ϑ as a function of $t_0 z = \varphi$. The parameter $t_0 \xi = 1$ belongs to the field free case. Values $t_0 \xi < 1$ are obtained with a negative anisotropy, whereas values $t_0 \xi > 1$ are obtained with a positive anisotropy of the field. For $t_0 \xi = \infty$ the helix becomes completely unwound. That means another critical field

$$H_c = t_0 (K/\mu_0 \chi_a)^{1/2} \tag{30}$$

which is nothing else as the critical Eq. (11) extrapolated to $d = \infty$.

§ 4. Discussion

To begin with let us elucidate the director field $\boldsymbol{n}(z)$ along the critical u-v curve more closely. In the case of an external field $\boldsymbol{H} = (H, 0, 0)$ parallel to the layer, $\boldsymbol{n}$ is analytically described by Eq. (6) or Equation (8). In Figs. 4 a, b you see a plot of the orthographic projection of the director $\boldsymbol{n}$ for $-d/2 < z < +d/2$. The critical v is chosen as a parameter. Owing to the homeotropic boundaries each curve begins and ends at the origin.

Figure 4 a holds for negative anisotropy ($u \leqq 0$). Here the external field stabilizes the homeotropic texture. Decreasing the field strength at the critical point the director prefers a deviation normal to the external field direction. If we define a critical angle $\Delta\varphi_c = \varphi_c(d/2) - \varphi_c(-d/2)$, where φ has the same meaning as in Eq. (12) and the index c holds for the critical curve, we find $\Delta\varphi_c = \pi$ for all values of v.
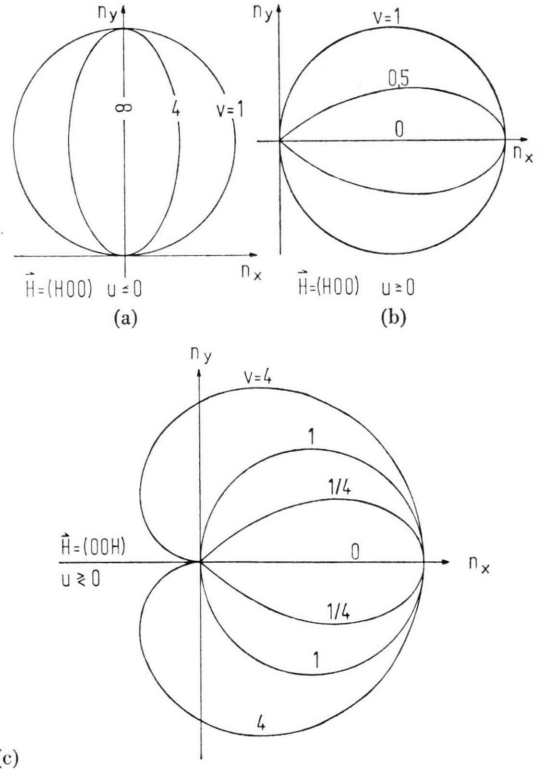

Fig. 4. Orthographic projection of the director $\boldsymbol{n}$ into the x-y plane at the critical u-v curve. One constant approximation. a) $\boldsymbol{H} = (H, 0, 0)$; negative anisotropy. b) $\boldsymbol{H} = (H, 0, 0)$; positive anisotropy. c) $\boldsymbol{H} = (0, 0, H)$ normal to the film; positive and negative anisotropy. Parameter is the critical v.

Figure 4 b holds for positive anisotropy ($u \geqq 0$). Here the external field helps to destroy the homeotropic conformation. Increasing the field strength at the critical point the director prefers to turn parallel to the external field direction. Here one finds $\Delta \varphi_c = \pi v$. For $v = 0$ we have the well known Fredericks transition.

For $u < 0$ as well as for $u > 0$ there are two equivalent conformations above the critical u-v curve. They transform into one another by a π rotation around the z axis. Let us define * with $\boldsymbol{c}$ in the x-y plane the direction of maximum deflection of the director in the middle of the layer ($z = 0$). Then in case of $u < 0$ we either have $\boldsymbol{c} = \boldsymbol{y}$ or $\boldsymbol{c} = -\boldsymbol{y}$. In case of $u > 0$, however, we either have $\boldsymbol{c} = \boldsymbol{x}$ or $\boldsymbol{c} = -\boldsymbol{x}$. In both cases this allows the formation of walls normal to the layer with a completely homeotropic orientation in their interior.

At the limit $u = 0$ in the non homeotropic regime ($v \geqq 1$), which you find as a dotted line in Fig. 1, $\boldsymbol{c}$ can obtain any direction within the x-y plane. This allows the formation of umbilics of the strength ± 1 already without an external field. By crossing the limit $\boldsymbol{c}$ has to be turned by $\pm \pi/2$. Such a crossing should be accomplished by combining a magnetic and an electric field ($\varepsilon_a < 0$), both parallel to $\boldsymbol{x}$. However walls of higher order cannot be expected becauses of the homeotropic boundaries.

In the case of an external field $\boldsymbol{H} = (0, 0, H)$ normal to the layer by using Eq. (10) we obtain the graph shown in Fig. 4 c as the orthographic projections of the director $\boldsymbol{n}$. There is no preferential orientation anymore in the x-y plane. Any rotation of the curves around the z axis is admitted. This degeneration above the critical u-v curve (Fig. 1) provides the conditions under which umbilics can be formed. This simply means a steady extension from the pure nematic ($v = 0$) into the cholesteric domain, worth mentioning the existence of umbilics also at positive anisotropy. The intersection of the critical u-v curve with the abscissa $v = 0$ (Fig. 1) belongs to the well known Fredericks transition.

The critical angle is found to be $\Delta \varphi_c = \pi \sqrt{v}$ $= \varkappa_2 \cdot t_{0c} \, d$. That means it can be very large. The reason is seen by consulting Equation (18). By applying an external field normal to the layer the unperturbed slope of the helix can at most be extended by a factor of K_3/K_2. On the contrary a

* $\boldsymbol{c}, \boldsymbol{n}, \boldsymbol{y}, \boldsymbol{x}$, are unit vectors.

sufficient strong field parallel to the layer unwinds the helix completely.

By moving off the critical u-v curve into the planar regime at constant v (Fig. 1) we approach a saturation in $\Delta \varphi$, namely $\Delta \varphi_{max} = t_{0c} \, d$. Consequently in case of a normal field we have

$$\varkappa_2 = \Delta \varphi_c / \Delta \varphi_{max} \, . \qquad (31)$$

The experimental determination of $\Delta \varphi_c$ and $\Delta \varphi_{max}$ probably will cause certain difficulties. Here also a detailed analysis of the optical behaviour of such a layer at normal incidence has to be performed. In a qualitative way we expect circular modes for visible light in the immediate neighbourhood of the critical u-v curve because of the very small optical anisotropy which is developing from zero. With increasing ϑ_2 at $z = 0$ the circular modes will turn more and more into wave guide modes leaving the circular nature only near the homeotropic boundaries.

Of a certain interest concering the stability of a planar conformation with homeotropic boundaries is the elastic energy stored in such a film. In the one constant approximation one can find an exact solution for the halfspace. The stored energy per surface area comes out to be

$$f_d = K \left| t_0 \right| \, . \qquad (32)$$

Assuming a film of thickness d the homeotropic conformation yields

$$f_d = \tfrac{1}{2} K \, t_0^2 \, d \, . \qquad (32)$$

At the critical point $\left| t_0 \right| d = \pi$ we have $f_d = (\pi/2) K \left| t_0 \right|$. Here the homeotropic conformation becomes unstable. With increasing $\left| t_0 \right| d$ the stored energy density approaches the limit $2 K \left| t_0 \right|$.

The transitions within the cholesteric phase treated so far in the literature [1] are always restricted to the case $\left| t_0 \right| d \gg 2 \pi$. In this paper yet the range $0 \leqq \left| t_0 \right| d \leqq 2 \pi$ is of special interest. Because of the constraint, introduced into our calculations, that the director field only depends on z, the results might only be good for small values of $\left| t_0 \right| d$.

Let us compare the statements given in this paper with the experimental results obtained by Brehm et al. [2] on MBBA with optically active additives. They have found that the fingerprint texture already dominates the homeotropic conformation at $\left| t_0 \right| d$ values between 4.8 and 5.5. The transformation of the homeotropic into the planar texture however should happen at $\left| t_0 \right| d = \pi K_3/K_2$. Using values out

of the literature [6] this gives about $|t_0| d = 8 \pm 1$. So without external fields the homeotropic planar transition should not be observable, because the fingerprint texture will appear before. In our laboratory Wahl [7] is studying the influence of optically active additives upon the critical voltage. These measurements however cover the whole critical u-v curve form $v = 0$ to $v = 1$.

Finally let me mention possible technical applications. The well defined addition of small amounts of an optically active substance to a nematic liquid crystal with negative dielectric anisotropy will allow to reduce the critical voltage of the Fredericks transition in a specified way. Also nematics with positive dielectric anisotropy could be used above $v = 1$. Here the homeotropic deformation would appear when the voltage is on. In addition we may expect the optical rotary power of the film to be reversibly controllable by an overcritical ($\varepsilon_a < 0$) or subcritical ($\varepsilon_a > 0$) voltage.

[1] P. G. de Gennes, Solid State Comm. 6, 163 [1968]; R. B. Meyer, Appl. Phys. Lett. 12, 281 [1968]; F. M. Leslie, Mol. Cryst. Liq. Cryst. 12, 57 [1970]; W. Welfrich, Appl. Phys. Letters 17, 531 [1970]; W. Helfrich, J. Chem. Phys. 55, 839 [1971]; J. P. Hurault, J. Chem. Phys. 59, 2068 [1973].
[2] M. Brehm, H. Finkelmann, and H. Stegemeyer, Berichte der Bunsengesellsch. 78, 883 [1974].
[3] P. E. Cladis and M. Kléman, Mol. Cryst. Liq. Cryst. 16, 1 [1972].
[4] G. Durand, L. Leger, F. Rondelez, and M. Veyssie, Phys. Rev. Letters 22, 227 [1969].
[5] Jahnke-Emde-Lösch, Tables of Higher Functions, Stuttgart 1966.
[6] P. G. de Gennes, The Physics of Liquid Crystals, Oxford 1974, p. 66.
[7] J. Wahl, to be published.