

THEORETICAL STUDIES ON THE PROPERTIES OF THE LIQUID CRYSTALLINE STATE

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By
U. DEVAPPA KINI

Liquid Crystals Laboratory
RAMAN RESEARCH INSTITUTE
Bangalore • 560006 (India)

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DECLARATION

I hereby declare that the thesis
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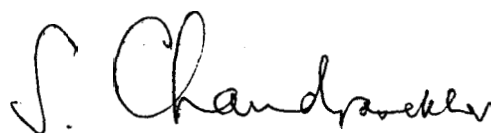
U. DEVAPPA KINI

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S. Chandrasekhar

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I certify that this thesis has been composed by Mr. U. Devappa Kini based on investigations carried out by him at the Liquid Crystals Laboratory, Raman Research Institute, under my supervision. The subject matter of this thesis has not previously formed the basis of the award of any degree, diploma, associate-ship, fellowship or other similar title.



Professor S. Chandrasekhar
Liquid Crystals Laboratory
Raman Research Institute
Bangalore 560006

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PREFACE

It has long been known that certain organic materials exhibit 'liquid crystalline' phases which have the mechanical properties of a fluid (e.g., viscosity, surface tension, etc.) and at the same time show optical, dielectric and diamagnetic anisotropy rather like a crystal. This type of behaviour is due to the preferred alignment of highly anisotropic elongated molecules of which these materials are composed. Thermotropic liquid crystals are classified broadly into three types: nematic, cholesteric and smectic. In the nematic type the molecules are aligned approximately parallel to one another with no positional order. The cholesteric type is essentially a twisted nematic with the axis of twist normal to the preferred molecular direction. In smectics the molecules are packed in layers with their long axes normal or tilted with respect to the planes of the layers.

This thesis reports some theoretical studies on nematics and cholesterics. Part One (Chapters I to VII) deals with the continuum theory of nematics and cholesterics; Part Two (Chapters VIII and IX) embodies studies on ^{the} optical properties of cholesterics.

Part I

Chapter I gives a brief description of the Ericksen-Leslie continuum theory for incompressible nematics (Ericksen 1962, Leslie 1968) which is essential to many of the problems considered here. In this theory the preferred direction of orientation is described by a unit vector field called the director, which is assumed to be of constant magnitude. Conservation laws are written down for mass, linear momentum, angular momentum and energy and the equations governing the rate of change of linear velocity and change in director orientation are obtained. The invariance principle which enables a selection of primary variables (using which alone the mechanics of the system can be described) together with the Clausius-Duhem entropy inequality gives explicit expressions for quantities like stress, free energy and body torques in terms of these variables. For instance the free energy density should depend only on the director and its gradients. Also stresses and body forces can be resolved into equilibrium (static) and non-equilibrium (hydrodynamic) parts. The equilibrium parts are shown to be related to functional derivatives of the free energy density, while the non-equilibrium parts can be expressed in terms of the components of velocity gradients and of the director.

The conclusions of the Ericksen-Leslie theory of nematics are the following: (1) The stress tensor of a nematic is asymmetric; (2) There are in general six viscosity coefficients and four elastic constants for a nematic; but one of the elastic constants has no part to play in the equations of motion; (3) The Oseen-Frank elasticity theory of nematics (Oseen 1933, Frank 1958) becomes a special case of this general theory; (4) In any flow problem the equations for the director orientation and those for the velocity field have to be solved simultaneously. This is a direct consequence of the intimate coupling between the velocity and director fields, which manifests itself in the non-Newtonian flow behaviour of liquid crystals. The viscous torques which try to deform the director orientation are opposed by the restoring elastic torques which arise from the anchoring of the director at the boundary. Many of the problems in this thesis deal with details of this non-Newtonian flow. The differential equations of motion are in general highly non-linear and cannot be solved exactly. Numerical techniques such as the fourth order Runge-Kutta method and the orthogonal collocation method have been used in this thesis for solving the equations.

The shear flow of nematics (flow between two plane parallel plates with one plate moving relative to the

other with a constant velocity) is one of the simplest of the flow geometries wherein many features of the Ericksen-Leslie theory become apparent. This forms the subject matter of Chapter II. Earlier (experimental) studies on this problem (Porter and Johnson 1962) indicated that at high shear rates the apparent viscosity η (defined as the ratio of applied shear to the average velocity gradient) approaches a constant value, independent of shear rate and the distance between the plates. Leslie (1968) showed that thin behaviour can be accounted for on the basis of the continuum theory. He even worked out (Leslie 1971) the effect of a magnetic field applied in the plane of shear. Numerical calculations of apparent viscosity in the presence of a magnetic field in one particular geometry (perpendicular director orientation at the plates and a magnetic field applied perpendicular to the plates) was carried out by Finlayson (1974). However a complete analysis of the problem needs a detailed consideration of other possible geometries for this flow. In this chapter η has been studied as a function of shear rate and of magnetic field, for fields applied either parallel or perpendicular to the plates and for symmetric or asymmetric director alignment at the plates. This results in eight possible geometries in this flow. Flows in which the field is perpendicular

to both the velocity and to the velocity gradient and in which the director does not lie in a plane are difficult to analyse and have not been considered. The other four geometries have been treated in detail. The orthogonal collocation method has been used for solving the differential equations. Though the calculations pertain to PAA the conclusions are general. It is found that for symmetric director orientation η has a value η_A which is independent of shear rate at low shear rates. However as the shear rate is increased η decreases to lower values approaching again a constant limiting value $\eta_{||}$ at very high shear rates. For the asymmetric case η at low shear rates is about $0.5 \eta_A$ but approaches η as the shear rate is increased. A field applied perpendicular to the plates increases η while a field applied along the flow direction decreases it. Another interesting result is that at low shear rates for the symmetric boundary condition with a magnetic field parallel to the flow $\eta = \eta_A$ and is independent of the field till the field attains a critical value H_0 . As the field is increased beyond H_0 η decreases approaching the value $\eta_{||}$ at very high fields. However this type of critical behaviour is absent in the case of asymmetrical director alignment. Orientation and velocity profiles at different fields and shear rates for both types of boundary condition also

exhibit some interesting features. With increasing shear rate or field strength, director orientation in the fluid changes from the equilibrium value. At high values of shear rate or field applied along the flow the director orientation is nearly parallel to the flow except near the boundaries where it reverts back to the boundary value. There are indications of boundary layers existing at high enough shear rates.

In Chapter III the flow of a nematic in a circular tube (i.e., Poiseuille flow) has been studied. The experimental investigations of Fisher and Fredrickson (1969) indicate that η is a sensitive function of shear rate and director alignment at the wall of the tube. Their observations were neatly accounted for by Tseng et al. (1972) who solved numerically the differential equations obtained by Atkin (1970). In this chapter the effect of an axial magnetic field on Poiseuille flow has been considered. By a proper coordinate transformation the equations of motion can be solved numerically by the Runge-Kutta method to yield director orientation and velocity profiles. Calculations of η as a function of the rate of flow for different values of the magnetic field show some interesting results. Even for magnetic fields of moderate strength η decreases considerably due to the alignment effects of the field. At any shear rate, increasing the

field decreases η . The field also has a significant effect on the velocity and orientation profiles. The velocity profile becomes parabolic and the orientation profile flat at very Ugh fields. It has also been found that in the field free case non-homeotropic director alignment at the tube wall considerably alters η from its value for the homeotropic case. This feature of the calculations is in qualitative agreement with the experimental observations of Fisher and Fredrickson.

Chapter IV deals with Couette flow of nematics, i.e., the flow confined do the annular space between two coaxial cylinders which rotate with different angular velocities. Porter and Johnson (1962) in their Couette viscometric studies ON PAA Pound that η , at very high shear rates attains a value which is independent of shear rate and that it increases with decreasing gap width. Atkin and Leslie (1970) worked out the exact theory in the field-free case and found qualitative agreement with the observations of Porter and Johnson. Currie (1970) extended their theory to include the effects of a magnetic field and investigated a number of possible solutions of the equations of motion. However ha, did not investigate apparent viscosity. In this chapter the differential equations of Couette flow in the presence of radial or azimuthal magnetic fields hare been arrived

at in a more simple manner, and have been solved numerically. Calculations of η as a function of shear rate, of the ratio of radii of the cylinders and of magnetic field for symmetric and asymmetric director orientation at the two cylinders have also been presented. The important results are (i) η decreases when the ratio of the outer cylinder to the inner one increases. This is in qualitative agreement with the results of Porter and Johnson, (ii) In general, for any value of the shear rate a radial field enhances η whereas an azimuthal field diminishes it. (iii) For gap widths which are small compared to the average radius, the results of the simple shear flow are recovered. Thus for example in the perpendicular director orientation, at low values of shear rate when an azimuthal field B/r is applied a critical value $B = B_c$ is found. For $B < B_c$ η stays constant at η_A . For higher values of B , η decreases, ^($B > B_c$) ultimately attaining the value $\eta_{||}$ for very high fields. This critical behaviour is absent for asymmetric director orientation at the cylinders. An expression for B_c has been derived here for the first time. It is found to depend on the ratio R_1/R_2 of the radii of the inner and outer cylinders. When R_1/R_2 increases from a low value B_c also increases till for values of R_1/R_2 approaching unity, B_c approaches H_0 , the corresponding value of the critical

field in shear flow. Orientation and velocity profiles also exhibit some interesting features. For small gap widths and for symmetric alignment of director at the walls of the cylinders, the orientation profiles are very nearly symmetric. In general the distortion increases with increasing shear rate and azimuthal field. A radial field tends to decrease the extent of distortion. But for gap widths comparable to the *radii* the orientation profile is distinctly asymmetric, the asymmetry decreasing with the ratio R_2/R_1 . For the asymmetric case the orientation profile becomes more and more distorted with increasing shear rate and with increasing value of azimuthal or radial field.

The non-Newtonian behaviour of cholesteric liquid crystals is strikingly different; from that of nematics. For example η of cholesterics can increase a million-fold as the shear rate decreases to a low value, Helfrich (1969) proposed an explanation of the anomalously high value of η for low shear rates in the Poiseuille flow geometry by assuming that; the cholesteric flows along its helical axis with the molecules spiralling as they move down this axis (but without the helical structure itself moving due to the anchoring effects of the boundary) and that the velocity profile is flat. He showed that η should then be directly proportional to the square of the

tube radius and inversely proportional to the square of the pitch and independent of the shear rate. This behaviour has been analysed in Chapter V by using the continuum theory of cholesterics given by Leslie (1968a). The main features of Helfrich's model (referred to in the literature as the permeation model) follow as a natural consequence of the continuum theory without it being necessary to make assumptions about the anchoring of the structure at the boundary. In all practical situations the velocity is found to be flat, ^{except} over a negligibly thin *layer* near the boundary. Also the expression for η for Poiseuille flow reduces to that given by Helfrich to a very high degree of accuracy. The case of a cholesteric flowing along the helical axis between two fixed parallel plates under the action of a pressure gradient has also been worked out in this Chapter. Again the apparent viscosity and the velocity profile exhibit an anomalous behaviour.

Cholesteric flow perpendicular to the helical axis was theoretically studied by Leslie (1969) for the shear flow geometry. The theory predicts that at very high shear rate η should attain a constant value which is independent of shear rate. In Chapter VI the differential equations of Leslie have been numerically solved by the collocation method for shear flow normal to the helical axis of twisted MBBA. The apparent viscosity η has been studied as a function of the velocity V of the moving plate. At low shear rates (or equivalently for low values of V) η remains almost constant. On increasing the shear rate above a certain critical value η decreases and at high shear rates attains a constant lower limiting value. This is in qualitative agreement with the experimental results of Candau et al. (1973) on the Poiseuille flow of twisted nematic Merck IV.

The variation of η with the pitch of the structure is also equally interesting. To facilitate an analytical solution the region of very low shear rate has been considered in the following geometries (1) flow between plates with one plate moving

relative to the other; (ii) Poiseuille flow (This has been considered here for the first time). Though the differential equations for general values of shear rates are quite complicated they become very simple at low shear rates where distortions can also be assumed to be law,. The results for low shear rates are the following:

(1) η is independent of the shear rate, (2) η is a function of the pitch for a given gap width (or tube radius). As the pitch is increased η exhibits an oscillatory behaviour the oscillations becoming more and more pronounced till at a particular value of the pitch (determined by the sample thickness) η shoots to a peak value η_M and then decreases continuously approaching the value $\eta_{||}$ corresponding to the ordinary nematic at pitches approaching infinity, (3) The peak value η_M can be as high as 1.65 $\eta_{||}$ in Poiseuille flow. It should be possible to observe these interesting effects experimentally.

So far the hydrodynamical properties of nematics and cholesterics have been discussed. In Chapter VII are considered certain static distortions in nematics which give rise to characteristic optical textures when a thin film of the liquid crystal is viewed through a

polarising microscope. These textures arise from line singularities which have come to be termed as disclinations. A disclination is assigned a strength s defined as one fourth the number of (bright or dark) brushes starting from it and a sign which is positive or negative depending upon whether, when the polarisers are rotated, the brushes rotate in the same direction or in the opposite direction. The molecular alignment around these disclinations were described by Oseen (1933) and Frank (1958) and their properties were investigated in greater detail by Nehring and Saupe (1972). ~~and Meyer (1969)~~ However the assumption that is usually made in these discussions is that the splay and bend elastic constants are equal. This assumption is generally not accurate and in particular fails completely near a smectic-nematic transition point (exhibited for instance by CBOOA) where the bend elastic constant increases to very high values. Under these circumstances many of the features exhibited by disclinations may be expected to change drastically. In Chapter VII the differential equation governing the director orientation around a singularity has been set up for the general case of unequal splay and bend elastic constants. The equation which is nonlinear has been solved numerically by the orthogonal collocation method for CBOOA using the experimental data for the elastic constants of this compound

(Cheung et al. 1973). The variation of deformation energy, interaction energy and the director orientation pattern have been computed for $\pm\frac{1}{2}$ and ± 1 singularities at different temperatures in the neighbourhood of the smectic-nematic transition of CBOOA. All these quantities change gradually as the temperature approaches the transition. In particular the following results are worthy of special mention: (i) The interaction energy between $+\frac{1}{2}$ and $-\frac{1}{2}$ singularities increases much more rapidly than that between $+1$ and -1 *U* the smectic phase is reached, showing that the former pair has a greater probability of being annihilated than the latter near the smectic-nematic transition. (ii) The energies of $+1$ and $-\frac{1}{2}$ singularities do not vary much with temperature, while those of -1 and $+\frac{1}{2}$ singularities increase many-fold as the smectic transition is approached.

Part II

The second part of the thesis deals with some theoretical work on the optical properties of cholesterics. In particular the regime of large pitch, much larger than the wavelength of light is considered. The optical properties in this regime have been studied experimentally in detail in mixtures of right- and left-handed cholesterics where pitch can be continuously varied (Friedel 1922).

The mixture adopts the helical structure of a cholesteric with a pitch which is a function of temperature and composition. For any particular composition the pitch approaches infinity at a particular temperature (called the nematic temperature, T_N) beyond which it changes handedness. The optical rotatory power undergoes inversion as the temperature is varied across T_N . In ^{the} literature such systems have been referred to as compensated cholesterics. In Chapter VIII a rigorous theory of the optical behaviour of compensated cholesterics has been developed, Chandrasekhar and Srinivasa Rao (1968) used Jones calculus for working out the optical behaviour at wavelengths much smaller than the pitch. This theory has been extended here to the case of compensated cholesterics. The twisted structure is treated as a helical stacking of birefringent layers. Jones matrices of the various layers are multiplied together to get the Jones matrix for the system. The final Jones matrix gives the polarisation state of the emergent light for a given incident state of polarisation. The de Vries equation for optical rotatory power (which holds for $\mu P > \lambda > (\Delta \mu)P$, where μ is the average refractive index, λ the wavelength, P the pitch and $\Delta \mu$ the birefringence) has been shown to be valid for temperatures which are far removed from T_N and not in the vicinity of T_N where the pitch is large. The optical rotatory power of a typical

compensated mixture has been calculated as a function of the temperature. It is found^{that} on heating the optical rotatory power increases, attains a maximum before falling to zero at T_N . On further heating the rotatory power changes sign, increasing to a second maximum before dropping again to lower values. Also as the sample thickness is increased the temperatures corresponding to the maxima of optical rotatory power approach T_N . The maxima also increase in magnitude with increasing sample thickness. All these conclusions are in conformity with the detailed experimental observations carried out recently by Suresh (1976).

The optical behaviour of absorbing compensated cholesterics is the subject matter of the IX Chapter. Sackmann and Voss (1972) observed that when linearly dichroic molecules are dissolved in a cholesteric the medium exhibits circular dichroism in the wavelength region of the absorption band of the dye molecule. A much more detailed study of the circular dichroism as a function of temperature and of sample thickness of compensated cholesterics, with absorbing dye molecules dissolved in them, have been carried out recently by Suresh (96). Again it is found that the de Vries equation extended to absorbing systems fails to account for the behaviour near T_N . In this chapter, the rigorous

theory developed in Chapter VIII has been extended to include the effect of absorption. Circular dichroic power has been calculated as a function of temperature and of sample thickness. The dichroic power, like the rotatory power, increases on increasing the temperature, attains a maximum and then decreases becoming zero at the nematic temperature T_N . On increasing the temperature further the dichroic power changes sign, again attains a maximum and then decreases approaching a low value. The dichroic power exhibits weak oscillations at temperatures far removed from T_N . Also at any given temperature the dichroic power exhibits pronounced oscillations when the thickness is varied. The theoretical predictions are in qualitative agreement with the experimental observations of Suresh (1976).

Some of the results described above have been reported in the following publications of which the present writer is a co-author:

- 1 Theory of the optical properties of non-absorbing compensated cholesteric liquid crystals (with S. Chandrasekhar, G.S.Ranganath and K.A.Suresh) - Mol. Cryst. Liquid Cryst. (1973) 24, 201.
- 2 Optical properties of mixtures of right-handed and left-handed cholesteric liquid crystals (with G.S. Ranganath, S. Chandrasekhar, K.A. Suresh and S. Ramaseshan) - Chem. Phys. Lett. (1973) 19, 556.

- 3 Circular dichroism in mixtures of right- and left-handed cholesterics (with G.S. Ranganath, K.A.Suresh and S.R. Rajagopalan) - International Liquid Crystals Conference, Bangalore, 1973 - Pramana Supplement No.1, p. 353
- 4 Effect of an axial magnetic field on the Poiseuille flow of a nematic liquid crystal (with G.S.Ranganath) - Pramana (1975) 4, 19.
- 5 Flow of cholesteric liquid crystals - I: Flow along the helical axis (with G.S.Ranganath and S.Chandrasekhar) Pramana (1975) 5, 101.
- 6 The effect of magnetic fields and boundary conditions on the Couette flow of nematics - Pramana (1975) 7, 223
- 7 The effect of magnetic fields and boundary conditions ON the shear flow of nematics - Pramana (1976) 7, 378
8. Singularities in nematics - the effect of elastic constant variation (with G.S.Ranganath) - Mol. Cryst. Liquid Cryst. (in press).

The present writer is also a co-author in the fallowing publications:

- 9 The theory of reflexion and transmission by plane parallel cholesteric films (with Rajaram Nityananda) - International Liquid Crystals Conference, Bangalore 1973 - Pramana Supplement No. 1, p. 311.
- 10 Anomalous transmission (Bormann effect) in absorbing cholesteric liquid crystals (with Rajaram Nityananda, S. Chandrasekhar and K.A.Suresh) - International Liquid Crystals Conference, Bangalore, 1973 - Pramana Supplement No.1, p. 325.

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