

CHAPTER 2

Experimental Methods and Theoretical Background

2.1 Introduction

This chapter deals with different experimental techniques that have been used to characterize various physical and mesomorphic properties like refractive index, optical birefringence, dielectric permittivity, dipole moment, density, splay elastic constant and rotational viscosity of binary liquid crystalline mixtures. The several instruments employed for the thesis work have also been introduced. The molecular statistical theories of the nematic [1-7] and smectic A (SmA) phase [8-9] have been discussed. Since, liquid crystals (LCs) manifest a number of phase transitions between different phases upon variation of temperature, an introductory overview on the phenomenological Landau-de Gennes theory of phase transition [4-7,10-14] has been given in this chapter. Finally, the elastic continuum theory [15-18] and the effects of external field [19,20] on the orientation of nematic LC have been briefly introduced.

2.2 Experimental methods

2.2.1 Texture studies

To construct the phase diagram of a binary liquid crystal system it is important to know the range of different liquid crystalline mesophases and also the exact phase transition temperatures. Therefore, polarizing optical microscopy (POM) has been employed to identify different liquid crystalline phases and locate

the phase transition temperatures. This POM study provides us an exclusive window into the phase behavior of liquid crystals and at the same time is exquisite owing to the colorfulness of the textures. The optical textures of different phases have been studied by means of a polarizing optical microscope Motic BA300 equipped with a Mettler Toledo FP90 hot stage with an temperature accuracy of $\pm 0.01^\circ\text{C}$. First, a very little amount of LC sample was taken in a glass slide and covered with a cover slip, and then the slide was placed between crossed polarizer and analyzer *i.e.* the optic axis of the polarizer and analyzer are perpendicular to each other. When the sample is illuminated with a polarized light, optical textures are observed in microscope due to the defects present in structure. Therefore, the defect in liquid crystal system plays a major role in the identification of different phases. Textures of different mixtures have been observed as a function of temperature and the associated phases are identified. Demus [21] and Dierking [22] provide a more detailed and well illustrated description of different liquid crystal textures with photographs.

2.2.2 Optical birefringence measurement

When a beam of light propagates through an anisotropic media such as LCs, the interaction between the electric field vector of incident light and constituent atoms of the material depends on the direction of propagation of light and also the orientation of electric field with respect to the liquid crystal structure. If the direction of propagation of light beam is other than the parallel direction to optic axis, then the incoming light ray splits into two rays which pass through the material with different velocities. These two rays have two different refractive indices *viz.* extraordinary refractive index (n_e) and ordinary refractive index (n_o) with their plane of polarizations perpendicular to each other. This phenomenon is known as double refraction. The difference between the extraordinary and ordinary refractive indices is known as the birefringence (Δn), which is given by

$$\Delta n = n_e - n_o \quad (2.1)$$

Optical birefringence (Δn) has been measured by means of two different ways. In the first case, the extraordinary and ordinary refractive indices (n_e , n_o) were determined by the thin prism technique [23-27] and hence the birefringence (Δn)

was calculated from the difference between them. In the later method, a high resolution temperature scanning technique has been used to determine the birefringence (Δn) of different mesophases with high precision [28-32].

2.2.2.1 Thin prism technique

The extraordinary and ordinary refractive indices (n_e , n_o) of the binary liquid crystalline mixtures have been measured by using the thin prism technique at a wavelength $\lambda=632.8\text{nm}$. The experimental setup for the refractive index measurements is shown in Figure 2.1. First, the thin prisms with refracting angle less than 2° have been prepared by using two optically flat rectangular glass plates. These plates have been washed with detergent and water, and after that treated in an acid mixture at a temperature near about 60°C for one hour. Then, the glass plates have been cleaned further with distilled water and again treated in 1 molar solution of KOH at 60°C for the next one hour. After repeatedly washing with distilled water, the glass plates have been immersed into acetone in order to remove any organic impurities. The two glass plates have been made into a wedge shape by placing a thin glass spacer at one of the vertical edge, which provides a desired refracting angle of the prism. Finally, the glass plates of the prism have been sealed together by means of a high temperature adhesive and then baked in an oven for 8 to 10 hours.

For filling the LC samples, the prism has been heated up to the clearing temperature of the corresponding sample and then introduced into the prism from its top open side. After that, the sample filled prism has been placed inside a specially designed electrically powered thermostat brass block provided with a transparent opening at the centre. The temperature of the heater has been maintained at a fixed value by a temperature controller (Eurotherm PID 2404) with an accuracy of $\pm 0.1^\circ\text{C}$. The heater with the prism inside has been placed between the two pole pieces of an electromagnet and a magnetic field of about 0.8 Tesla has been applied to align the liquid crystalline sample. A He-Ne laser beam ($\lambda=632.8\text{nm}$) has been allowed to be incident normally on the prism. After passing through the aligned LC sample the laser beam splits into two rays *i.e.* ordinary and extraordinary rays and two spots have been observed on the screen. From the high

resolution photograph of the two spots the ordinary (n_o) and extra ordinary refractive indices (n_e) have been calculated using the prism angle. The angle of the prism was first measured with the help of pure water. In the present experimental setup the accuracy of the refractive index measurement has been found to be ± 0.0006 .

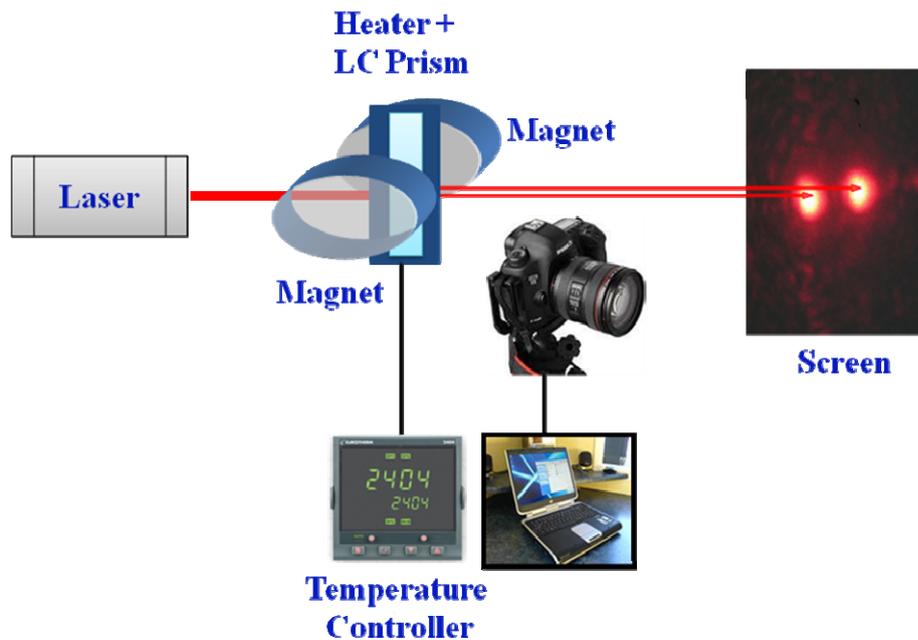


Figure 2.1 Schematic diagram of the experimental set-up for refractive index measurement from the thin prism technique.

2.2.2.2 Optical transmission (OT) method

High resolution optical birefringence (Δn) measurements have been carried out by measuring the intensity of a laser beam transmitted through a planar aligned LC cell. To probe its phase retardation ($\Delta\phi$), a He-Ne laser beam ($\lambda = 632.8\text{nm}$) has been used. The LC filled cell has been placed in a custom built heater made of brass between a pair of crossed polarizers (Glan-Thomson) and its temperature has been simultaneously regulated and measured with a temperature controller (Eurotherm PID 2404) with an accuracy of $\pm 0.1^\circ\text{C}$. The transmitted light intensity has been measured with the aid of a photodiode at an interval of 3 seconds while the heater temperature has been varied at a rate of $0.5^\circ\text{C min}^{-1}$, this translates into a temperature difference of 0.025°C between two successive readings [30-32]. A precision multimeter (Keithley model 2000) has been employed to measure the

photodiode output. The whole experimental set up is automated and controlled by the computer. The schematic diagram of the present experimental set up is given in Figure 2.2. The planar or homogeneously aligned Indium Tin Oxide (ITO) coated cells of thickness 5 μ m (procured from AWAT Co. Ltd., Warsaw, Poland) have been used for the present study.

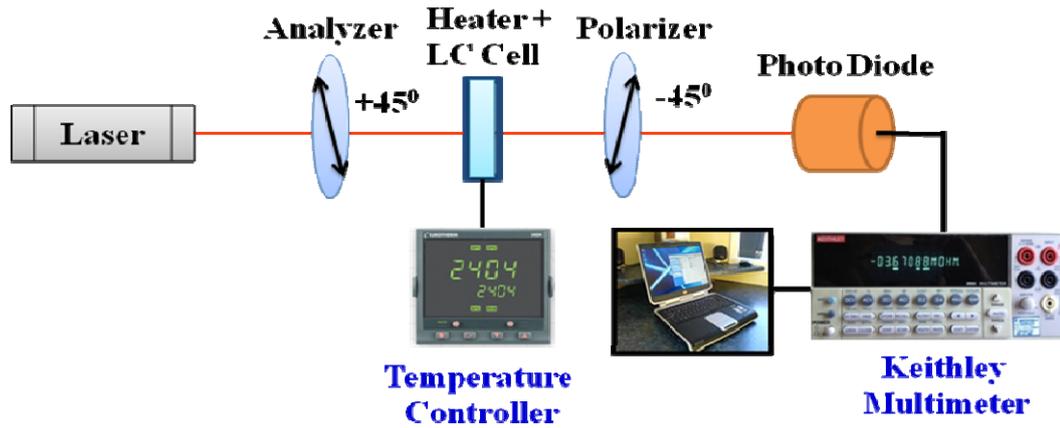


Figure 2.2 Schematic diagram of the experimental set-up for high resolution optical birefringence (Δn) measurement.

The liquid crystalline samples are believed to be a uniaxial birefringent slab with a spatially uniform orientation of the optical axis. The normalized transmitted light intensity (I_t) of the laser beam emerging from the planar aligned LC medium can be written as [33,34]:

$$I_t = \frac{\sin^2 2\theta}{2} [1 - \cos \Delta\phi] \quad (2.2)$$

where θ is the angle made by the polarizer with the optical axis. $\Delta\phi$ is the related phase retardation which is given by the following expression:

$$\Delta\phi = \frac{2\pi\Delta n d}{\lambda} \quad (2.3)$$

where Δn is the optical birefringence, d is the LC cell thickness and λ is the wavelength of the light used. The angle θ has been kept fixed at 45° in order to obtain maximum sensitivity. The transmitted intensity (I_t) is an oscillatory function which have minima and maxima for $\Delta\phi = 2p\pi$ and $(2p+1)\pi$, where p is an integer. Therefore, analyzing the intensity data the related phase retardation

($\Delta\phi$) has been calculated. Finally, using the known value of the cell thickness (d) and wavelength (λ) of the laser beam, birefringence (Δn) has been determined [33,34]. In the present method, the precision of measurement of the birefringence values is found to be slightly higher than 10^{-5} . Apart from the He-Ne laser ($\lambda = 632.8\text{nm}$), a solid state green laser ($\lambda = 532\text{nm}$) have also been employed to determine the birefringence of some binary liquid crystalline mixtures [30].

2.2.3 Static dielectric permittivity measurement

Any material which is polarizable but non-conducting is known as the dielectric material. As the liquid crystals are uniaxial and anisotropic in nature, it has two different dielectric permittivities *i.e.* along the direction of long molecular axis and perpendicular to it. Measurement of these permittivities endows with very fruitful information about the dipole-dipole interaction in various liquid crystalline mesophases. The parallel and perpendicular components of the dielectric permittivity (ϵ_{\parallel} and ϵ_{\perp}) depend on the temperature, spatial configuration of the LC molecules and also on the degree of molecular ordering present within the mesophases.

For the capacitance measurements planar and homeotropically aligned liquid crystal cell of thickness $5\mu\text{m}$, procured from AWAT Co. Ltd., Warsaw, Poland, have been used. The cell consists of two plane parallel glass plates in between which the liquid crystalline material was encapsulated. The parallel glass plates are coated on the inside by a conducting Indium Tin Oxide (ITO) layer and a rubbed polymer layer, both of which are transparent. The conducting layer is required for applying an electric field to the cell whereas the polymer coating is used to control the orientation of the LC molecules within the cell. The LC sample was filled into the empty cell by capillary action at the high temperature isotropic phase. The capacitance of the LC filled cells has been measured as a function of temperature at a frequency 1 kHz using Agilent E4980A digital LCR-bridge with a relative accuracy of 0.05% [35-40]. In order to obtain the temperature variation of the dielectric parameters, the LC filled cell was kept inside an electrically powered thermostat brass block, the temperature of which was controlled and measured by a temperature controller (Eurotherm PID 2404) with an accuracy of $\pm 0.1^{\circ}\text{C}$.

For this dielectric study, first the cell calibration was performed by measuring the capacitances of some standard dielectric liquids within an accuracy of 1%. The parallel and perpendicular components of the dielectric permittivity (ϵ_{\parallel} and ϵ_{\perp}) were computed by measuring the capacitances of the cell filled with air, benzene (as standard materials) and the liquid crystal sample respectively, applying an electric field parallel and perpendicular to the director and using the following expression

$$\epsilon_x = 1 + \frac{(C_x - C_a)}{(C_b - C_a)}(\epsilon_b - 1) \quad (2.4)$$

where C_a , C_b and C_x are the capacitances of the cell filled with air, benzene (as standard materials) and the liquid crystal sample respectively. ϵ_x and ϵ_b presents the relative permittivities of the liquid crystalline material and benzene, and that of the air is taken as unity.

2.2.4 Dipole moment measurement

A molecule is said to have a permanent dipole moment when there is a net separation of the centre of positive charge and the centre of negative charge within the molecule. The free molecular dipole moment of some pure liquid crystalline compounds has been determined by using the Guggenheim method [41], based on the Debye equation. This method necessitates the value of the refractive index (n) and dielectric permittivity (ϵ) of the compound dissolved in a non-polar solvent like *p*-xylene. Therefore, by measuring the concentration (in wt%) dependence of the dielectric permittivity (ϵ) and refractive index (n) of the solution at 30°C, the free molecular dipole moment have been determined as a function of the molar concentration (c). The dielectric permittivities at 1kHz and 0.3Volt have been determined by measuring the capacitance of the solution in a liquid crystal cell using Agilent E4980A digital LCR-bridge whereas the refractive index of the solution have been measured by the thin prism technique [23,24]. According to the Guggenheim [42,43], the effective dipole moment (μ) of a solute in solution of molar concentration c can be written as [41]:

$$\mu^2 = \frac{27kT}{4\pi N_A} \times \frac{(\epsilon_2 - n_2^2) - (\epsilon_1 - n_1^2)}{(\epsilon_1 + 2)(n_1^2 + 2)c} \quad (2.5)$$

where the suffixes 1 and 2 respectively refer to the solvent and solution parameters, k is the Boltzmann constant, N_A is the Avogadro's number and T is the absolute temperature. The concentration dependence of dipole moment is determined and its extrapolation to infinite dilution gives the value of the dipole moment of the isolated molecule. The experimentally obtained dipole moment (μ) of all the studied compounds has been compared with those obtained from the semi-empirical molecular orbital package MOPAC [44,45] in their minimum energy configuration.

2.2.5 Density measurement

The density measurement has been carried out by Anton Paar Digital density meter (model DMA4500) which provides accurate and convenient density measurements in a wide temperature range with an accuracy of ± 0.00005 g/cm³. The apparatus is equipped with a thermo stating device that assures constant temperature of the sample with an accuracy of $\pm 0.03^\circ\text{C}$. Measurement of density by the Anton Paar Digital density meter is based on the oscillating U-tube method. The LC sample was introduced into a U-shaped tube that was electronically excited to oscillate at its characteristic frequency. The characteristic frequency of oscillation changes depending on the density of the filled sample. Through an accurate determination of the characteristic frequency the density of the sample was determined. The measurements were performed during cooling from the isotropic to different liquid crystalline phases with a stability time equal to 30 minutes for each reading.

2.2.6 Splay elastic constant (K_{11}) measurement

Study of the elastic constants offers an insight into the microscopic configuration of the different liquid crystalline mesophases. The nematic director may vary spatially owing to the application of an external field such as electric or magnetic field. The elastic constants are the molecular parameters which describe the restoring forces on a molecule within a LC phase in response to an externally applied field that distorts the LC medium from its minimum energy configuration. The deformations of the nematic phase under the distorting force can be associated

by the three basic elastic deformation modes *i.e.* splay, bend and twist (shown in Figure 2.3). Each of these three deformation modes are described by an individual elastic constant which can be determined experimentally by different methods. One of the most useful methodology employed to determine the elastic constant of liquid crystalline phases is the electric field induced Fredericksz transition [19,20,46,47]. The schematic representation of the director configuration of a liquid crystal sample above and below the Fredericksz transition is shown in Figure 2.3.

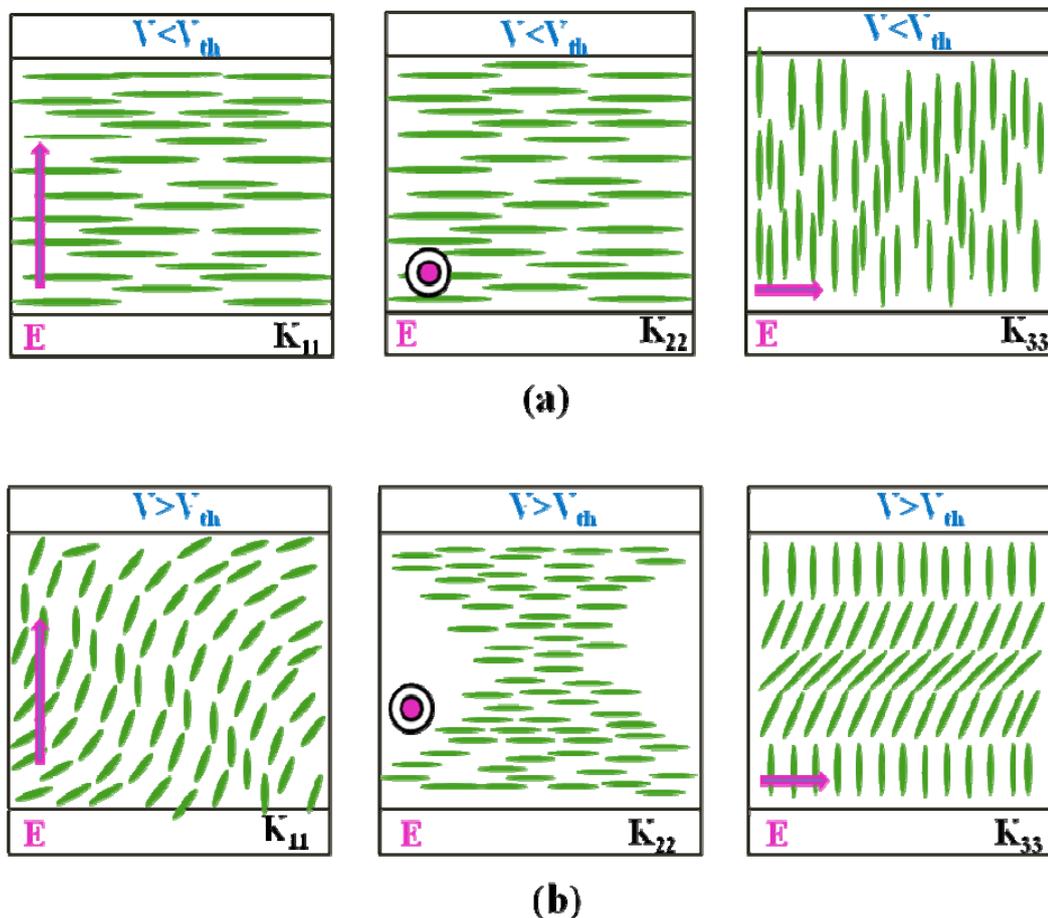


Figure 2.3 Schematic representation of the director configuration is shown (a) below threshold voltage (V_{th}) and (b) above the threshold voltage (V_{th}) respectively.

For the splay elastic constant (K_{11}) measurement, the liquid crystalline sample was first heated upto the isotropic phase and then cooled very slowly to the low temperature phase. After stabilizing the LC cell at a particular temperature, a sinusoidal voltage of frequency 1 kHz was applied to the cell. The applied voltage

was then increased in small steps from a value much lower than the Freedericksz threshold voltage to 20V. The temperature of the cell was regulated and measured by a temperature controller (Eurotherm PID 2404) with an accuracy of $\pm 0.1^\circ\text{C}$ while the variation in the capacitance value was recorded by the Agilent E4980A precession LCR-bridge as a function of the applied voltage [48-51]. The capacitance value changes significantly near a definite voltage which is known as the threshold voltage (V_{th}) (within $\pm 0.5\%$) for the Freedericksz transition (Figure 2.4). The splay elastic constant (K_{11}) is related to the threshold voltage (V_{th}) by the following equation [52-54]

$$K_{11} = \frac{\epsilon_0 \Delta\epsilon V_{th}^2}{\pi^2} \quad (2.6)$$

where ϵ_0 is the permittivity of free space and $\Delta\epsilon$ is the dielectric anisotropy. Therefore, using the value of V_{th} and $\Delta\epsilon$ the splay elastic constant has been calculated.

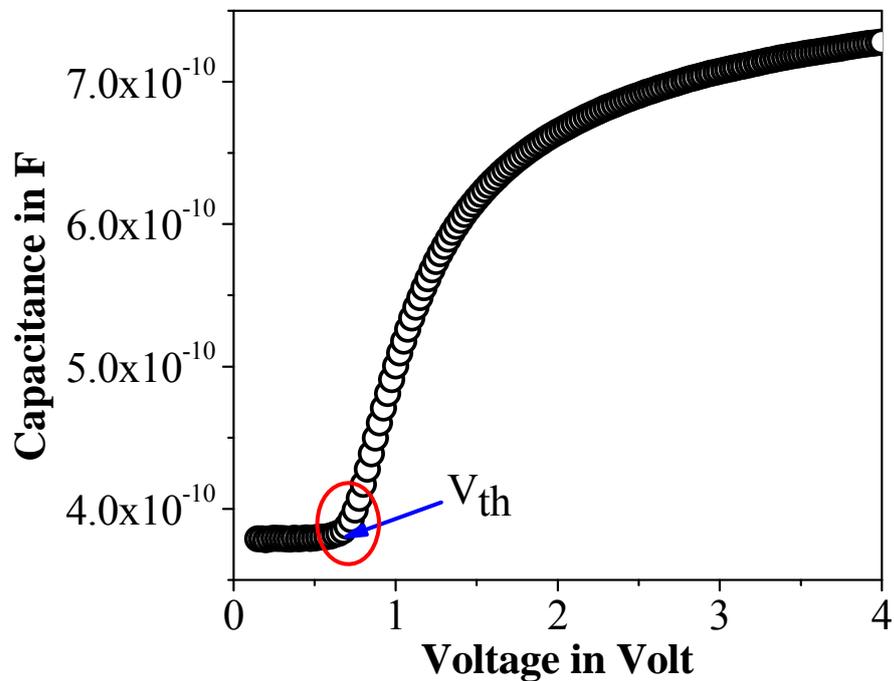


Figure 2.4 Voltage dependent capacitance change due to Freedericksz transition in a liquid crystal. The arrow indicates the Freedericksz threshold voltage (V_{th}).

2.2.7 Rotational viscosity measurement

Rotational viscosity (γ_1) is an important parameter in characterizing the dynamic physical properties of liquid crystals. It is correlated to the torque associated with the rotation of LC directors during molecular rotations and represents the force of internal friction between the liquid crystal directors. The rotational viscosity exhibits an intriguing dependence on the molecular structure and temperature. A capacitive relaxation method [37,50,55] have been used to measure the rotational viscosity of some binary liquid crystalline mixtures. First a voltage higher than the corresponding Freedericksz threshold voltage (V_{th}) was applied to the LC cell for a time of about 1 min. Then, this voltage was suddenly removed and the director re-orientes to the equilibrium state owing to the relaxation of elastic distortions with a characteristic relaxation time τ_0 . During relaxation, the change in the cell capacitance with time was recorded by the Agilent E4980A precession LCR-bridge in programmable mode and suitably interfaced with a computer. The operating frequency was kept fixed at 10kHz and a delay time of 30ms was introduced between the successive readings. In the small signal regime the difference between the instantaneous capacitance C_t (at time t) and the capacitance of the equilibrium state *i.e.* C_{\perp} follows a simple exponential decay with the following form [55]

$$\Delta C_t = C_t - C_{\perp} = \Delta C_0 \cdot \exp\left(-\frac{2t}{\tau_0}\right) \quad (2.7)$$

where $\Delta C_0 \sim C_{\perp} (\Delta\epsilon/2\epsilon_{\perp}) \cdot \phi_m$ for the LC molecules aligned in a planer geometry. ϕ_m is the tilt angle of the director in the middle of the layer at initial stage (*i.e.* $t = 0$). The experimental results [55] reveal that Equation (2.7) is a good approximation for $\phi_m < 1$. Therefore, variation of the transient capacitance was recorded against the time at various temperatures and from the slope of the logarithmic plot of $\Delta C_t/C_{\perp}$ vs time, the characteristic relaxation time τ_0 has been calculated. For a planar aligned LC cell of thickness d , the relaxation time (τ_0) is related to the rotational viscosity (γ_1) by the following relation [37,50,52,55]

$$\gamma_1 = \frac{\tau_0 K_{11} \pi^2}{d^2} \quad (2.8)$$

where K_{11} is the splay elastic constant. The temperature variation of the relaxation time and hence the rotational viscosity have been determined by placing the LC cell in a custom built brass made heater, the temperature of which was controlled and measured by a temperature controller (Eurotherm PID 2404) with an accuracy of $\pm 0.1^\circ\text{C}$.

2.2.8 Determination of activation energy

The temperature dependent rotational viscosity (γ_1) values has been fitted to the following expression [50,56-58]

$$\gamma_1 = \gamma_0 \langle P_2 \rangle \exp\left(\frac{E_a}{kT}\right) \quad (2.9)$$

where T is the absolute temperature, k is the Boltzmann constant, γ_0 is the fitting parameter, $\langle P_2 \rangle$ is the orientational order parameter which can be obtained from the birefringence (Δn) measurement and E_a is the associated activation energy. From the slope of the $\ln(\gamma_1/\langle P_2 \rangle)$ vs $1/T$ curve, the activation energy E_a can be determined.

2.3 Theoretical background

2.3.1 Maier-Saupe theory for the nematic phase

In the theoretical description of thermotropic nematics the Maier-Saupe mean field theory [1-3] is of historical importance. This theory is structurally simplest, technically most significant and also most successful among all the theories based on the molecular mean field approximation. The molecular statistical theory of Maier and Saupe is very much thriving in accounting for the main characteristics of the nematic phase (N) and nematic to isotropic (N-I) phase transition [4-7]. In the nematic phase, the constituent molecules are assumed to be rod-like and possess cylindrical symmetry with a tendency to orient their molecular long axis along a definite direction (\mathbf{n}), known as the director. It is assumed that a molecule orients under the action of a mean field due to the all other molecules present in the LC system and the orientational ordering in the nematic phase is developed by the anisotropic part of the dispersion interaction

between the constituent molecules. In addition, Maier and Saupe [1-3] further considered the following points:

- (i) for the long range nematic ordering the influence of the permanent dipoles can be ignored.
- (ii) the induced dipole-dipole interaction plays a key role in stabilization of the nematic phase; so the effect of this interaction should be considered.
- (iii) the liquid crystal molecules possess cylindrical symmetry with respect to the molecular long axis.
- (iv) with respect to a particular molecule, the centre of mass of the neighbouring molecules are distributed in a spherically symmetric configuration.

In case of nematics the molecular long axis makes an angle (θ) with the director, thus the distribution of molecular long axis about the director can be characterized by an orientational distribution function $\rho(\cos\theta)$. The rod-like nematic molecules have up-down symmetry *i.e.* the heads and tails of the constituent molecules are not distinguished separately. This makes $\rho(\cos\theta)$ an even function of $\cos\theta$. Accordingly, the orientational distribution function $\rho(\cos\theta)$ can be expressed as

$$\rho(\cos\theta) = \sum_{L\text{-even}} \frac{(2L+1)}{2} \langle P_L(\cos\theta) \rangle P_L(\cos\theta) \quad (2.10)$$

where $P_L(\cos\theta)$ is the L^{th} even order Legendre polynomial and $\langle P_L(\cos\theta) \rangle$ is the statistical average given by

$$\langle P_L(\cos\theta) \rangle = \int_0^1 P_L(\cos\theta) \rho(\cos\theta) d(\cos\theta) \quad (2.11)$$

$\langle P_L \rangle$ are called the orientational order parameters and the first term (*i.e.* for $L=2$) $\langle P_2 \rangle$ is generally known as the order parameter. In the disordered phase (isotropic phase) $\langle P_2 \rangle = 0$ whereas in the perfectly ordered state *i.e.* crystalline state $\langle P_2 \rangle = 1$. From the mean field theory the effective single molecule potential function $V(\cos\theta)$ of the cylindrically symmetric molecules is given by

$$V(\cos\theta) = \sum_{L\text{-even}} U_L \langle P_L \rangle P_L(\cos\theta) \quad (L \neq 0) \quad (2.12)$$

where U_L are the functions of the intermolecular distance between the central molecule and its neighbours only. Putting $L = 2$ in Equation 2.11 we can write

$$\langle P_2(\cos\theta) \rangle = \int_0^1 P_2(\cos\theta) \rho(\cos\theta) d(\cos\theta) \quad (2.13)$$

Keeping the first term (*i.e.* for $L=2$) of the right hand side of Equation 2.12, the orientational potential energy function of a single molecule can be written as

$$V(\cos\theta) = -v P_2(\cos\theta) \langle P_2 \rangle \quad (2.14)$$

where $v = -U_2$. Hence, the orientational distribution function in terms of the potential function (V) for a single molecule is expressed as

$$\rho(\cos\theta) = Z^{-1} \exp[-V(\cos\theta)/kT] \quad (2.15)$$

where k is the Boltzmann constant and Z is the single molecule partition function given by

$$Z = \int_0^1 \exp[-V(\cos\theta)/kT] d(\cos\theta) \quad (2.16)$$

Substituting the value of $\rho(\cos\theta)$ from Equation 2.15 into Equation 2.11, one can write

$$\langle P_2(\cos\theta) \rangle = \frac{\int_0^1 P_2(\cos\theta) \exp[P_2(\cos\theta) \langle P_2 \rangle / T^*] d(\cos\theta)}{\int_0^1 \exp[P_2(\cos\theta) \langle P_2 \rangle / T^*] d(\cos\theta)} \quad (2.17)$$

where $T^* = kT/v$

Equation 2.17 is a self-consistent equation because the term $\langle P_2 \rangle$ appears on both sides and can be solved by iterative method to obtain the temperature variation of $\langle P_2 \rangle$. For each value of T^* or temperature (T) there is a $\langle P_2 \rangle$ value which satisfies the above self-consistent equation. Now, $\langle P_2 \rangle = 0$ is a solution for all temperatures, which corresponds to the isotropic or disordered phase. Whereas for the temperatures $T^* < 0.22284$, two other solutions of Equation 2.17 emerge. It has been observed that the nematic phase becomes stable when T^* satisfies the condition $0 \leq T^* \leq 0.22019$ while for $T^* > 0.22019$, a thermodynamically stable isotropic phase with $\langle P_2 \rangle = 0$ appears. As the temperature increases, the orientational order parameter $\langle P_2 \rangle$ shows a decreasing tendency from unity to a minimum value of 0.4289 at $T^* = 0.22019$. A discontinuous change in $\langle P_2 \rangle$ from 0.4289 to 0 is observed at $T^* = 0.22019$. This sharp discontinuity indicates a first

order nature of the N-I phase transition.

Moreover, the entropy change in the vicinity of transition determines the order of that phase transition. Experimentally it has been observed that the entropy change near the N-I transition is relatively lesser than the same at the solid to liquid transition. Hence this phase transition is often called a weakly first order phase transition. Temperature dependent order parameter ($\langle P_2 \rangle$) can be determined by solving the self consistent Equation 2.17 iteratively. Although there are some approximations in the Maier-Saupe mean field theory but for a number of nematic liquid crystals the experimentally obtained order parameter values concur fairly well with those envisaged by the theoretical values [6,59,60].

2.3.2 McMillan theory for the smectic A phase

The smectic A phase is characterized by one dimensional positional ordering along with the long range nematic orientational order. The formation of layered structure in the smectic A phase can be described by a periodic density variation along the layer normal (along the z-axis). McMillan extended the Maier-Saupe mean field theory to explain the smectic A to nematic (SmA-N) phase transition in liquid crystals [8,9]. A parallel but more general formalism, based on the theory of melting [61], was proposed separately by Kobayashi [62,63]. However, in the Kobayashi model two particle distribution of the ordered phase makes the numerical calculation for a realistic potential very difficult. Several modifications and extensions were suggested [64-68] but the McMillan model still remains the easiest one for its usefulness in describing the qualitative behavior of the smectic A phase or the SmA-N phase transition.

In the McMillan theory, in addition to the orientational order parameter, a new order parameter which is related to the amplitude of the one dimensional density wave of the smectic A phase is introduced in the mean field potential energy function. Due to the presence of orientational as well as translational ordering in the smectic A phase the molecular distribution function of the same should be such that it can describe both the tendency of the molecules to orient along the director (\mathbf{n}) and to form layers perpendicular to the director. Hence, the normalized distribution function is a function of $\cos\theta$ and z and can be written as

$$\rho(\cos\theta, z) = \sum_{L\text{-even}} \sum_n A_{L,n} P_L(\cos\theta) \cos\left(\frac{2\pi n z}{d}\right) \quad (2.18)$$

with the normalized condition given by

$$\int_{-1}^1 \int_0^d \rho(\cos\theta, z) dz d(\cos\theta) = 1 \quad (2.19)$$

where d is the thickness of smectic layer. Following Kobayashi [62,63] McMillan [8,9] expressed the pair potential as:

$$V_M(\cos\theta, z) = -v \left[\delta \alpha' \tau \cos\left(\frac{2\pi z}{d}\right) + \left\{ \eta + \alpha' \sigma \cos\left(\frac{2\pi z}{d}\right) \right\} P_2(\cos\theta) \right] \quad (2.20)$$

where α' and δ are the two parameters of the pair potential. α' increases with increasing the length of the molecules and δ represents the strength of the two parts of the interaction *i.e.* the ratio of the translational part of the potential to the orientational part of the same. $\eta = \langle P_2(\cos\theta) \rangle$, $\tau = \langle \cos(2\pi z/d) \rangle$ and $\sigma = \langle P_2(\cos\theta) \cos(2\pi z/d) \rangle$ are the orientational, translational and mixed order parameters respectively, and $\langle \dots \rangle$ represents the statistical average of the quantities inside. The parameter v can be obtained from the relation $kT_{NI}/v = 0.22019$, knowing the nematic-isotropic (N-I) phase transition temperature (T_{NI}).

Now, the single molecule distribution function corresponding to the potential function can be written as:

$$\rho_M(\cos\theta, z) = Z^{-1} \exp[-V_M(\cos\theta, z)/kT] \quad (2.21)$$

where Z is the single particle partition function given by:

$$Z = \int_0^1 \int_0^d \exp[-V_M(\cos\theta, z)/kT] d(\cos\theta) dz \quad (2.22)$$

Again, three self consistent equations containing η , τ and σ appears which can be solved iteratively and are given by

$$\eta = \int_0^1 \int_0^d P_2(\cos\theta) \rho_M(\cos\theta, z) d(\cos\theta) dz \quad (2.23)$$

$$\tau = \int_0^1 \int_0^d \cos\left(\frac{2\pi z}{d}\right) \rho_M(\cos\theta, z) d(\cos\theta) dz \quad (2.24)$$

$$\sigma = \int_0^1 \int_0^d P_2(\cos\theta) \cos\left(\frac{2\pi z}{d}\right) \rho_M(\cos\theta, z) d(\cos\theta) dz \quad (2.25)$$

Depending on the values of different potential parameters, the following three solutions are possible:

- (i) $\eta = 0, \tau = 0, \sigma = 0$, this solution corresponds to the isotropic phase;
- (ii) $\eta \neq 0, \tau = 0, \sigma = 0$, this solution corresponds to the nematic phase in conformity with the Maier-Saupe theory;
- (iii) $\eta \neq 0, \tau \neq 0, \sigma \neq 0$, this solution corresponds to the smectic A phase.

The temperature dependence of η , τ and σ can be obtained by using the three self consistent equations for different values of α' and δ . For $\alpha' < 0.7$ and the dimensionless ratio of smectic A-nematic (T_{SN}) to nematic-isotropic (T_{NI}) phase transition temperatures *i.e.* T_{SN}/T_{NI} is less than the value 0.87, the McMillan theory envisages a second order nature of the smectic A to nematic (SmA-N) phase transition. When $\alpha' > 0.98$, a direct transition from smectic A phase to isotropic phase takes place, but for $\alpha' < 0.98$ there is a SmA-N phase transition trailed by a nematic-isotropic (N-I) transition at relatively higher temperature. Therefore, $\alpha' = 0.7$ and $T_{SN}/T_{NI} = 0.87$ confers to a tricritical point (TCP) at which the SmA-N phase transition changes its nature from second order to first order.

2.3.3 Landau theory of phase transition

Phase transitions involve breaking of symmetry of a thermodynamic system. In general, the high temperature phase (disordered phase) is more symmetric than the low temperature phase (more ordered phase). This symmetry breaking can be described by an order parameter, the exact nature of which depends on the system under study. According to the Landau theory of phase transition [13,14], different thermodynamic parameters of a system can be obtained by expanding the free energy density in a power series of order parameter near the transition. Landau theory relates the free energy density near the phase transition to the order parameter of the system. The information about the change in different physical quantities as well as the change of symmetry of the system is collected in the order parameter. This theory is of central importance in many

fields of condensed matter physics including magnetism, superconductivity, structural phase transition *etc.* The essential feature of the Landau theory of phase transition [13,14] is that it is a phenomenological theory which is based on the general considerations of symmetry and analyticity. It is not concerned with the details of the interactions at the atomic level that ultimately govern the behavior of any thermodynamic system. Instead, Landau theory is chiefly concerned with the symmetry of the system, indeed it only applies to phase transitions entailing a change in symmetry. One of the outcomes of this theory is that systems with similar symmetries- even very different system with different microscopic theories would look very identical within the Landau theory. Therefore, Landau theory offers a unified description of almost all the critical phenomena in the vicinity of phase transition and especially divulges the role of symmetry in phase transition.

Near the phase transition the free energy density f can be expressed in power series of a spatially invariant, dimensionless scalar order parameter (S) and sufficiently close to the transition point, only the leading terms of the power series are important, so that the free energy density expansion becomes a simple low order polynomial which can be expressed as

$$f(T,P,S) = f(T,P,0) + qS + \frac{1}{2}AS^2 + \frac{1}{3}BS^3 + \frac{1}{4}CS^4 + \dots \quad (2.26)$$

where $f(T,P,0)$ is the free energy density in the disordered phase ($S = 0$). All the coefficients q, A, B, C, \dots are phenomenological and function of temperature and pressure. The equilibrium conditions are obtained by minimizing f with respect to the order parameter (S) for fixed temperature (T) and pressure (P), and the conditions are given by

$$\frac{df}{dS} = 0 \quad (2.27)$$

and
$$\frac{d^2f}{dS^2} > 0 \quad (2.28)$$

Therefore, at the transition it gives

$$\left(\frac{df}{dS} \right)_{S=0} = q = 0 \quad (2.29)$$

and
$$\left(\frac{d^2f}{dS^2} \right)_{S=0} = A \quad (2.30)$$

The coefficient in the linear term of the free energy density expansion *i.e.* $q = 0$ confirms the stability of the high temperature phase. In the disordered phase ($S = 0$) the minimum in f is ensured by assuming the coefficient $A > 0$ while in the ordered phase ($S \neq 0$) the minimum in f is ensured by assuming $A < 0$. Moreover, near the phase transition the second order term in Equation (2.26) *i.e.* $\frac{1}{2}(AS^2)$ becomes increasingly significant. Thus, to ensure that the value $S = 0$ corresponds to a minimum of free energy, the coefficient A should depend on temperature and also must change sign as a function of temperature. Landau assumed that $A = a(T - T_C)$, where T_C is the transition temperature and a is constant. Therefore, Equation (2.26) can be written as

$$f(T,P,S) = f(T,P,0) + \frac{1}{2}a(T - T_C)S^2 - \frac{1}{3}BS^3 + \frac{1}{4}CS^4 + \dots \quad (2.31)$$

In the vicinity of phase transition two solutions are obtained from Equation (2.27) as

$$S = 0 \quad (2.32)$$

and
$$S = \frac{B \pm [B^2 - 4aC(T - T_C)]^{1/2}}{2C} \quad (2.33)$$

The negative sign of the coefficient B is preferred for the reason of convenience. But, the symmetry of the order parameter requires that the cubic and all other higher order odd terms are not allowed; only the terms containing even powers of S will survive in the free energy density expansion. So the free energy density can be written as

$$f(T,P,S) = f(T,P,0) + \frac{1}{2}a(T - T_C)S^2 + \frac{1}{4}CS^4 + \dots \quad (2.34)$$

The equilibrium value of the order parameter for the low temperature phase is given by

$$S = \frac{a(T - T_C)^{1/2}}{C} \quad (2.35)$$

with positive C values. It should be mentioned that the Landau theory can be extended to the first order phase transition by two different ways [7]. The first condition is that the coefficient B is equal to zero and C is less than zero. In addition the sixth order term with the corresponding coefficient E>0 is required to confirm the stability of the ordered phase. The other possibility is to consider the presence of a third order term BS³ in the free energy expansion (Equation 2.26). When the order parameter is a tensorial quantity the cubic term BS³ cannot be removed from the free energy expansion, therefore a first order phase transition can also be obtained for B≠0.

2.3.3.1 Nematic-Isotropic (N-I) phase transition

Landau theory of phase transition [4-7,10-14] is basically a theory of second order phase transition but de Gennes [6] was the first to successfully apply this theory to the first order nematic-isotropic (N-I) phase transition in liquid crystals. de Gennes built a detailed mean field theory, based on the Landau theory that describes at least qualitatively the main characteristics of the LCs and their phase transitions. The strengths of the Landau-de Gennes [6,10-14] theory lies in the fact that it provides a satisfactory explanation of the phase transition from a phenomenological point of view. The nematic phase can be described by a symmetric tensorial order parameter **Q** with trace equal to zero *i.e.* Q_{ii} = 0 [7]. According to Landau-de Gennes theory the first order nematic-isotropic phase transition in LCs can be well explained by expanding the free energy density up to the fourth order in the tensor order parameter **Q** in the vicinity of transition. As the free energy is a scalar quantity, only those terms which are invariant combinations of Q_{ij} of the order parameter are present in the expansion [5]. Therefore, the free energy density can be written as

$$g_n = g_i + \frac{1}{2} A_{ijkl} Q_{ij} Q_{kl} - \frac{1}{3} B_{ijklmn} Q_{ij} Q_{kl} Q_{mn} + \frac{1}{4} C_{ijklmnuv} Q_{ij} Q_{kl} Q_{mn} Q_{uv} \quad (2.36)$$

where g_n and g_i are the Gibbs free energy density of the nematic and isotropic phases respectively. The coefficients A, B and C are tensorial in nature and function of temperature (T) and pressure (P). The negative sign of B is chosen for convenience. In the above expression there is no term linear in the order parameter

owing to the different symmetry of the two phases. Also absence of the linear term in the free energy expansion is in accordance with the stable isotropic phase. In case of an externally applied field, a linear term has to be incorporated in the free energy density expansion, making the high temperature isotropic phase impossible [5]. Now, instead of the Gibbs free energy density the Helmholtz free energy density in Equation (2.36) has been found to be more suitable because most of the molecular statistical calculations are generally performed at constant density. For the uniaxial nematic phase the Helmholtz free energy density f_n can be expanded in the following way [5]:

$$f_n = f_i + \frac{1}{2} A Q_{ij} Q_{ji} - \frac{1}{3} B Q_{ij} Q_{jk} Q_{ki} + \frac{1}{4} C (Q_{ij} Q_{ji})^2 \quad (2.37)$$

where f_n and f_i are the Helmholtz free energy densities of the nematic and isotropic phases respectively. The variation of pressure near the transition is so small that it can be neglected from the free energy expansion. Therefore, it can be considered that the tensors A, B and C are independent of pressure and solely depend upon the temperature. Equation (2.37) has been formulated in terms of the invariants $Q_{ij} Q_{ji}$ and $Q_{ij} Q_{jk} Q_{ki}$. All the higher order invariants can be constructed by these two invariants.

The nematic-isotropic (N-I) phase transition occurs near $A = 0$. It has been assumed that in the vicinity of N-I transition the temperature dependence of the free energy density is contained only in the coefficient A and the other two coefficients B and C can be regarded as temperature independent terms. The phase transition can be described by writing

$$A = a(T - T^*) \quad (2.38)$$

where T^* is the temperature slightly below the transition temperature T_{NI} and a is a temperature independent positive constant. Using the representation of the order parameter described in chapter 1 (Equation 1.2) it can be shown that $Q_{ij} Q_{ji} = (2/3)S^2$ and $Q_{ij} Q_{jk} Q_{ki} = (2/9)S^3$. Putting these values in Equation (2.37) and using Equation (2.38) the corresponding Landau-de Gennes free energy density is given by

$$f_n = f_i + \frac{1}{3} a(T - T^*) S^2 - \frac{2}{27} B S^3 + \frac{1}{9} C S^4 \quad (2.39)$$

Minimizing f_n with respect to S , the equilibrium value of the corresponding order parameter can be obtained. S can be calculated from the following expression

$$a(T - T^*)S - \frac{1}{3}BS^2 + \frac{2}{3}CS^3 = 0 \quad (2.40)$$

The solutions of Equation (2.40) are $S = 0$, corresponds to the high temperature stable isotropic phase and

$$S_{\pm} = \frac{B}{4C} \left[1 \pm \left(1 - \frac{24aC(T - T^*)}{B^2} \right)^{1/2} \right] \quad (2.41)$$

The temperature dependence of the order parameter in the nematic phase is correctly illustrated by S_+ . The phase transition temperature T_{NI} can be calculated by using the condition $f_n = f_i$, which yields

$$a(T_{NI} - T^*)S_{NI}^2 - \frac{2}{9}BS_{NI}^3 + \frac{1}{3}CS_{NI}^4 = 0 \quad (2.42)$$

while the other expression which relates T_{NI} and S_{NI} as obtained from Equation (2.40) is given by

$$a(T_{NI} - T^*)S_{NI} - \frac{1}{3}BS_{NI}^2 + \frac{2}{3}CS_{NI}^3 = 0 \quad (2.43)$$

Combining the above two equations it can be written that

$$\frac{1}{9}BS_{NI}^3 = \frac{1}{3}CS_{NI}^4 \quad (2.44)$$

Therefore, the possible solutions are

(a) $S_{NI} = 0$, $T_{NI} = T^*$

(b) $S_{NI} = \frac{B}{3C}$, $T_{NI} = T^* + \frac{B^2}{27aC}$

Evidently the S_- solution offers the results $S_{NI} = 0$ at $T_{NI} = T^*$ while the S_+ , the thermodynamically stable solution gives $S_{NI} = \frac{B}{3C}$ at $T_{NI} = T^* + \frac{B^2}{27aC}$. Equation (2.41) representing the two solutions (S_+ and S_-) determine a third temperature T^{**} given by

$$T^{**} = T_{NI} + \frac{B^2}{24aC} \quad (2.45)$$

When the temperature T is higher than T^{**} both the solutions are no longer valid owing to their complex nature. Therefore, the Landau-de Gennes theory differentiates four temperature regions [5]:

(i) when $T > T^{**}$, the minimum corresponds to the stable high temperature isotropic phase with $S = 0$.

(ii) when $T_{NI} < T < T^{**}$, $S = 0$ is also a solution which gives minimum free energy density. Moreover, there is a relative minimum and maximum for $S = S_+$ and $S = S_-$ respectively. Therefore, an energy density barrier results in between the two minima ($S = 0$ and $S = S_+$) with an effective height $[f_n(S_-) - f_n(S_+)]$. It signifies that a metastable nematic phase region can be obtained in this temperature range because of overheating. The barrier height becomes zero at T^{**} for $S_+(T^{**}) = S_-(T^{**}) = \frac{B}{4C}$ and the associated point in the free energy density curve is a point of inflection.

(iii) when $T^* < T < T_{NI}$, the minimum corresponds to a nematic phase. In addition there is a relative local minimum which give rise to a possible super-cooled isotropic phase.

(iv) when $T < T^*$, the minimum corresponds to thermodynamically stable nematic phase. The S_+ solution has the lowest free energy density while S_- and $S = 0$ solutions correspond to a relative minimum and maximum respectively. The energy barrier height between the S_+ and S_- solution is given by $f_i - f_n(S_-)$.

Figure 2.5 illustrates the variation of $\Delta f = f_n - f_i$ on the order parameter (S) for different characteristic temperatures. A critical temperature can be identified for which the two phases can co-exist with the same free energy density. There exists an energy barrier at the transition temperature $T = T_{NI}$ between the nematic and isotropic phase and the height is given by $H = \frac{B^4}{11664C^3}$. The existence of this energy barrier owing to the presence of the cubic term in the free energy density expansion is the characteristic signature of a first order phase transition [5]. The general behavior of the order parameter (S) vs. temperature in case of a first order phase transition is shown in Figure 2.6. The order parameter vanishes at the nematic-isotropic (N-I) phase transition temperature (T_{NI}). The Landau coefficients have been experimentally determined by Oswald *et al.* [69] and Vertogen *et al.* [5]

for the two liquid crystalline compounds 4-n-pentyl-4'-cyanobiphenyl (5CB) and 4-methoxybenzylidene-4-n-butylaniline (MBBA) respectively.

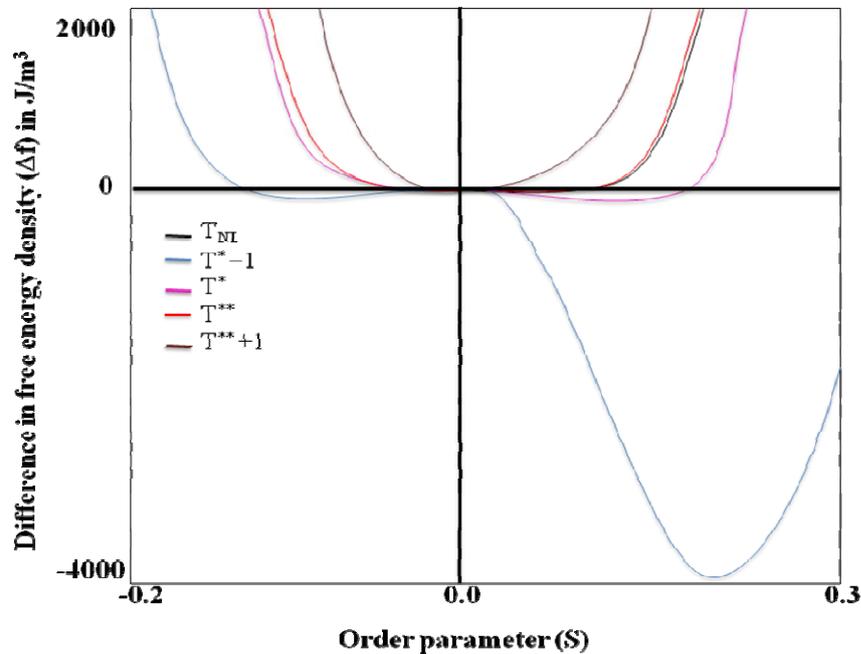


Figure 2.5 Difference in the free energy density (Δf) as a function of scalar order parameter S .

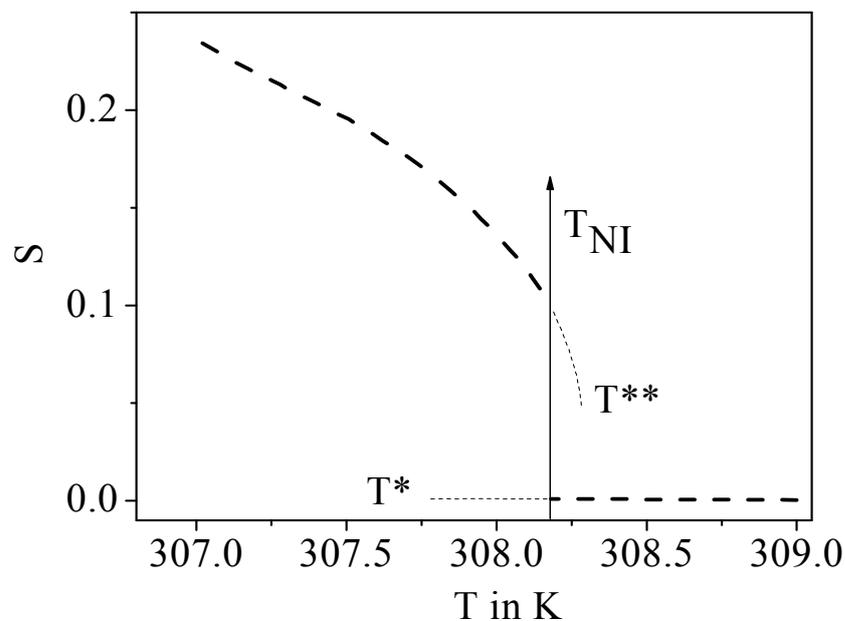


Figure 2.6 The nematic order parameter (S) vs. temperature. T^* and T^{**} are the temperatures slightly lower and higher than T_{NI} respectively. T^* and T^{**} are also known as the spinodal temperatures.

2.3.3.2 Smectic A-Nematic (SmA-N) phase transition

The smectic A-nematic (SmA-N) phase transition entails a re-arrangement of the LC molecules in a layered structure. On an average the centre of mass of the LC molecules in the smectic A (SmA) phase are arranged in equidistant plane. Within the layers the molecules can move freely with the director perpendicular to the smectic layers [7]. In the thermodynamic limit, the SmA phase do not possesses true long range translational ordering, hence the theory of SmA-N phase transition is a theory of one dimensional melting. The SmA-N phase transition is accompanied by a spontaneous translational symmetry breaking due to the appearance of a one dimensional density wave in the SmA phase [7]. According to McMillan [8] and de Gennes [6] the SmA-N phase transition could be either first order or second order. The crossover from the second order to first order nature takes place through a tricritical point (TCP). On the other hand, Halperin *et al.* [70] envisaged that the SmA-N transition is always first order in nature which rules out the possibility of a tricritical point.

The phenomenological Landau-de Gennes theory for the nematic-isotropic (N-I) phase transition can be extended to the SmA-N transition by defining a suitable order parameter for the SmA phase. The order parameter for the SmA-N transition has been defined to be the amplitude of the density wave ($|\Psi|$) which describes the formation of layered structure in the SmA phase. The difference between $|\Psi|$ and $-|\Psi|$ simply depends on the selection of origin, thus the free energy density expansion contains only the even power terms. The SmA phase is described by a density modulation in the \mathbf{z} direction perpendicular to the layers [6,7]

$$\eta(\mathbf{r}) = \eta_0 + \eta_1 \cos(mz - \phi) \quad (2.46)$$

where η_1 stands for the first harmonic of the density modulation, m is an integer and ϕ is an arbitrary phase angle. In case of nematic η_1 is zero while for the smectic A phase it is the main candidate governing the SmA order parameter. The free energy density (f_{SmA}) near the SmA-N transition can be expanded in power series of η_1 :

$$f_{\text{SmA}} = \frac{1}{2} \lambda_2 \eta_1^2 + \frac{1}{4} \lambda_4 \eta_1^4 \quad (2.47)$$

The coefficient λ_2 is assumed to be equal to $\lambda_0(T-T_0)$ where T_0 is a temperature very close to the SmA-N transition temperature (T_{SN}). λ_2 changes its sign on crossing T_0 . When $T>T_0$, λ_2 is positive and for $T<T_0$, λ_2 is negative while the other coefficient λ_4 is always positive. From these considerations only the second order (continuous) phase transition could be obtained at $T_{SN} = T_0$. Moreover, to account for the influence of the smectic layering on the orientational order parameter a coupling term (f_{AN}) should be added to the free energy density expansion. Denoting the orientational order parameter in the SmA phase by $S(T)$, f_{AN} can be written as [7]

$$f_{AN} = -\xi\eta_1^2\delta S \quad (2.48)$$

where ξ is a constant with positive value and $\delta S = S-S_0(T)$, $S_0(T)$ being the nematic order parameter in absence of the smectic phase. In addition to this another term i.e. the nematic free energy density (f_N) should also be added. f_N can be expressed as

$$f_N = f_N(S_0) + \frac{1}{2\chi}\delta S^2 \quad (2.49)$$

where $\chi(T)$ is the response function which is small for $T < T_{NI}$ owing to the saturation of the nematic order parameter but large near the nematic-isotropic (N-I) phase transition. Therefore the total free energy density [7] is

$$f = f_{SmA} + f_N + f_{AN} = \frac{1}{2}\lambda_2\eta_1^2 + \frac{1}{4}\lambda_4\eta_1^4 + f_N(S_0) + \frac{1}{2\chi}\delta S^2 - \xi\eta_1^2\delta S \quad (2.50)$$

Minimization of f with respect to δS gives

$$\delta S = \chi\xi\eta_1^2 \quad (2.51)$$

and

$$f = f_N(S_0) + \frac{1}{2}\lambda_2\eta_1^2 + \frac{1}{4}\lambda'_4\eta_1^4 \quad (2.52)$$

with

$$\lambda'_4 = \lambda_4 - 2\chi\xi^2 \quad (2.53)$$

λ'_4 depends upon the values of χ and ξ . The sign of λ'_4 determines the order of the SmA-N phase transition. There are three cases as follows: (i) when $T_0 \sim T_{NI}$, $\chi(T_0)$ is large and λ'_4 is negative. In this case the SmA-N transition is first order in nature

and takes place $T_{SN} > T_0$. Additionally, to ensure the stability a sixth order term with positive coefficient must be added to Equation (2.52).

(ii) when $T_0 \ll T_{NI}$, $\chi(T_0)$ is small and $\lambda_4 \sim \lambda_2 > 0$. The SmA-N transition is second order in nature and takes place at $T_{SN} = T_0$.

(iii) when $\lambda'_4 = 0$, $\chi(T_{SN}) = \lambda_4/2\xi^2$; a crossover from second order to first order behavior occurs through a tricritical point (TCP) due to the coupling between the nematic and smectic order parameter.

Thus, the strong coupling between the nematic and smectic order parameter drives the SmA-N phase transition towards the tricritical behavior [71]. The McMillan ratio (T_{SN}/T_{NI}) *i.e.* the ratio of the SmA-N phase transition temperature and N-I phase transition temperature is a convenient parameter governing the strength of the SmA-N phase transition.

2.3.4 Elastic continuum theory

Different molecular theories of liquid crystalline phases are not always useful to describe some large scale phenomena. There exist a number of physical phenomena which involves the response of bulk liquid crystalline materials to external stimuli that cannot be explained in the light of molecular theories rather can be described by assuming the liquid crystal as a continuous media [4,15] with a set of elastic constants. Generally, these elastic constants are named splay (K_{11}), twist (K_{22}) and bend (K_{33}) elastic constant and collectively they are known as the Frank elastic constant. The Frank elastic constants are correlated to the energy cost of re-orienting the LC director from an equilibrium value. The foundations of the elastic continuum theory of liquid crystals were developed by Oseen [16], Zocher [17] and later on reformulated by Frank [18]. This continuum theory has proved to be very much useful in describing the behavior of uniaxial LCs under the different perturbing fields such as electric or magnetic fields. In case of nematics, the parallel arrangement of the LC directors corresponds to a stable state with minimum free energy. But, if an external perturbation is applied to the system, then the orientation of the LC directors will no longer remains spatially uniform. In this way the free energy of the LC system increases and this deformed state have higher free energy than the equilibrium state.

According to the continuum theory, the free energy (or Frank energy) density (F_{def}) of a deformed liquid crystal in its minimum energy configuration can be expressed by three basically independent elastic constants as [4,15]

$$F_{\text{def}} = \frac{1}{2} [K_{11} (\nabla \cdot \mathbf{n})^2 + K_{22} (\mathbf{n} \cdot \nabla \times \mathbf{n})^2 + K_{33} (\mathbf{n} \times \nabla \times \mathbf{n})^2] \quad (2.54)$$

where \mathbf{n} is the director. The above equation is the standard expression for the elastic free energy density related to the distortion of the director field for a nematic LC in absence of any chirality. The free energy density F_{def} must have positive value so as to confer stability for the uniformly aligned LC phase. Therefore, all the elastic constants associated with the splay, twist and bend deformations are positive quantity [72].

2.3.5 Freedericksz transition

Liquid crystalline compounds are composed of anisotropic molecules, which is responsible for the anisotropy of all their physical properties. In case of a nematic LC, the minimum energy configuration is reached when all the rod-like molecules are, on an average, aligned along a definite direction which is pointed out by the director \mathbf{n} . The orientation of the LC director can be experimentally specified either by an externally applied field or by imposing some surface anchoring conditions. Moreover, if a liquid crystal layer between two parallel plates is subject to an externally applied electric, magnetic or optical field then a competition between the surface anchoring and the reorienting externally applied field would cause a transition at which the undistorted configuration of the LC director would change to a distorted configuration. This transition is generally known as field induced Freedericksz transition [4,5,19,20,57]. It depends on the different boundary conditions at the substrates and on the sign and magnitude of the dielectric anisotropy ($\Delta\epsilon$). For a weak applied field the elastic contribution wins over the external perturbation and the director stays unaffected by the field whereas for an adequate applied field, the initial configuration of the LC molecules due to the surface anchoring vanishes and the sample is switched to other configuration. This particular field is called Freedericksz threshold. The threshold voltage of the Freedericksz transition depends on the geometry of the set up *i.e.* on the orientation of the surface anchoring related to the external field.

Furthermore, the total free energy of the nematic phase encompasses two components: first, the elastic free energy which originates from the elastic deformation and secondly, the dielectric free energy which arises from the interaction between the anisotropic liquid crystal molecules and the applied field. In order to solve the steady state director distribution, this total free energy of the system should be minimized. Conversely, to accomplish the dynamic response of the directors, the field induced torque and the elastic torque must be balanced with the viscous torque.

In an aligned (parallel) nematic liquid crystal cell, the LC directors are along the x axis and the two bounding surfaces are at $z = 0$ and $z = d$ (cell thickness). When the applied voltage (V) along the z-axis is greater than the Freedericksz threshold voltage (V_{th}), the LC system endures an elastic deformation; accordingly the directors become tilted in the xz plane. The amount of tilt depends on the distance from the boundary surface with a minimum value of zero at the boundaries and a maximum value at $z = d/2$.

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