INVESTIGATIONS ON SOME FIELD INDUCED INSTABILITIES IN NEMATIC LIQUID CRYSTALS

Thesis submitted to the

UNIVERSITY OF MYSORE

for the *degree of*

Doctor of Philosophy

by

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MARCH 1989

DECLARATION

I hereby declare that this thesis was composed by me independently and that it has not formed the basis for the award of any Degree, Diploma, Associateship, Fellowship or other similar title.

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CERTIFICATE

I certify that this thesis has been composed by Mr. V. A. Raghunathan based on investigations carried out by him at the Liquid Crystal Laboratory, Raman Research Institute, Bangalore, under my supervision. The subject matter of this thesis has not previously formed the basis of the award of any Degree, Diploma, Associateship, Fellowship or other similar title.

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ACKNOWLEDGEMENTS

It is with great pleasure that I acknowledge all the help received from Prof. N. V. Madhusudana. I am greatly indebted to him for his invaluable guidance and constructive criticisms.

I am very grateful to Prof. S. Chandrasekhar for his advice and constant encouragement.

I am grateful to Dr. G. S. Ranganath for the numerous stimulating discussions I have had with him.

I wish to thank Dr. 5. K. Sadashiva, Dr. B. S. Srikanta and Dr. U.D. Kini for many useful discussions. I thank Mr. S. Raghavachar, Mr. A. Ratnakar, Mr. G. Manjunath, Mr. Hanumappa and Mr. C. Ramachandra Rao for their timely assistance and co-operation. I acknowledge the considerable assistance received from Mr. K. Sukumarsn, Mr. B.V. Nataraj, Mrs. Jayanthi Ramachandran and Mr. R. Nandakumar in carrying out the computations. I am grateful to Mr. H. Subramonyam, Mr. K. Subramanya, Mr. A. Dhason, Mr. V. Nagaraj and Mr. M. Mani for technical assistance. Finally I thank all my friends in the institute for their help and encouragement.

V.A. RAGHUNATHAN

CONTENTS

PREFACE

This thesis describes studies on some static and hydrodynamic instabilities induced in nematic liquid crystals by external electric and magnetic fields. A major part of the work presented deals with the influence of flexoelectricity on electrohydrodynamic instabilities.

Nematic liquid crystals exhibit convective instabilities under the action of an external electric field. These electrohydrodynamic (EHD) instabilities have been the subject of many experimental and theoretical studies [1,2]. The first theoretical analysis of the problem for DC excitation was developed by Helfrich [3], based on a suggestion by Carr [43 that the anisotropy of the electrical conductivity can lead to the formation of space charges in a nematic in the presence of suitable director deformations. This model was later extended to the case of AC excitation by Dubois-Violette et al. [5], who showed that the Carr - Helfrich mechanism leads to two types of EHD instabilities in nematics, depending on the frequency of the applied field. These are called the conduction and dielectric regimes and occur respectively for frequencies less than and greater than a cut-off frequency. These models show that the EHD instabilities are influenced greatly by many of the physical properties of nematics, like elasticity, the dielectric properties, viscosity and electrical conductivity. In this thesis it is shown that these instabilities are also influenced by the flexoelectric property [6] of nematics.

Chapter 1 gives a general introduction to liquid crystals with special emphasis on the nematic phase. The various physical properties of this phase, which are relevant to the discussion in the later chapters, are described here. The hydrodynamics of nematics is discussed in some detail, as it provides the framework for the description of the convective instabilities.

The EHD instabilities induced in a nematic by an external electric field are discussed in chapter 2. We confine our attention to instabilities exhibited by homogeneously aligned nematic layers, since only these are dealt with in the later chapters. The Carr - Helfrich mechanism, which is responsible for most of these instabilities, is also discussed in detail. Further, we describe some experimental observations which cannot be accounted for by the Orsay model [5,7]. These include the oblique roll instability observed at low frequencies in the conduction regime, in which the wavevector of the rolls makes an angle a with the direction of initial orientation of the director [8,9], the oblique rolls found in the dielectric regime [10] and the EHD instabilities found in nematics with negative conductivity anisotropy [11-13]. Some theoretical models [14], including an alternative instability mechanism [13], have been proposed to explain these observations. However, these models are not entirely satisfactory and in later chapters we show that the inclusion of the flexoelectric effect in the theory of EHD instabilities leads to a natural explanation of many of these observations.

In chapter 3 we present a one-dimensional linear analysis of the EHD instability in nematics under DC excitation, which takes into account the flexoelectric effect. Splay and bend distortions of the director give rise to a flexoelectric polarization in a nematic, given by [6]

$$\vec{P} = e_1 \hat{n} (\operatorname{div} \hat{n}) + e_3 (\operatorname{curl} \hat{n}) \times \hat{n}.$$

where e_1 and e_3 are the two flexoelectric coefficients. On the basis of the dipolar model of flexoelectricity proposed by Meyer [6], only nematics consisting of polar molecules having certain shapes **can** be expected to show the flexoelectric effect. Prost and Marcerou [15] later pointed out that flexoelectricity can also arise from the electric quadrupolar moments of the molecules. Unlike the dipoles, the quadrupoles contribute substantially to the flexoelectric effect irrespective of the molecular shape. As nematogenic molecules generally have nonzero quadrupole moments, the theory of Prost and Marcerou implies that flexoelectricity is a universal property of all nematics. Flexoelectricity influences the problem in two ways. Firstly, the flexoelectric polarization $\vec{P}$ can supplement the space charge density in the medium. Secondly, the action of the external field on $\vec{P}$ can create additional torques on the director. When the boundary conditions are neglected both these flexoelectric contributions are non-zero only if the convective rolls are oblique. This mode1 leads to the following expression for the threshold voltage of the instability

$$V_{th}^2 = M\ L\ \pi^2/[\{\epsilon_a\sigma_\perp/\sigma_c + (\alpha_2/\eta_1)\epsilon_c(\epsilon_r - \sigma_r)c^2\}(L/4\pi) + F\ s^2]$$

where $M = K_2 s^2 + K_3 c^2$, $L = K_1 s^2 + K_3 c^2$, $\epsilon_a = \epsilon_\parallel - \epsilon_\perp$,
$\sigma_a = \sigma_\parallel - \sigma_\perp$, $\epsilon_c = \epsilon_\perp + \epsilon_a c^2$, $\sigma_c = \sigma_\perp + \sigma_a c^2$, $\epsilon_r = \epsilon_a/\epsilon_c$,
$\sigma_r = \sigma_a/\sigma_c$, $\eta_1 = \frac{1}{2}[\alpha_4 + (\alpha_5 - \alpha_2)\ c^2]$,
$F = (e_1 - e_3)^2 - (e_1 + e_3)^2\ \sigma_r \alpha_2 c^4/\eta_1 + (e_1^2 - e_3^2)(\alpha_2/\eta_1 - \sigma_r)c^2$,
$c = \cos a$, $s = \sin a$, $\epsilon_\parallel$ and $\epsilon_\perp$ are the principal

dielectric constants, $\sigma_{\parallel}$ and a, the principal electrical conductivities and K_1, K_2 and K_3 the splay, twist and bend elastic constants, respectively. When a = 0, all the flexoelectric terms drop out of the problem and the above expression reduces to that given by Helfrich [3]. On the other hand, when a □ 2 all the hydrodynamic terms drop out and we get the threshold for the flexoelectric domains [16]. Fig.1 shows the variation of the critical voltage V_{th} for the onset of the instability with the angle a. It is clear from the figure that oblique rolls characterized by a non-zero value of a are favoured when the flexoelectric terms are included. We have also calculated the dependence of V_{th} and a on some of the material parameters of the medium. We have experimentally studied the EHD instability in a room temperature nematic mixture under DC excitation. The oblique rolls obtained at the threshold are shown in Fig.2. An interesting feature of this domain pattern is that the domain width is approximately twice the layer thickness. Fig.3 shows the dark bands obtained when the sample was viewed through a tilting compensator, at a voltage slightly above the threshold. It is clear from the figure that the curvature of the director field is sharper in regions corresponding to the bright lines of the domain pattern than in regions mid-way between two bright lines. Thus the

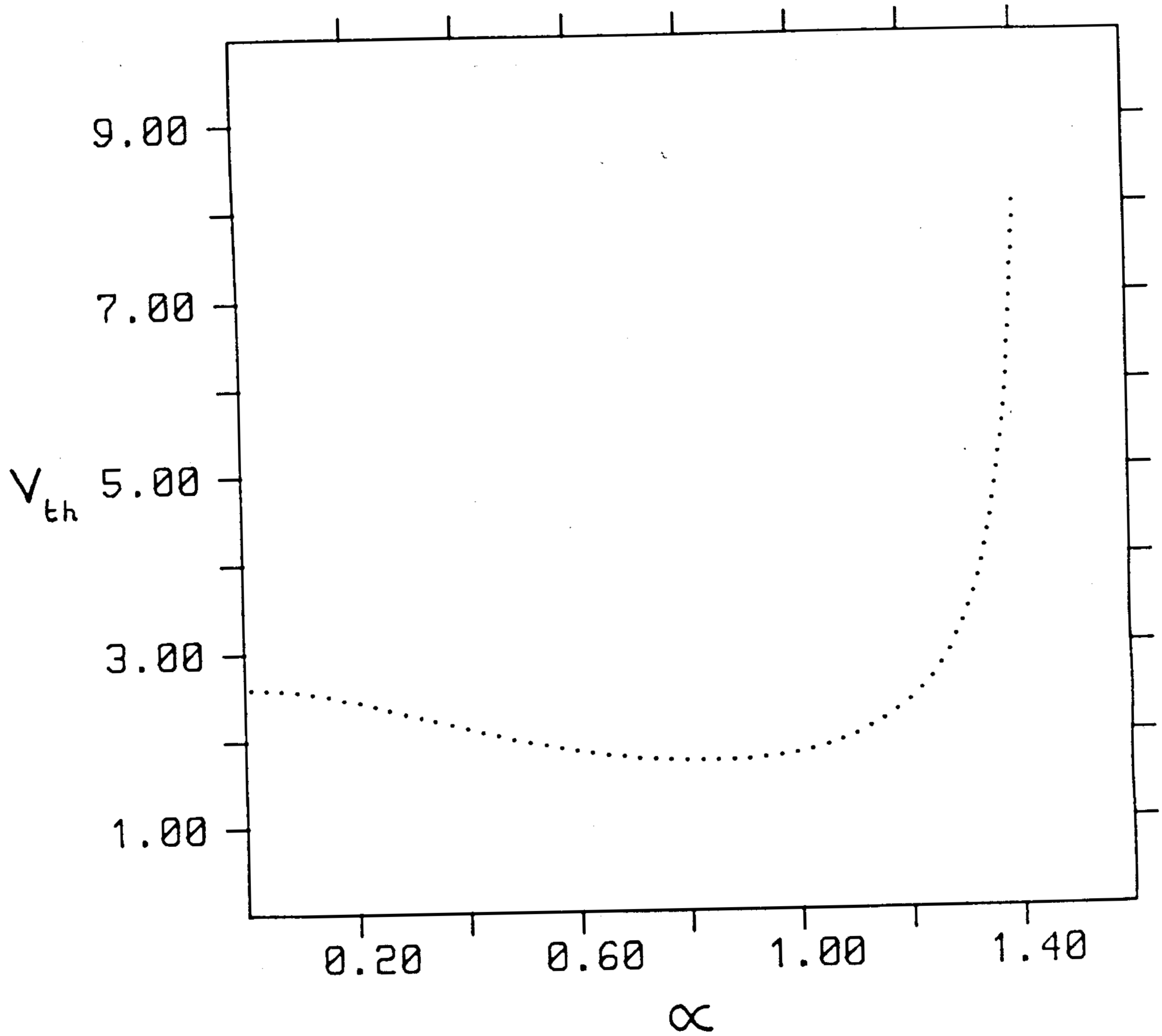

Fig.. Variation of the threshold voltage V_{th} (in volts) with the angle a (in radians) calculated for the standard MBBA values of the material parameters.

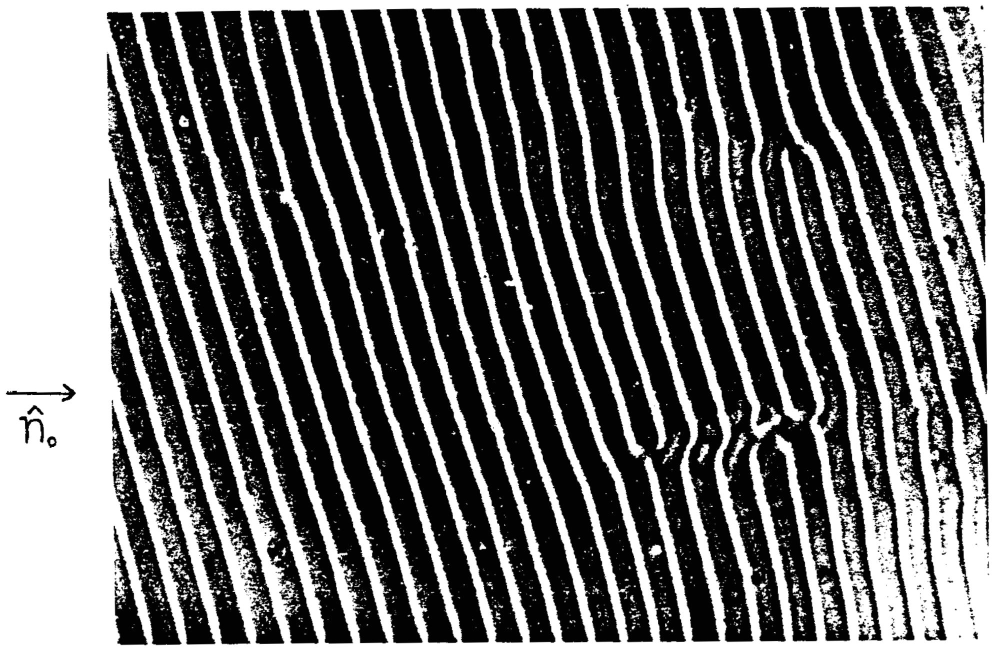

Fig.2. Photograph of the EHD pattern obtained slightly above the threshold of the DC instability in a room temperature nematic. The orientation of the undistorted director $\mathbf{n}_o$ is indicated in the figure. (Magnification: x 250).

Fig.3. The dark fringes obtained when the sample was viewed in sodium light through a tilting compensator, at a voltage slightly above the threshold.

asymmetry in the optical domain pattern is caused by non-sinusoidal director profile within the rolls. We show that such a director profile can be obtained if the lowest order non-linear term, which is flexoelectric in origin, is taken into account (Fig.4).

The one-dimensional analysis presented in chapter 3 neglects the boundary conditions at the two surfaces of the nematic layer. These boundary conditions are taken into account in the calculations of chapter 4. When the flexoelectric terms are neglected, these calculations show that oblique rolls are not favoured at the threshold of the instability, for the standard MBBA values of the material parameters. However, they can be obtained by varying suitably any one of these parameters, keeping others fixed, as found by Zimmermann and Kramer [14] by using stress free boundary conditions. On including the flexoelectric terms oblique rolls are obtained for the standard MBBA values of the material parameters. Fig.5 shows V_{th} as a function of a, obtained from the theory. The curves labelled (a) and (b) correspond to calculations without and with flexoelectricity, respectively. It is clear from the figure that flexoelectricity strongly favours the formation of oblique rolls at the threshold. The difference in the V_{th} values at

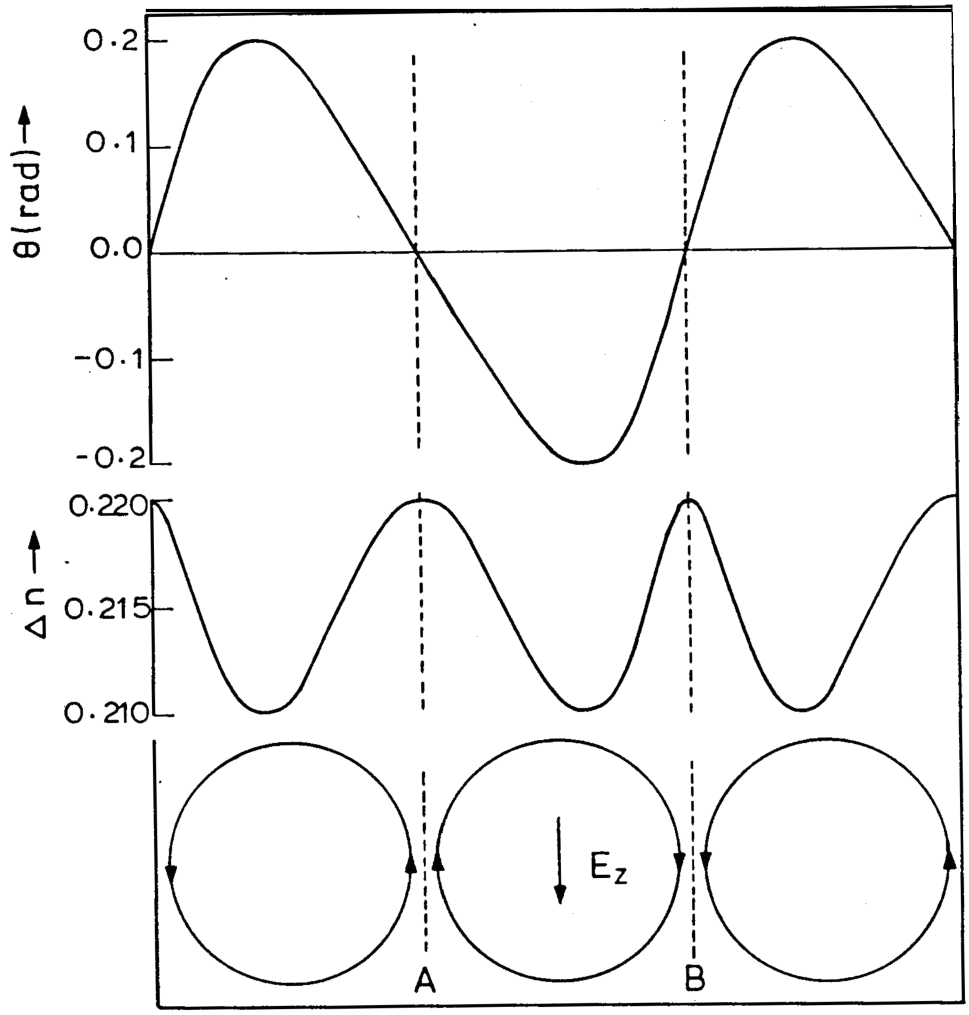

Fig.4. The non-sinusoidal director profile obtained on including the non-linear flexoelectric term (top). The resulting variation of the effective birefringence along the wavevector of the rolls (middle). The disposition of the convective rolls (bottom) agrees with the observed tracer particle motion, regions B corresponding to the bright lines of Fig.2.

$a = 0$ in the two cases arises from the additional space charge formation due to the flexoelectric polarization, which is non-zero at $a = 0$, when the boundary conditions are taken into account. Further, flexoelectricity is found to lead to an open helical flow of the fluid particles within the rolls (Fig.6). Such an helical flow has been observed in our experiments.

The one-dimensional analysis of chapter 3 is extended to the case of AC excitation in chapter 5. Following Smith et al.[7] we solve the problem for the case of square wave excitation. As in the Orsay model [5,7] we find two regimes of instability. The stability diagram obtained from the calculations, using the MBBA values of the material parameters, is shown in Fig.?. Oblique rolls are obtained upto a frequency f_o at the onset of the conduction regime and upto a frequency f_r along the restabilization branch, with $f_r > f_o$. Therefore, in the frequency range $f_o < f < f_r$, though oblique rolls are not favoured at the threshold, they can be expected to occur at higher fields. However, a non-linear analysis of the problem is required to predict the transition between the normal and oblique rolls. The above mentioned results are in agreement with the observations of Ribotta et al. [9]. The stability diagram obtained from their

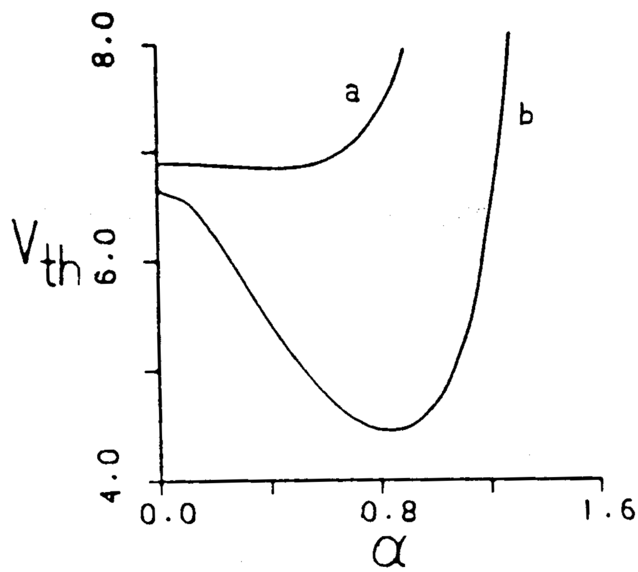

Fig.5. Variation of the threshold voltage V_{th} (in volts) with the angle a (in radians). The curves labelled a and b correspond to calculations without and with flexoelectricity, respectively.

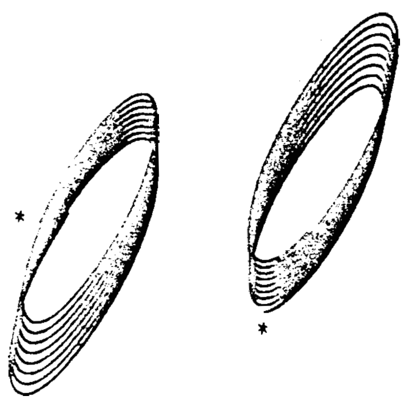

Fig.6. The helical trajectories of two fluid particles in neighbouring rolls obtained when the flexoelectric terms are included. The asterisks indicate the initial positions of the particles.

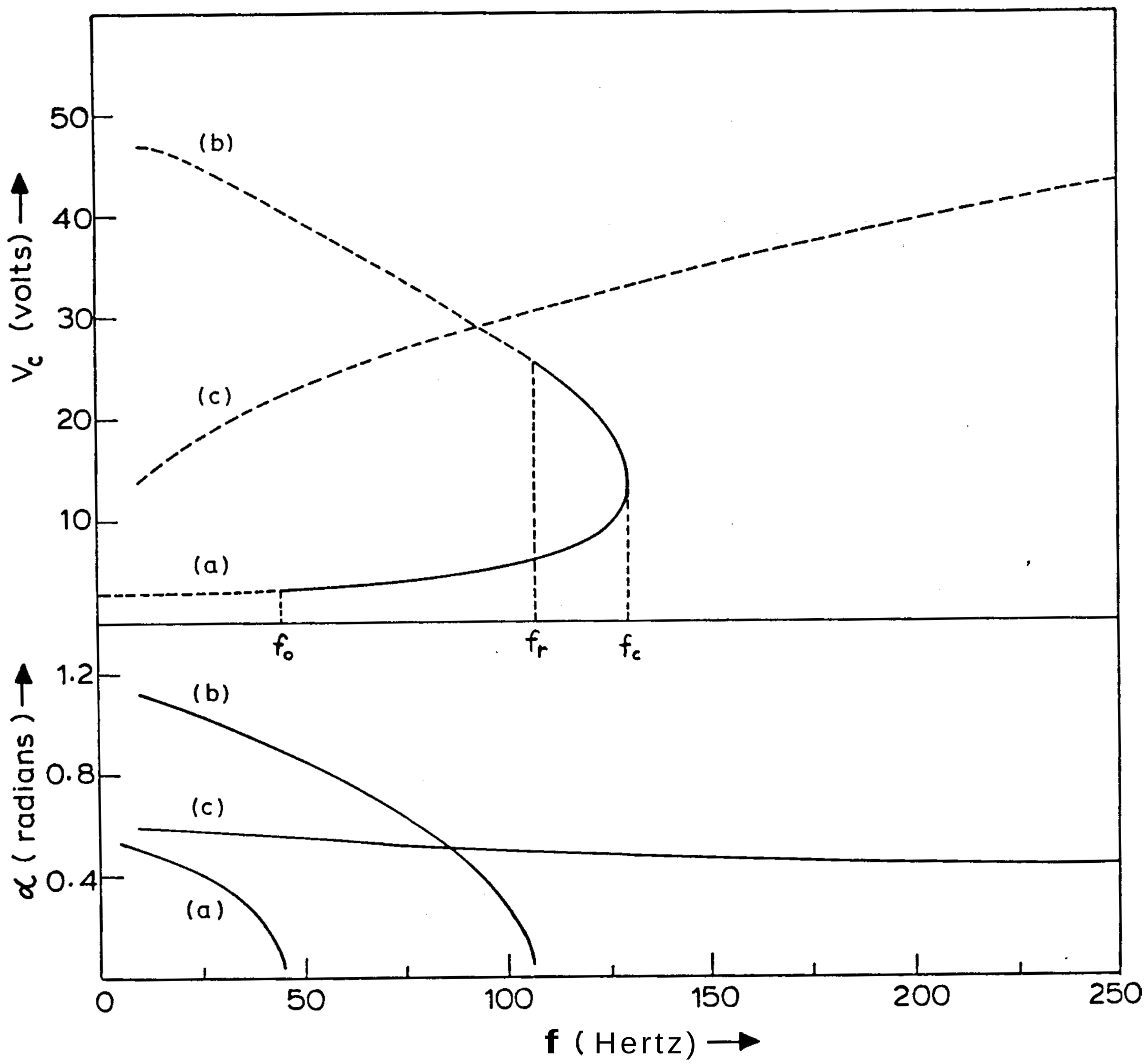

Fig.7. Upper section: Threshold voltage (curve a) and the restabilization voltage (cure b) as a function of the frequency in the conduction regime for MBBA with $\sigma_{\parallel} = 3 \times 10^{-10}$ ohm^{-1} cm^{-1}. The frequency dependence of the voltage at the threshold of the dielectric regime in a 20 μm thick sample is shown in curve c. The dashed lines indicate regions characterized by a non-zero value of a. Lower section: Variation of the tilt angle a of the oblique rolls with the frequency. a, b and c correspond to the same branches as in the upper section.

experiments is reproduced in Fig.8 for the sake of comparison. Oblique rolls are also obtained at the threshold of the dielectric regime and the value of a is not very sensitive to the frequency. However, experiments on MBBA [10] show normal rolls at the threshold in the dielectric regime. Nevertheless, with a slight increase in the field above the threshold the chevron pattern consisting of oblique rolls is observed. Our calculations indicate that if the flexoelectric coefficients are decreased by a factor S, keeping the ratio $(e_1 - e_3)/(e_1 + e_3)$ at the MBBA value, normal rolls are obtained for $S < 0.74$ (Fig.9).

The introduction of the flexoelectric terms also leads to an explanation of the low frequency EHD instabilities observed in nematics with negative conductivity anisotropy (σ_a). Taking σ_a to be negative, we find solutions corresponding to the dielectric regime. At the onset of the instability the convective rolls are found to be almost longitudinal, with their axes making a small angle with the direction of initial alignment of the director. The width of the rolls is found to be determined by the sample thickness. Further, the instability is characterized by a field threshold. All these results are in agreement with the experimental observations on the low frequency

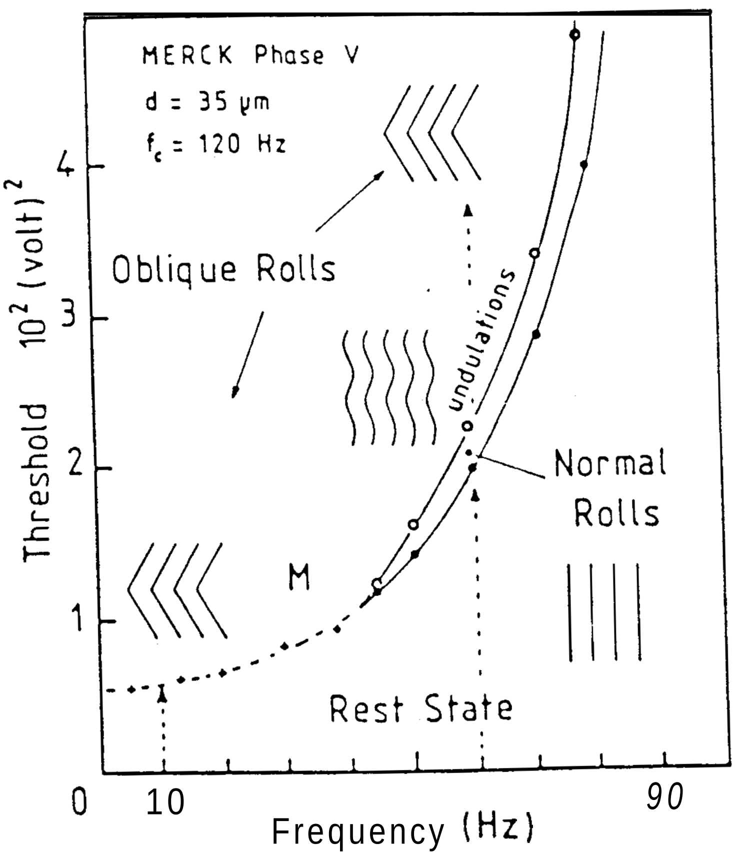

Fig.3. The stability diagram obtained from the experiments of Ribotta at al.[9]. Below the triple point M oblique roils are obtained at the threshold. Beyond M, normal rolls are obtained at the shreshold and as the field strength is further increased, they first become undulatory and shen change continuosly into oblique rolls.

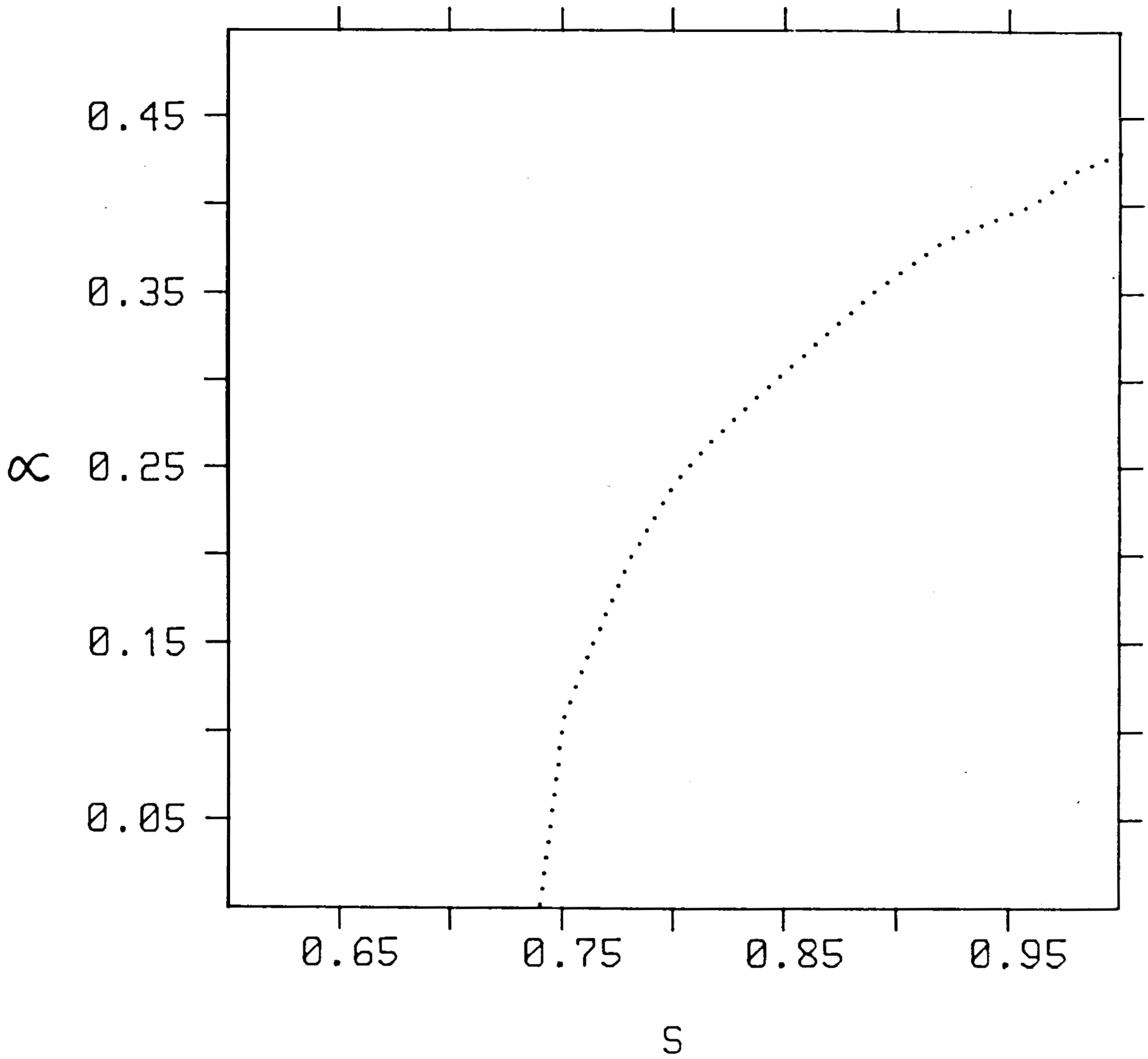

Fig.9. Variation of a (in radians) with the factor S by which the flexoelectric coefficients are decreased, keeping the ratio $(e_1 - e_3)/(e_1 + e_3)$ fixed at the standard MBBA value.

instability in these materials [11-13] (see Fig.10).

Static periodic distortions in nematics is a topic of current interest. A periodic splay-twist distortion of the director field induced by an external magnetic field was first observed by Lonberg and Meyer in a polymeric nematic [17]. From their analysis of the problem it follows that such a distortion is preferred to the uniform splay Freedericksz transition if the ratio of the splay and twist elastic constants, $R = K_2/K_1$, is less than a critical value $R_c \approx 0.303$. Periodic distortion induced by an external electric field has been the subject of many experimental and theoretical studies [1]. Neglecting the elastic anisotropy Bobylev and Pikin [16] showed that the flexoelectric effect could give rise to such a distortion, if the dielectric anisotropy is sufficiently small. In chapter 6 we show that the periodic distortion observed by Lonberg and Meyer follow from the theory of Bobylev et al. for the flexoelectric domains [18], which includes the elastic anisotropy, when the electric field is replaced by a magnetic field. A far more interesting result presented in this chapter deals with the influence of flexoelectricity on the director distortions in the twist geometry, induced by an electric field. Fig.11 shows the variations of the product of the threshold field and

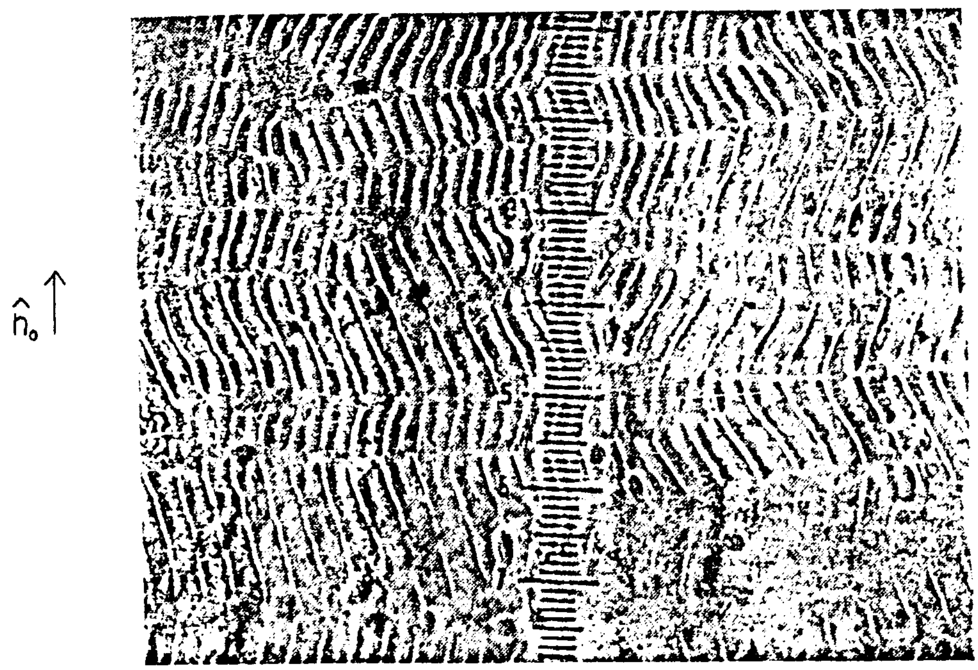

Fig.10. The low frequency 'longitudinal' domains observed in a nematic with negative σ_a. (from Ref.11).

the sample thickness ($E_{y_c}.d$) and the wavevector of the distortion, q_y, with the ratio $R' = K_1/K_2$. When the flexoelectric terms are neglected, we find periodic distortions upto a critical value $R'_c \approx 0.303$, as found by Kini [19] and Oldano [20] in the analogous magnetic case. Flexoelectricity does not favour a periodic distortion in the twist geometry. Therefore, when it is taken into account the critical value R'_c decreases. However, for $R' > R'_c$ flexoelectricity gives rise to a new type of transition characterized by a non-periodic non-planar director distortion. This transition has a lower threshold than the twist Freedericksz transition, for all positive values of ϵ_a. Further, it can also be obtained for negative values of ϵ_a, smaller than a critical value. We have detected this transition in a nematic mixture with $\epsilon_a \approx 0$.

In chapter 7 we describe the experimental determination of the flexoelectric coefficients of two nematics. The combination ($e_1 - e_3$) was measured by using the method of Dozov et al [21]. The sample is taken in a hybrid cell with homeotropic alignment at one of the plates and homogeneous alignment at the other. The distortion of the director in such a cell gives rise to a flexoelectric polarization, given by

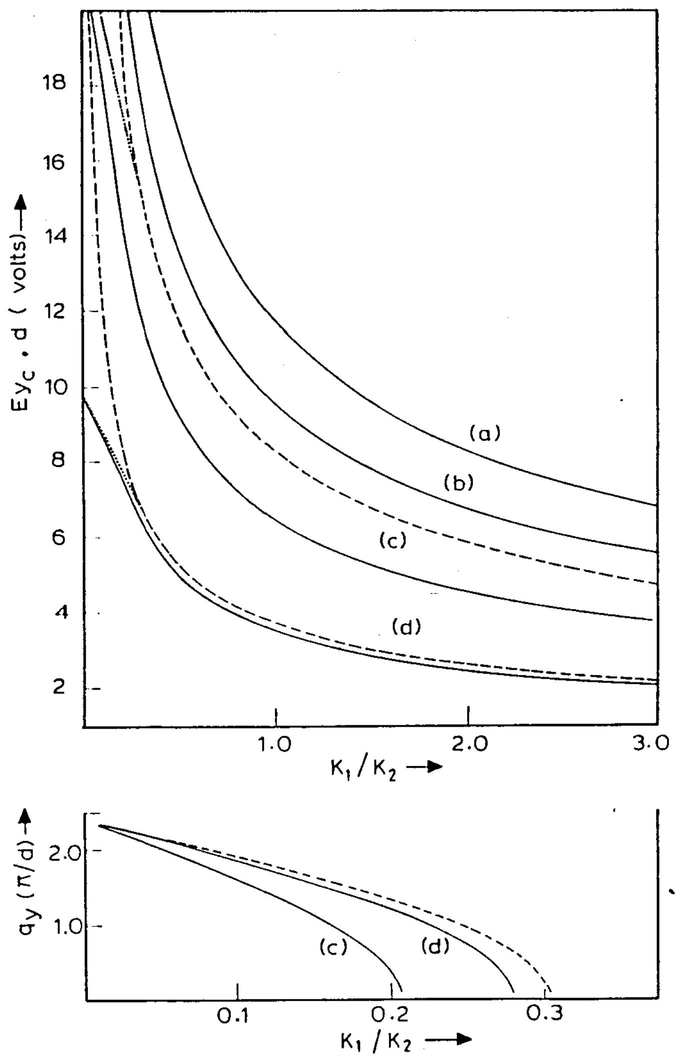

Fig.11. Upper section: The product $E_{y_c}.d$ as a function of $R' = K_1/K_2$ in the twist geometry. (a) $\epsilon_a = -0.1$, (b) $\epsilon_a = 0$, (c) $\epsilon_a = 0.1$ and (d) $\epsilon_a = 0.5$. In the last two cases the dotted lines correspond to the periodic distortion and the dashed lines to the twist Freedericksz transition in the absence of flexoelectricity. The solid lines are obtained from calculations including the flexoelectric terms. Lower section; Variation of the wavevector q_y with R'. The dashed line is obtained when the flexoelectric terms are neglected and the solid lines are obtained when they are included. (c) $\epsilon_a = 0.1$ and (d) $\epsilon_a = 0.5$. Note that $q \rightarrow 0$ at some R'.

$$\vec{P} = (e_1 - e_3)\, \hat{n}\, (\mathrm{div}\, \hat{n})$$

When a transverse electric field $\vec{E}$ is applied in a direction normal to the plane containing the director, a twist distortion is created in the sample, due to the action of $\vec{E}$ on P. The maximum **tilt** angle of the director ($\Phi(o)$) in the sample can be measured using the waveguide property of the structure. By measuring $\Phi(o)$ as a function of E, $(e_1 - e_3)$ can be calculated using the relation [21]

$$\Phi(o) = -(e_1 - e_3)\, E\, d/(\pi\, K)$$

where d is the thickness of the sample and K the elastic constant.

The combination $(e_1 + e_3)$ was measured using a wedge shaped sample with homeotropic alignment at the two surfaces. When an electric field is applied between the two surfaces, field gradients are created in the sample due to the wedge shape of the cell. These field gradients give rise to a destabilizing flexoelectric torque on the director. The resulting distortion of the director can be detected, **if** the dielectric anisotropy of the material under study is negligible, by observing the **tilt** of the conoscopic pattern obtained between crossed polarizers. Neglecting the dielectric anisotropy and assuming the distortion to be small, the conoscopic pattern can be expected to **tilt** by an angle $n_o\bar{\theta}$, where n_o is the index of ordinary refraction and $\bar{\theta}$ is the average **tilt** angle of the director in the sample, given by

$$\bar{\theta} = (\alpha/2)\ [\ 1 + (e_1 + e_3)\ V\ /(6\ K)]$$

where a is the wedge angle and V the applied voltage. By measuring θ for a few values of V, $(e_1 + e_3)$ can be calculated. The values of $(e_1 - e_3)$ and $(e_1 + e_3)$ of the nematic mixture used for studying the EHD instabilities were found to be 100 and -180 cgs units, respectively.

Chapter 8 deals with the measurement of the splay and bend elastic constants of a discotic nematic. The material studied is hexa-n-dodecanoyloxy truxene (C_{12}HATX). The elastic constants were determined independently from the thresholds of the splay and bend Freedericksz transitions. Their values are found to be comparable to those of nematics with rod-like molecules, as has already been found by Mourey et al. [22] in another discotic nematic. Further the ratio K_1/K_3 was found to be less than 1. **It** has been theoretically shown [23,24] that **if** the elastic properties of a discotic nematic are governed by long range orientational order alone, then this ratio should be greater than 1. However, if short range columnar order is present in the medium, then this ratio can be expected to be less than 1. Such short range columnar order has been found in some discotic nematics [25]. Then the observed reversal in the trend of K_1/K_3 is similar to that observed in nematics with rod-like molecules having smectic-like cybotactic groups [26,27]. It may be noted here that our data are comparable to those obtained from recent measurements on two homologues of C_{12}HATX [28].

The author has also carried out some experimental studies on binary mixtures of mesogenic compounds. As these do not fall under the main topic of the thesis, they are described in the appendices. In appendix 1 we describe the studies on a system exhibiting an enhanced smectic A phase and appendix 2 deals with the induction of a smectic C phase in a binary mixture.

Some of the results presented in this thesis are reported in the following publications:

1. Induction of smectic C phase in binary mixtures of compounds with cyano end groups.
   N.V. Madhusudana, V.A. Raghunathan and M. Subramanya Raj Urs, Mol. Cryst. Liq. Cryst., 106, 161 (1984).

2. Enhanced smectic A mesophase in mixtures of terminally polar compounds.
   V.A. Raghunathan, M. Subramanya Raj Urs and N.V. Madhusudana, Mol. Cryst. Liq. Cryst., 131, 9 (1985).
3. Bend and splay elastic constants of a discotic nematic.
   V.A. Raghunathan, N.V. Madhusudana, S. Chandrasekhar and C. Destrade, Mol. Cryst. Liq. Cryst., 148, 77 (1987).
4. Flexoelectric origin of oblique roll electrohydrodynamic instability in nematics.
   N.V. Madhusudana, V.A. Raghunathan and K.R. Sumathy, Pramana - J. Phys., 28, L311 (1987).
5. Flexoelectric origin of oblique rolls with helical flow in electroconvective nematics under DC excitation.
   V.A. Raghunathan and N.V. Madhusudana, Pramana - J. Phys., 31, L163 (1988).
6. Influence of flexoelectricity on electrohydrodynamic instabilities in nematics under AC fields.
   N.V. Madhusudana and V.A. Raghunathan, Mol. Cryst. Liq. Cryst.Lett., 5, 201 (1988).
7. A new threshold flexoelectric instability in nematic liquid crystals.
   V.A. Raghunathan and N.V. Madhusudana, Mol. Cryst. Liq. Cryst., (in press).

8. Influence of flexoelectricity on electrohydrodynamic instabilities in nematics.
   N.V. Madhusudana and V.A. Raghunathan, Liq. Cryst., (in press).

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