



1.1 General Background on Liquid Crystals

Liquid crystals^{1,2} possess many physical properties found either in a liquid or a crystal. The anisotropy of the liquid crystal molecule leads to many interesting anisotropic optical, electrical, and magnetic properties. Nearly all liquid crystals found are organic compounds³. These organic molecules may be of a variety of chemical types, such as acids, azo- and azoxy- compounds, and cholesteric esters.

According to the arrangement of the rod-like molecules in the system, G. Friedel⁴ classified liquid crystal phases into three classes : nematic, cholesteric, and smectic (see Fig. 1).

¹O. Lehmann, Flüssige Kristalle (Engelmann, Leipzig, 1904)

²M.J. Stephen, and J.P. Straley, Rev. Mod. Phys. 46(1974), 617.

³W. Kast, Landolt-Bornstein Tables (Springer, Berlin) Vol. 2, Part 2a, p. 266. (1969)

⁴G. Friedel, Ann. Phys. 19(1922), 273.

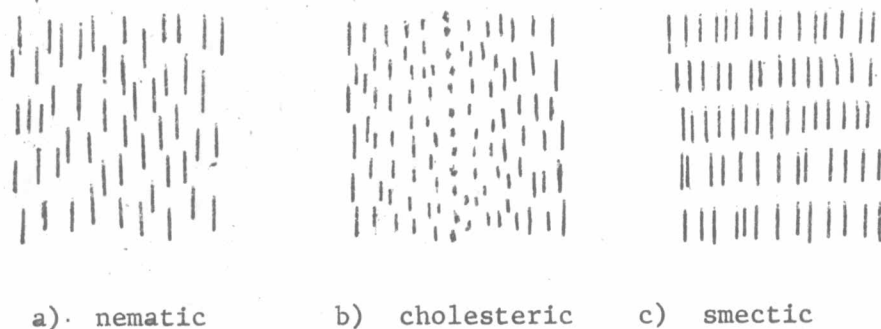


Fig. 1. Schematic of arrangement of molecules in the three major liquid crystal phases.

1.2 The Curvature Elasticity Theory

Useful for understanding physical phenomena in liquid crystal systems is the curvature elasticity theory developed by Zocher⁵, Oseen⁶, and Frank⁷. This theory is reviewed briefly in the following.

Oseen assumed that the energy of a liquid crystal could be written as a sum of the pairwise interactions of the molecules. The interaction of these pairs depends on the relative orientations of the molecules. A unit vector $\underline{n}(\underline{r})$ may be introduced to represent the direction of the preferred axis at any point \underline{r} . We use a local right-handed Cartesian coordinate system x, y, z with z parallel to \underline{n} . The six local components of curvature at the point \underline{r} are defined by :

⁵H. Zocher, Trans. Faraday Soc. 29(1933), 945.

⁶C.W. Oseen, Trans. Faraday Soc. 29(1933), 883.

⁷F.C. Frank, Discuss. Faraday Soc. 25(1958), 19.

$$\text{splay} : s_1 = \frac{\partial n_x}{\partial x}, \quad s_2 = \frac{\partial n_y}{\partial y},$$

$$\text{twist} : t_1 = \frac{-\partial n_y}{\partial x}, \quad t_2 = \frac{\partial n_x}{\partial y},$$

$$\text{bend} : b_1 = \frac{\partial n_x}{\partial z}, \quad b_2 = \frac{\partial n_y}{\partial z} \cdot \dots\dots\dots(1.1)$$

The three fundamental curvature strains, labelled as splay, twist and bend respectively, are shown in Fig. 2.

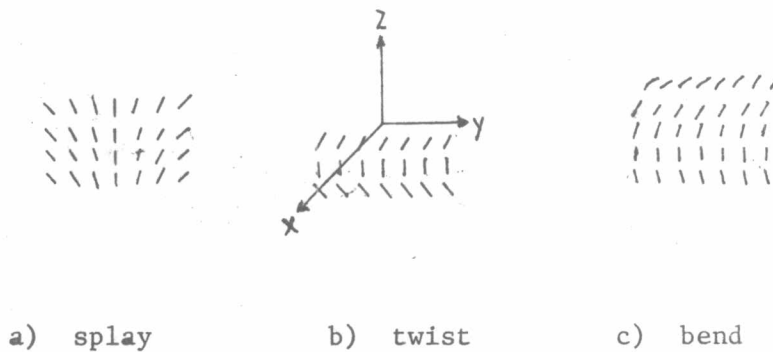


Fig. 2 The three distinct curvature strains of a liquid crystal in a given region

These curvature strains can also be defined by expanding the preferred orientational vector $\underline{n}(\underline{r})$ in a Taylor Series in powers of x, y, z measured from the origin :

$$\begin{aligned} n_x &= a_1 x + a_2 y + a_3 z + 0(r^2), \\ n_y &= a_4 x + a_5 y + a_6 z + 0(r^2), \\ n_z &= 1 + 0(r^2), \quad r^2 = x^2 + y^2 + z^2. \end{aligned} \quad \dots\dots(1.2)$$

It may be seen that

$$\begin{aligned} s_1 &= a_1, \quad t_2 = a_2, \quad b_1 = a_3, \\ -t_1 &= a_4, \quad s_2 = a_5, \quad b_2 = a_6. \end{aligned} \quad \dots\dots(1.3a)$$

The Gibbs free energy density g of a liquid crystal, relative to its free energy density in the state of uniform orientation, can be expanded in terms of the six curvature strains :

$$g' = \sum_{i=1}^6 k_i a_i + \frac{1}{2} \sum_{i,j=1}^6 k_{ij} a_i a_j \quad \dots\dots(1.3b)$$

where k_i and k_{ij} are the curvature elastic constants.

Frank considered the symmetry of the liquid crystal system and showed that the free energy density can be written in the form

$$\begin{aligned} g' &= k_1(s_1+s_2) + k_2(t_1+t_2) + \frac{1}{2} k_{11}(s_1+s_2)^2 \\ &+ \frac{1}{2} k_{22}(t_1+t_2)^2 + \frac{1}{2} k_{33}(b_1^2+b_2^2) \\ &+ k_{12}(s_1+s_2)(t_1+t_2) - (k_{22}+k_{24})(s_1 s_2 + t_1 t_2) \dots\dots(1.4) \end{aligned}$$

It is to be noted that only eight independent elastic moduli are needed. By introducing

$$s_o = -k_1/k_{11}, \quad t_o = -k_2/k_{22}, \quad \dots\dots\dots(1.5)$$

and

$$g = g' + \frac{1}{2} k_{11} s_o^2 + \frac{1}{2} k_{22} t_o^2, \quad \dots\dots\dots(1.6)$$

we can write

$$g = \frac{1}{2} k_{11} (s_1 + s_2 - s_o)^2 + \frac{1}{2} k_{22} (t_1 + t_2 - t_o)^2 + \frac{1}{2} k_{12} (b_1^2 + b_2^2) + k_{12} (s_1 + s_2)(t_1 + t_2) \dots\dots\dots(1.7a)$$

The free energy density can be written in a vector notation as follows :

$$g = \frac{1}{2} k_{11} (\text{div } \underline{n} - s_o)^2 + \frac{1}{2} k_{22} (\underline{n} \cdot \text{curl } \underline{n} + t_o)^2 + \frac{1}{2} k_{33} (\underline{n} \cdot \text{grad } \underline{n})^2 - k_{12} (\text{div } \underline{n})(\underline{n} \cdot \text{curl } \underline{n}) \dots\dots\dots(1.7b)$$

where $s_o = -\frac{k_1}{k_{11}}, \quad t_o = -\frac{k_2}{k_{22}} \cdot$

The magnitude of curvature elastic moduli of liquid crystals is generally 10^{-6} dyn. and the energy associated with the curvature in liquid crystals is very small compared with the energy required to elastically deform a solid.

1.3 The Effects of Magnetic Field

The diamagnetic susceptibility of liquid crystal, owing to the anisotropic structure of the molecules composing it, is also anisotropic in form. In the uniaxial state the magnetic susceptibility may be written as a second rank tensor :

$$\chi_{ij} = \chi \delta_{ij} + \chi_a n_i n_j, \dots\dots\dots(1.8)$$

where $\chi_a = \chi_{\parallel} - \chi_{\perp}$ is the anisotropy in the susceptibility and is generally positive and χ_{\parallel} and χ_{\perp} are the susceptibilities per unit volume along and perpendicular to the molecular axis respectively.

Two more terms are added to the free energy equation in the presence of magnetic field :

$$g_m = -\frac{1}{2} \chi H^2 - \frac{1}{2} \chi_a (\underline{n} \cdot \underline{H})^2. \dots\dots\dots(1.9)$$

In general, the first term can be omitted as it is independent of the orientation of the director. The last term gives rise to a torque on the molecules, and will align them parallel to the field if χ_a is positive.

1.3.1 Effect of magnetic field on a nematic system : Fredericksz transition

When contained between two parallel glass slides, a nematic system is constrained to lie either perpendicular or parallel to the glass at the boundaries. When a magnetic field, applied perpendicular to the director, exceeds a certain critical value, the optical properties of the system change abruptly. This effect, first observed by Fredericksz and Zolina⁸, can be used to determine some of the elastic constants. There are three principal cases which have been studied by Saupe⁹, Pieranski, Brochard, and Guyon¹⁰ and Rapini¹¹. Other geometries have been considered by Dafermos¹² and Leslie¹³.

a). Perpendicular case

In the perpendicular case the director is constrained to be perpendicular to the surfaces and the x-axis along the magnetic field. Defining ϕ to be the angle between the director $\underline{n}(z)$ and the z axis, the director will have the form

$$n_z = \cos \phi(z) \quad , \quad n_x = \sin \phi(z) \quad . \quad \dots\dots\dots(1.10)$$

The free energy per unit area may be written

⁸V. Fredericksz, and V. Zolina, Kristallogr. 79(1931), 225

⁹A. Saupe, Z. Naturforsch. A 15(1960), 815.

¹⁰P. Pieranski, F. Brochard, and E. Guyon, J.Phys. 34(1973),35.

¹¹A. Rapini, M. Papoular, and P. Pincus, C.R. Acad. Sci. B 267(1968), 1230.

¹²C.M. Dafermos, SIAM J. Appl. Math. 16(1968), 1305.

$$g_A = \frac{1}{2} \int_{-d/2}^{d/2} dz \left[(k_{11} \sin^2 \phi + k_{33} \cos^2 \phi) \left(\frac{\partial \phi}{\partial z} \right)^2 - \chi_a H^2 \sin^2 \phi \right]$$

where d is the thickness of the sample.

We will assume, for simplicity, that $k_{11} = k_{33} = k$, then

$$g_A = \frac{1}{2} \frac{k}{\xi} \int_{-d/2}^{d/2} dz \left[\xi^2 \left(\frac{\partial \phi}{\partial z} \right)^2 - \sin^2 \phi \right] \dots\dots\dots(1.11)$$

where $\xi = \sqrt{\frac{k}{\chi_a H^2}}$ is the magnetic coherence length.

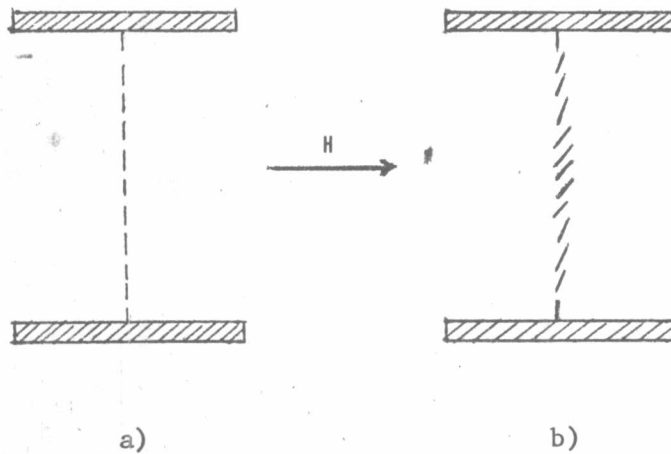


Fig. 3. Molecular orientation in the Fredericksz transition, perpendicular case :

- a) Below a certain critical field, H_c , the alignment is not affected
- b) Slightly above H_c

The equilibrium configuration is determined by minimizing the free energy with respect to z which gives rise to the equation :

$$\xi^2 \frac{d^2 \phi}{dz^2} + \sin \phi \cos \phi = 0 \quad \dots\dots\dots(1.12)$$

The general solution of Eq. (1.12) has been found. The first integral is

$$\begin{aligned} \xi \left(\frac{d\phi}{dz} \right) &= \lambda^{-1} (1 - \lambda^2 \sin^2 \phi)^{1/2} \\ &= (\sin^2 \phi_m - \sin^2 \phi)^{1/2} \quad \dots\dots\dots(1.13) \end{aligned}$$

where the constant λ is determined by the condition that $\frac{d\phi}{dz} = 0$ at the midplane of the system ($z = 0$):

$$\lambda^{-1} = \sin \phi_m \quad \dots\dots\dots(1.14)$$

and ϕ_m is the maximum value of ϕ which lies half way between the glass surfaces at $z = 0$. The equation may be further integrated to give

$$\begin{aligned} \left(\frac{1}{2} d - z \right) &= \xi \int_{\phi}^0 \frac{d\phi'}{(\sin^2 \phi_m - \sin^2 \phi')^{1/2}} \\ &= \xi \operatorname{csc} \phi_m F(\operatorname{csc} \phi_m, \phi) \quad \dots\dots\dots(1.15) \end{aligned}$$

where F is the incomplete elliptic integral of the first kind.

If we use the boundary condition $\phi = 0$ at $z = \frac{d}{2}$ the maximum distortion is found by putting $z = 0, \phi = \phi_m$:

$$\begin{aligned} \frac{1}{2} d &= \xi \operatorname{csc} \phi_m F(\operatorname{csc} \phi_m, \phi_m) \dots\dots\dots(1.16) \\ &= \xi K(\sin \phi_m) \end{aligned}$$

where K is the complete elliptic integral of the first kind.

This equation has a solution (other than $\phi_m = 0$) only for $d > \pi \xi$ giving the critical field H_c from $d = \pi \xi_c$

or
$$H_c = \frac{\pi}{d} \left(\frac{k_{33}}{\chi_a} \right)^{\frac{1}{2}} \dots\dots\dots(1.17)$$

For $k \sim 10^{-6}$ dyn, $\chi_a \sim 10^{-6}$ cgs. This gives $H_c d$ of order unity.

For $(H - H_c) / H_c \ll 1$, $\phi_m \propto (H - H_c)^{\frac{1}{2}}$. This is shown in Fig.4.

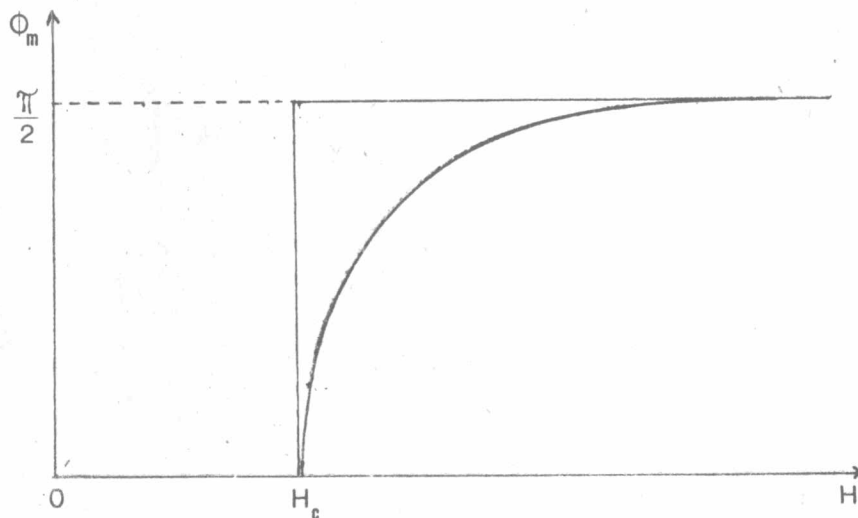


Fig. 4. The maximum distortion ϕ_m in the Fredericksz transition as a function of applied field

b). Parallel case

In this case, the director is constrained to be parallel to the surfaces. When a magnetic field applied parallel to the surfaces exceeded a critical field H_c the optical properties of the system change abruptly. H_c is given by

$$H_c = \frac{\pi}{d}(k_{11}/\chi_a)^{\frac{1}{2}} \dots\dots\dots(1.18)$$

This phenomenon has been considered in terms of the continuum theory¹⁴.

c). Twist case

A third case is that the field is applied in the plane of the glass, but perpendicular to the direction of the molecules which are parallel to the surface. Assuming that the molecules at the surface do not twist in the direction of the field, then the system shows a transition to a twisted state and observation of this effect can provide information on the elastic constant k_{22} . This geometry leads exactly to the same form as Eq. (1.17), the only change being the substitution of k_{22} for k . The equation is

$$H_c = \frac{\pi}{d}(k_{22}/\chi_a)^{\frac{1}{2}} \dots\dots\dots(1.19)$$

¹⁴A. Rapini, M. Papoular, and P. Pincus, C.R. Acad. Sci. B 267(1968), 1230.

and observation of this effect provides information on k_{22} ¹⁵. These twisted structures have been discussed theoretically by Leslie¹⁶. Twisted nematic and cholesteric structures have also been considered by Ericksen^{17,18,19}.

1.3.2 Effect of magnetic field on a cholesteric system: cholesteric-nematic transition

The effect of a magnetic field on a cholesteric liquid crystal which has a helicoidal structure had been explained thoroughly by de Gennes²⁰. For cholesteric helical structure, de Gennes has treated the unwinding of a cholesteric helix by magnetic field. Let the z-direction be the helical axis and the director be written in the form

$$n_x = \cos \phi(z) \quad , \quad n_y = \sin \phi(z) \quad , \quad n_z = 0 \quad \dots(1.20)$$

where in zero field $\phi(z) = t_0 z$.

¹⁵C. Williams, and P.E. Cladis, Solid State Commun. 16(1972), 357.

¹⁶F.M. Leslie, Mol. Cryst. Liq. Cryst. 12(1970), 57.

¹⁷J.L. Ericksen, J. Fluid Mech. 27(1967), 59.

¹⁸J.L. Ericksen, Q.J. Appl. Math. 25(1968), 474.

¹⁹J.L. Ericksen, Z. Angew. Math. Phys. 20(1969), 383.

²⁰P.G. de Gennes, Solid State Commun. 6(1968), 163.

An external magnetic field applied normal to the helical axis both distorts the structure and elongates the period $z_0 = 2\pi / t_0$. Taking the applied field along the y-axis, the distortion free energy per unit volume for xy-plane is

$$g = \frac{1}{2} \int dz \left[k_{22} \left(\frac{\partial \phi}{\partial z} - t_0 \right)^2 - \chi_a H^2 \sin^2 \phi \right] \dots\dots\dots(1.21)$$

The free-energy minimization is identical with as that for Eq.(1.12).

It leads to the result

$$\frac{z}{z_0} = \left(\frac{2}{\pi} \right)^2 K(\kappa) E(\kappa) \dots\dots\dots(1.22)$$

where κ , the integration constant for the first integration of Eq.(1.21), is determined by

$$\frac{E(\kappa)}{\kappa} = \frac{1}{2} \pi t_0 \xi_2$$

with
$$\xi_2 = \left[\frac{k_{22}}{\chi_a H^2} \right]^{\frac{1}{2}} \dots\dots\dots(1.23)$$

being the magnetic coherence length corresponding to the "twist" elastic constant k_{22} and z_0 the zero-field pitch.

$K(\kappa)$ is the complete elliptic integral of the first kind and $E(\kappa)$ is the complete elliptic integral of the second kind. Since we will compare Eq.(1.22) with our experimental results in detail, the numerical values were computed from values of elliptic integrals listed in the Handbook of Mathematical Functions (Abramowitz and Stegun). These values are tabulated in Table 1 and plotted in Fig. 5.

Table 1 Cholesteric Pitch as a Function of κ

$$\frac{z}{z_0} = \left(\frac{z}{\pi}\right)^2 K(\kappa) E(\kappa)$$

κ	$K(\kappa)$	$E(\kappa)$	z/z_0
0	1.57079	1.57079	1.00000
0.20	1.65962	1.48903	1.00155
0.30	1.71388	1.44536	1.00396
0.40	1.77751	1.39939	1.00812
0.50	1.85407	1.35064	1.01491
0.60	1.94956	1.29842	1.02592
0.65	2.00759	1.27070	1.03390
0.70	2.07536	1.24167	1.04438
0.75	2.15651	1.21105	1.05846
0.80	2.25720	1.17848	1.07808
0.85	2.38901	1.14339	1.10701
0.87	2.45533	1.12845	1.12293
0.89	2.53333	1.11285	1.14259
0.90	2.57809	1.10477	1.15433
0.91	2.62777	1.09647	1.16774
0.92	2.68355	1.08793	1.18323
0.93	2.74707	1.07912	1.20143
0.94	2.82075	1.06998	1.22321
0.95	2.90833	1.06047	1.24998
0.96	3.01611	1.05050	1.28411
0.97	3.15587	1.03994	1.33011
0.98	3.35414	1.02859	1.39825
0.99	3.69563	1.01599	1.52773
1.00	∞	1.00000	∞

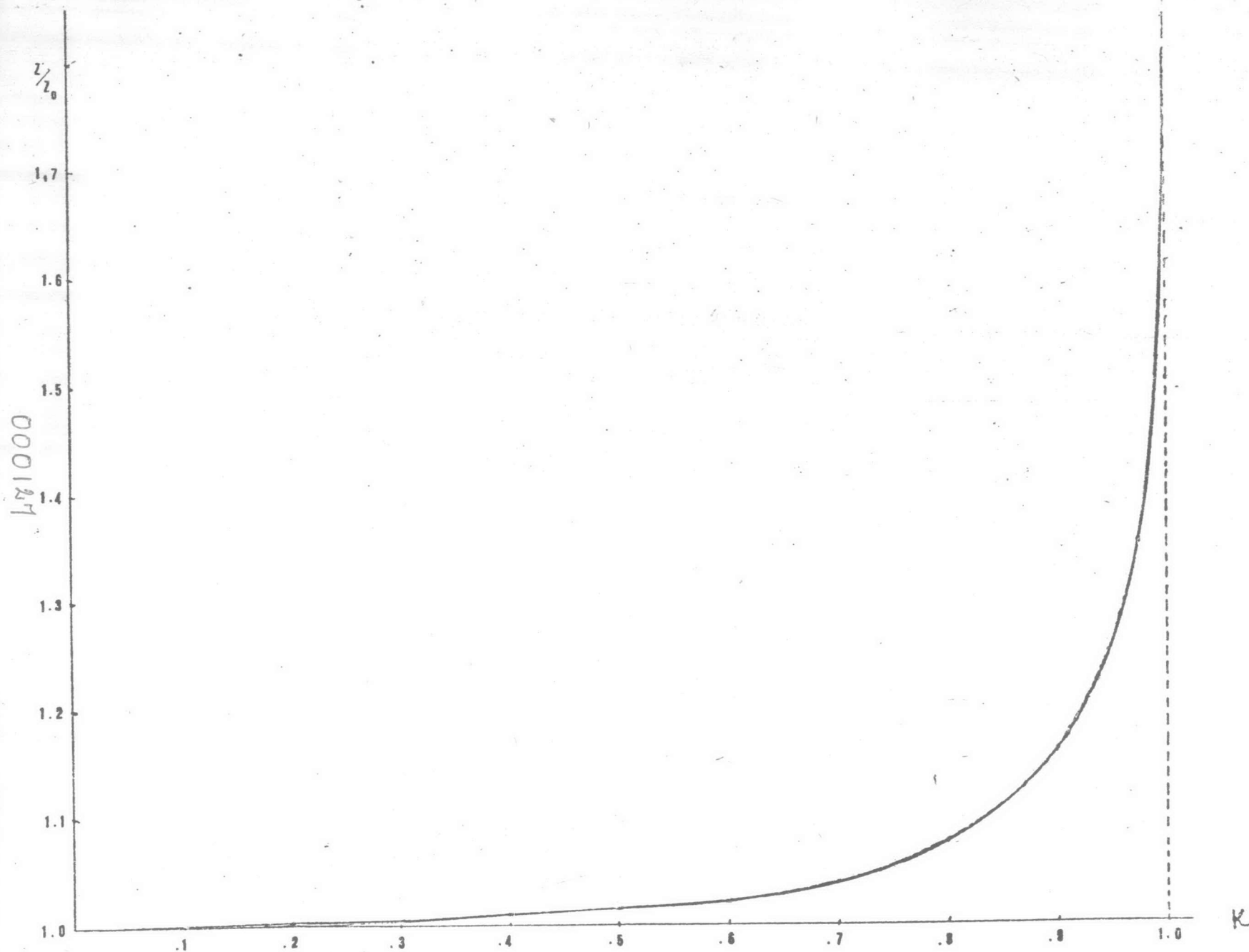


Fig.5 Divergence of cholesteric pitch in magnetic field

The logarithmic divergence of the cholesteric pitch z as the magnetic field approaches a critical value H_c can be clearly seen in Fig. 5.

At $H = H_c$, $\kappa = \kappa_c = 1$ and Eq. (1.23) gives

$$\frac{E(\kappa_c)}{\kappa_c} = \frac{1}{1} = \frac{1}{2} \pi t_o \xi_2 = \frac{1}{2} \pi t_o \left(\frac{k_{22}}{\chi_a H_c^2} \right)^{\frac{1}{2}},$$

so that
$$H_c = \left(\frac{\pi t_o}{2} \right) \left(\frac{k_{22}}{\chi_a} \right)^{\frac{1}{2}}; \quad t_o = \frac{2\pi}{z_o},$$

or
$$H_c = \frac{\pi}{z_o} \left[\frac{k_{22}}{\chi_a} \right]^{\frac{1}{2}}. \quad \dots\dots\dots(1.24)$$

The measurement of critical field can provide information on k_{22} if χ_a and t_o ($t_o = 2\pi/z_o$) are known. Typically, for $k_{22} = 10^{-6}$ dyne, $\chi_a = 10^{-6}$ ergs, and $t_o = 10^4 \text{ cm}^{-1}$, H_c is in the order of $10^4 - 10^5$ G.

1.4 Some Recent Experiments

In this section, some relevant recent experiments on magnetic field effects of liquid crystals, especially cholesteric liquid crystals, are reviewed.

The case of a cholesteric confined between parallel glass plates had been studied by Cladis and Kleman²¹ (see Fig. 6).

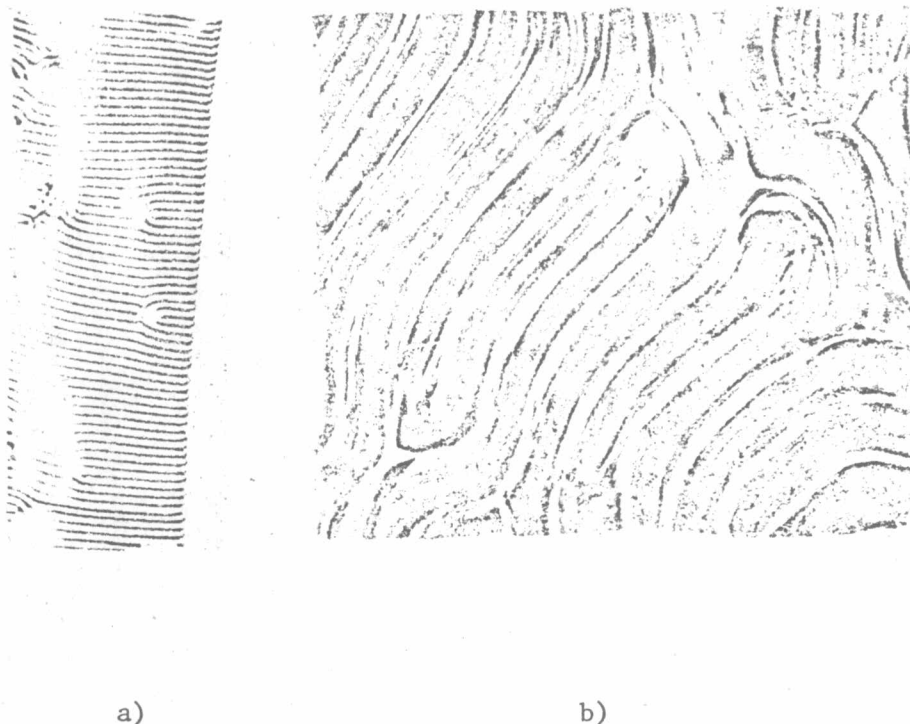


Fig. 6 a) The cholesteric texture when direction of vibration of incident light is perpendicular to the stripes
b) Large pitch (low concentration) cholesteric-nematic mixture held between rubbed glass plates

The cholesteric texture of Fig. 6b appears only when the film thickness of the optical cell is nearly the same as the helical pitch.

²¹P.E. Cladis, and M. Kleman, Mol. Cryst. Liq. Cryst. 16(1972),1.

Cholesteric pitch can therefore be effected by the thickness of the cell.

The variation of pitch with concentration for a nematic-cholesteric mixture was also studied by Cladis and Kleman.²¹ The magnitude of the induced pitch depends inversely on the concentration of the cholesteric dopant.

De Gennes's theory on the divergence of cholesteric pitch in a magnetic field has been verified by experiments by Meyer²² and Durand et al²³.

Magnetic field effects in a sample of p-azoxyanisole (PAA) doped with cholesteryl acetate (CA) were studied with a microscope by Meyer. At 119 °C, a critical field of about 8.3 kG. was obtained for a cholesteric-nematic system which has a zero field pitch, z_0 , of 13 μm . The experimental results were reproduced in Fig. 7 together with the theoretical curve of de Gennes.

²²R.B. Meyer, Appl. Phys. Lett. 14(1969), 208.

²³G. Durand, L. Leger, F. Rondelez, and E. Veyssie, Phys. Rev. Lett. 22(1969), 227.

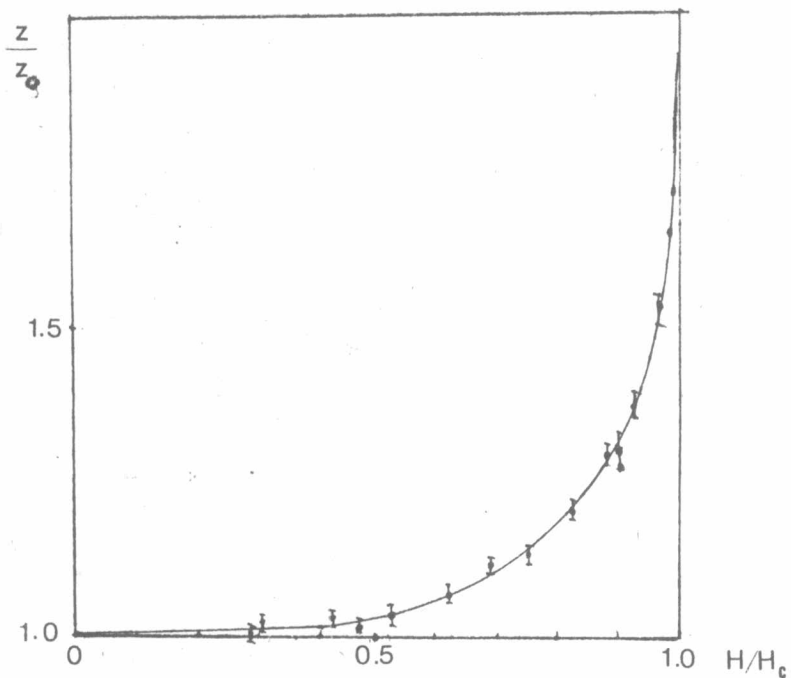


Fig. 7 The helical pitch z as a function of magnetic field strength H .

Durand and co-workers studied systems of PAA mixed with low concentration of cholesteryl decanoate (CD), cholesteryl nonanoate (CN), cholesteryl chloride (CC), cholesteryl acetate (CA), cholesteryl palmitate (CP). Using a different observational technique, de Gennes' theoretical prediction was again confirmed.

Durand and co-workers also studied the dependence of H_c on cholesteric concentration and found a linear dependence. Since the induced pitch is inversely proportional to the cholesteric concentration, the critical field was plotted against inverse pitch in Fig. 8.

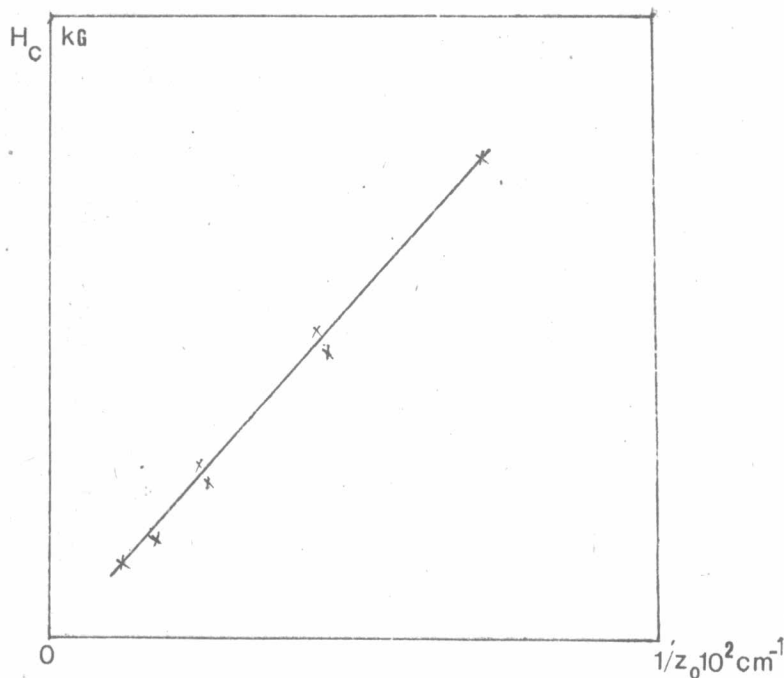


Fig. 8 Linear variation of critical field H_c with inverse pitch which is proportional to cholesteric concentration

The ratio $\frac{k_{22}}{\chi_a}$, where k_{22} is the twist elastic constant and χ_a the anisotropic susceptibility, of N-(p-Methoxybenzylidene)-p-butylaniline (MBBA) doped with 0.365 % cholesteryl propionate to produce a cholesterized nematic with a pitch of approximately 15 μm was measured by Williams and Cladis²⁴ using the magnetic field induced cholesteric nematic transition and the relation Eq.(1.24). The value of $\frac{k_{22}}{\chi_a}$ was 2.93 ± 0.28 cgs, at room temperature. Measuring the value of the ratio at different temperatures, Williams and Cladis obtained results which

²⁴C. Williams, and P.E. Cladis, Solid State Commun. 10(1972),357.

were related to the temperature dependence of the order parameter $S(t)$ as calculated by Maier and Saupe²⁵. Using $t = \frac{T}{T_c}$ to denote the reduced temperature and expressing the order parameter in the form $S(t) = \alpha \frac{k_{22}(t)}{\chi_a}$, the scaling parameter α was found to be 0.206 in fitting $\alpha \frac{k_{22}(t)}{\chi_a}$ to the values of $S(t)$ as calculated by Maier and Saupe.

The order parameter had been obtained to be $S = 0.52$ in PAA at 120°C by Alben, McColl, and Shih²⁶ by measuring the magnetic susceptibility.

1.5 The Scope of the Present Investigation

The objective of the present research is the investigation of the behaviour of cholesteric liquid crystals in a magnetic field. In particular, it was intended to study the effects of magnetic field on the cholesteric pitch in cholesteric-nematic mixtures with low concentration of cholesterics.

Firstly, it was planned to investigate thoroughly the properties of the cholesteric pitch, including the dependence of the magnitude of the pitch on cholesteric concentration in the mixture, temperature, film thickness and magnetic field strength. The investigation of the magnetic field effects of the cholesteric pitch includes verification of de Gennes' theoretical expression for the dilation of the cholesteric pitch in a magnetic field and the logarithmic divergence of the pitch near a

²⁵W. Maier, and A. Saupe, Z. Naturf. 15a (1960), 287.

²⁶R. Alben, J.R. McColl, and C.S. Shih, Solid State Commun. 11(1972), 1081.

critical field. These theoretical results, previously confirmed experimentally by Meyer and Durand's and co-workers, would be investigated in additional systems of nematic cholesteric liquid crystal mixtures. It was planned to investigate carefully the dependence of the critical field on the cholesteric concentration, temperature and film thickness.

Originally, it had been hoped to investigate the behaviour of a number of liquid crystal mixtures in the magnetic field using combinations of 6 or 7 cholesteric systems (CA, CN, CP, CB, CC, CD) with 3 or 4 nematics (PAA, PAP, MBBA) in different concentrations. The motivation was that, having information on the critical field strength for a large number of liquid crystal mixtures it might be possible to spot some trends in the values of critical field and their temperature dependence which may allow some inference to be drawn relating the critical field, and through it, the elastic constant of the mixture systems concerned with the molecular structures of and the interaction between the cholesteric and nematic systems forming the mixtures.

Because this was the first time liquid crystals were studied in magnetic field in our laboratory, a lot of time was taken in constructing and installing the experimental set up, therefore there was time to study only the PAA/CP system for cholesteric concentration ranging from 0.2 % to 0.75 % , However, it had been possible to undertake the complete range of the intended investigations, including a demonstration of the logarithmic divergence of the pitch in magnetic field and the dependence of the critical field on concentration, film thickness and temperature.

In Chapter 2, the experimental set up and the measurements are described. The results are also shown in this Chapter. In Chapter 3, the experimental results are discussed and summarized.