

# Chapter 1

## INTRODUCTION

### 1.1 Liquid Crystals

Liquid crystals are anisotropic liquids [1-4]. They consist of shape anisotropic (disc-like or rod-like) organic molecules. They occur in between the solid crystal and isotropic liquid phases, in certain compounds consisting of such molecules and are hence called *mesophases*. They exhibit some properties of liquids and some others of crystals: they can flow like a liquid and also exhibit properties such as birefringence.

There are basically two classes of liquid crystals, *viz.* **thermotropics** and lyotropics. Single compounds or mixtures which show mesomorphic behaviour as a function of temperature are called thermotropic liquid crystals. Lyotropic liquid crystals arise when amphiphilic compounds are dissolved in solutions like water. The **mesomorphism** occurs in some range of the **concentration**. In this thesis we will discuss some properties of thermotropic liquid crystals consisting of rodlike, achiral molecules.

### 1.2 Classification of Thermotropic Liquid Crystals

Thermotropic liquid crystals are classified depending on the symmetry of the medium. Liquid crystals consisting of rod-like achiral molecules exhibit nematic and/or smectic phases.

#### 1.2.1 Nematic Liquid Crystals

The nematic phase (N) is an orientationally ordered fluid. The distribution of the centres of mass of the molecules in the medium is liquid like. The long axes of the molecules are on average oriented about a specific direction denoted by a unit vector  $A$  (Figure 1.1) called the **director**.  $A$  and  $-A$  are indistinguishable *i.e.* the polarity of the molecules does not lead to a polarity in the medium **as** there are as many molecules 'pointing up' **as** there are 'pointing down'.

#### 1.2.2 Smectic A Liquid Crystals

Smectic liquid crystals are characterised by a 1-dimensional translational order in addition to the orientational order in the medium. This gives rise to a layered arrangement of the molecules **as** shown in Figure 1.2. Within the layers the distribution of the centres of mass of **the** molecules is liquid-like. In smectic A ( $S_A$ ) the director  $A$  is parallel to the layer **normal**. The one dimensional periodicity along the layer normal gives rise to large thermal fluctuations in the layers [1] and

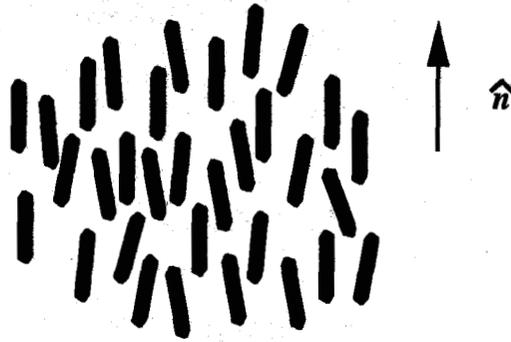


Figure 1.1: Schematic diagram of the molecular arrangement in a nematic liquid crystal

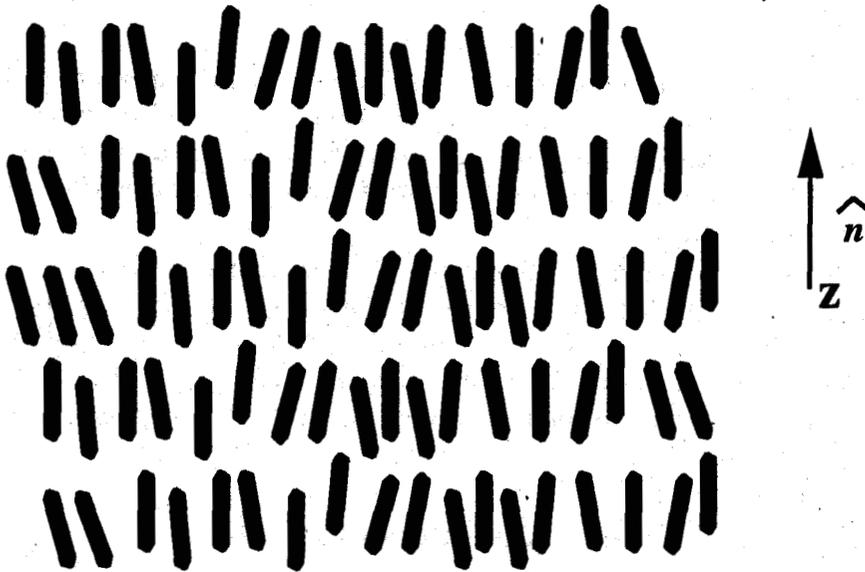


Figure 1.2: Schematic diagram of the molecular arrangement in a smectic A liquid crystal

is well described by a sinusoidal density wave given by

$$\rho = \rho_0 [1 + \text{Re}\{|\psi|e^{i(q_0 z + \phi)}\}] \quad (1.1)$$

where  $z$  is along the layer normal,  $\rho_0$  is the average density,  $|\psi|$  is the amplitude of the density wave,  $q_0 (= \frac{2\pi}{d})$  the wave vector and  $\phi$  is an arbitrary phase. The thickness ( $d$ ) of the layers is usually slightly less than the length of the molecules ( $l$ ). However, when there is a dipole moment positioned at the end of the molecule a variety of smectic A phases can be observed, with layer spacings varying from  $\sim l$  to  $2l$ .

### 1.2.3 Reentrant Liquid Crystalline Phases

Normally, it is expected that as the temperature is decreased the symmetry of the lower temperature phase is lower than that of the higher temperature phase. Accordingly, the smectic A phase which has a lower symmetry than the nematic phase, can be expected to occur at lower

## Introduction

temperatures. Indeed in most of the liquid crystals this sequence is followed. However it was discovered by Cladis [5] that a certain mixture of polar compounds exhibits the following phase sequence

$$\text{Isotropic (I) - N - S}_A \text{ - N}_R \text{ - Crystal (C).}$$

The lower temperature nematic phase ( $N_R$ ) has been termed as the reentrant nematic phase. Subsequently, she also found that a certain compound [6], at elevated pressures, shows a similar effect. Later pure compounds were found which exhibited the reentrant nematic phase even at atmospheric pressure [7, 8, 9]. It has been found that some compounds exhibit not only a reentrant nematic phase but also a reentrant smectic A phase ( $S_{AR}$ ) which is obtained on cooling the  $N_R$  phase [10, 11], the phase sequence being

$$\text{I - N - S}_A \text{ - N}_R \text{ - S}_{AR} \text{ - C.}$$

All of the systems which exhibit reentrant nematic and smectic A phases consist of molecules having a strongly polar end group.

As our experiments have been conducted on compounds which exhibit only the nematic, smectic A and reentrant nematic phases, we will not discuss the various other liquid crystalline phases exhibited by compounds with rod-like molecules.

### 1.3 Orientational Order Parameter

As mentioned earlier the nematic phase is characterised by an average orientational order of the long axes of the molecules about a specific direction called the director. The order parameter gives us a measure of the distribution of these molecules about this direction. In view of the apolar nature of the nematic liquid crystal the order parameter is a second rank tensor. For cylindrical molecules the order parameter is defined as [12]

$$S = \frac{3 \langle \cos^2 \theta \rangle - 1}{2} \quad (1.2)$$

If the distribution of the long molecular axes is random as in the isotropic phase then  $\langle \cos^2 \theta \rangle = 1/3$  and  $S = 0$ . In the fully aligned state  $\langle \cos^2 \theta \rangle = 1$  and  $S = 1$ . The nematic-isotropic phase transition is first order in nature. The order parameter at the phase transition point is  $-0.3$  to  $0.4$ . Deep in the nematic phase  $S$  can increase to about  $0.8$ . Thermodynamically the N-I transition is a weak transition, with a heat of transition  $\sim 0.2 \text{ kcal/mole}$ . On the other hand the N- $S_A$  transition can be either first order or second order in nature, depending on the length of the alkyl chains in the molecules.

### 1.4 Curvature Elasticity

In a nonuniformly oriented nematic the director orientation varies continuously in space. All the deformations of the director can be considered to be a combination of three basic curvature deformations. They are splay, twist and bend as shown in Figure 1.3. The deformation free energy density ( $F_d$ ) is given by

$$F_d = \frac{1}{2} K_1 (\nabla \cdot \hat{n})^2 + \frac{1}{2} K_2 (\hat{n} \cdot \nabla \times \hat{n})^2 + \frac{1}{2} K_3 (\hat{n} \times \nabla \times \hat{n})^2 \quad (1.3)$$

where  $K_1$ ,  $K_2$  and  $K_3$  are the splay, twist and bend elastic constants respectively. Usually, the order of magnitude of the elastic constants is  $\sim 10^{-7}$  dynes.

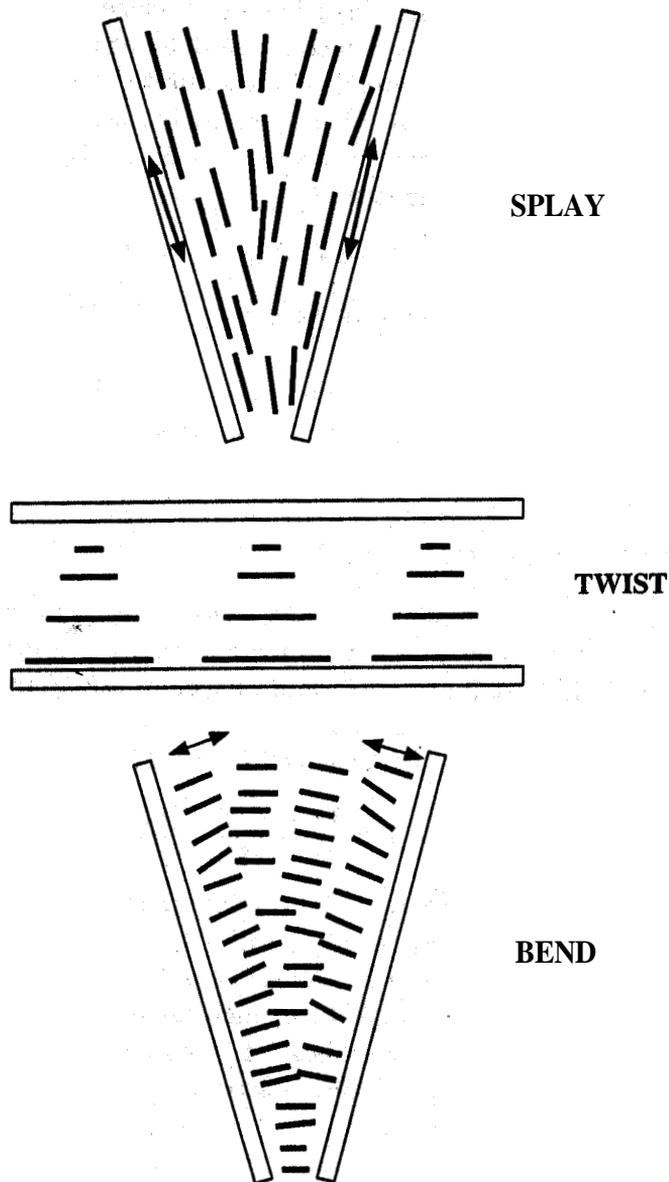


Figure 1.3: The three principal types of deformations in a nematic liquid crystal. Arrows indicate the direction of the **director**. In the **twist** geometry the lines represent the projection of the director on the page.

## 1.5 Anisotropic Physical Properties

A macroscopic anisotropy is found in a physical property because the molecular anisotropy related to this property does not average out to zero in the nematic phase. Many of these physical properties have the character of second rank tensors and can be used to measure the orientational order parameter. We describe the anisotropies in some **physical** properties which are relevant to the work presented in this thesis.

### 1.5.1 Refractive Index

The nematic liquid crystal, which is a uniaxial medium has two principal **refractive** indices,  $n_o$  and  $n_e$ . The ordinary index  $n_o$  is experienced by a light wave propagating orthogonal to A and polarised perpendicular to A. The extraordinary index  $n_e$  is experienced by a light wave propagating normal to A and polarised parallel to A. A similar definition applies to the smectic A phase. The birefringence is given by

$$\Delta n = n_e - n_o > 0. \quad (1.4)$$

$\Delta n$  for nematics is typically 0.1 to 0.2.

### 1.5.2 Dielectric Constant

The dielectric constant is a measure of the response of matter to an electric field [13, 14]. In a material consisting of nonpolar molecules the field induces a polarisation. In materials with polar molecules in addition to the induced polarisation an **orientation polarisation** occurs due to the tendency of the permanent dipole moments to orient **parallel** to the field. Due to fixed orientations of the molecules in a crystal the orientational polarisation does not contribute significantly to the permittivity of a solid. In liquid crystals, due to the possibility of the reorientations of the molecules the permanent dipoles can contribute significantly to the orientation polarisation and hence to the dielectric constant.  $\epsilon_{\parallel}$  and  $\epsilon_{\perp}$  are the dielectric constants measured with the field parallel and perpendicular to the director respectively. The dielectric **anisotropy**  $\epsilon_a$  is given by

$$\epsilon_a = \epsilon_{\parallel} - \epsilon_{\perp}. \quad (1.5)$$

For nematic liquid crystals consisting of polar molecules with the dipoles along the long axes,  $\epsilon_a$  usually has values between 10 to 20.

**Maier** and **Meier** [15] have developed a theory, which is an extension of **Onsager's** theory for polar molecules [14], in which they relate the macroscopic dielectric anisotropy with the anisotropies arising due to various molecular parameters. In their model they assume that the molecules have principal polarisabilities  $\alpha_l$  and  $\alpha_t$  along and transverse to the **long axis** of the molecule. Furthermore there is a permanent dipole  $\mu$  that **makes** an angle  $\beta$  with the long axis. Therefore  $\mu_l = \mu \cos \beta$  and  $\mu_t = \mu \sin \beta$ . It is assumed that the molecule is in a spherical cavity of radius  $a$  surrounded by a medium with dielectric constant  $\epsilon$  which **consists of** the remaining molecules.

Due to the polarisation of the medium the field experienced by the molecules is not **equal** to the external field. The actual field at the site of the **molecule** is called **the** internal field ( $\vec{E}_i$ ). The contribution of the orientation of the permanent dipole moments ( $\vec{\mu}$ ) to the polarisation is proportional to the Langevin function

$$\bar{\mu} = \frac{\mu^2}{3k_B T} E_d \quad (1.6)$$

where  $k_B$  is the **Boltzmann** constant and  $T$  is the **absolute** temperature.  $\vec{E}_d$  is a part of  $\vec{E}_i$  which reorients the **dipole**.  $\vec{E}_d$  is not **equal** to  $\vec{E}_i$  for the following reason: When a molecule with a permanent dipole moment is surrounded by other similar molecules the inhomogeneous field of the permanent dipole **also polarises** the medium. The field due the **permanent** dipole is called the reaction field  $\mathcal{R}$ . This reaction field is proportional to the permanent dipole moment and is given by

$$\vec{R} = f\vec{\mu} \quad (1.7)$$

where  $f$  is the reaction field factor. The reaction field for a polarisable dipole is given by

$$\vec{R} = f(\vec{\mu} + \alpha\vec{R}) \quad (1.8)$$

where  $\alpha$  is the polarisability. This reaction field contributes to  $\vec{E}_i$ , whereas it does not contribute to  $\vec{E}_d$  (as  $\vec{R}$  is along the direction of the dipole). Hence  $\vec{E}_i$  is a sum of the directing field and the reaction field

$$\vec{E}_i = \vec{E}_d + \mathcal{R}. \quad (1.9)$$

When a spherical cavity is surrounded by a dielectric medium of dielectric constant  $\epsilon$  the field experienced inside the cavity ( $\vec{E}_c$ ) is given by [14]

$$\vec{E}_c = \frac{3\epsilon}{2\epsilon + 1} \vec{E} = h\vec{E} \quad (1.10)$$

where  $\vec{E}$  is the applied electric field and  $h$  is called the cavity field factor. The directing field is a sum of the cavity field and the reaction field due to the induced dipole moment which is given by

$$\vec{E}_d = \vec{E}_c + f\alpha\vec{E}_d. \quad (1.11)$$

Taking the above described internal field and directing field into consideration the theory by **Maier** and **Meier** leads to the following expressions for  $\epsilon_{\parallel}$ ,  $\epsilon_{\perp}$  and  $\epsilon_a$

$$\epsilon_{\parallel} = 1 + 4\pi \frac{N_A \rho h F}{M} \left\{ t_i + \frac{2}{3} \Delta\alpha S + \frac{F\mu^2}{3k_B T} \left[ 1 - (1 - 3\cos^2\beta) S \right] \right\} \quad (1.12)$$

$$\epsilon_{\perp} = 1 + 4\pi \frac{N_A \rho h F}{M} \left\{ \bar{\alpha} - \frac{1}{3} \Delta\alpha S + \frac{F\mu^2}{3k_B T} \left[ 1 + \frac{1}{2} (1 - \cos^2\beta) S \right] \right\} \quad (1.13)$$

$$\epsilon_a = 4\pi \frac{N_A \rho h F}{M} \left[ A a - F \left( \frac{\mu^2}{2k_B T} \right) (1 - 3\cos^2\beta) S \right] \quad (1.14)$$

where  $N_A$  is the Avogadro number,  $\rho$  is the density,  $M$  is the molecular weight,  $h = 3\bar{\epsilon}/(2\bar{\epsilon} + 1)$  is the cavity field factor  $F = 1/(1 - f\bar{\alpha})$  (where  $f = (5-1)/[2\pi a^3(2\bar{\epsilon} + 1)]$  the reaction field factor for a spherical cavity [14]),  $\Delta\alpha = \alpha_l - \alpha_t$  and  $\bar{\epsilon}$  and  $\bar{\alpha}$  are the average dielectric constant and polarisability respectively. This model accounts satisfactorily for many essential features of the anisotropic permittivity of nematics. It can be seen from Equation 1.14 that the contribution of the **orientational polarisation** to the dielectric anisotropy is positive when the angle made by the dipole moment with respect to the long axis of the molecule is  $\leq 55^\circ$  and is negative otherwise. So if this negative quantity is larger than the **anisotropy** in the polarisability then this gives rise to a material with negative dielectric anisotropy. The contribution of the induced polarisation to  $\epsilon_a$  varies as  $S$  and that of the orientational polarisation varies as  $S/T$ .

The average dielectric constant is given by  $\bar{\epsilon} = (\epsilon_{\parallel} + 2\epsilon_{\perp})/3$  and from Equations 1.12 and 1.13 is given by

$$\bar{\epsilon} = 1 + \frac{4\pi N_A \rho h F}{M} \left( \bar{\alpha} + \frac{F\mu^2}{3k_B T} \right). \quad (1.15)$$

From Equation 1.15 it can be seen that at the nematic-isotropic transition due a small negative jump in the density  $\bar{\epsilon}$  should show a small negative jump.

However, experimental measurements of the dielectric constant [3] show that for compounds with highly polar end groups  $\bar{\epsilon}$  shows a small positive jump at the nematic-isotropic phase transition. In the Maier and Meier model short range order effects were not taken into consideration. Madhusudana and Chandrasekar [16] showed that antiferroelectric short range order (antiparallel arrangement of the permanent dipoles) gives rise to a slight increase of  $\bar{\epsilon}$  at the nematic-isotropic phase transition point. This is due to a small increase in the effective dipole moment of the antiparallel pairs due a decrease in the antiferroelectric order as the temperature is increased.

### 1.5.3 Electrical Conduction

The electrical conduction of liquid crystals is mainly due to residual ionic impurities, the nature of which is usually unknown. The conductivity is usually of the order of  $10^{-9}(\Omega\text{cm})^{-1}$ . The anisotropy of conductivity

$$\Delta\sigma = \sigma_{\parallel} - \sigma_{\perp} \quad (1.16)$$

where  $\sigma_{\parallel}$  and  $\sigma_{\perp}$  are the principal components of conductivity parallel and perpendicular to A. Usually for nematics  $\Delta\sigma$  is positive as the ions can move more freely along A than perpendicular to it. In smectics usually  $\Delta\sigma$  is negative as it is easier for the ions to flow in the layers than perpendicular to the layers. The finite conductivity of the sample leads to large heating effects when a strong electric field is applied to the sample. In this thesis we will be describing an experimental technique which takes into account the local heating of the sample due to the ionic heating effects.

### 1.5.4 Magnetic Susceptibility

Most organic molecules are diamagnetic in nature, the diamagnetism being particularly strong when the molecule is aromatic. A benzene ring, for instance, when subjected to a magnetic field  $\vec{H}$  normal to its plane, builds up a current inside the ring, which tends to reduce the flux through it: thus the lines of force tend to be expelled and this raises the energy. On the other hand if  $\vec{H}$  is applied parallel to the ring, no current is induced and the lines of force are almost undistorted and the energy is not raised. Thus a benzene molecule tends to choose an orientation such that  $\vec{H}$  is in the plane of the ring. Nematogens typically have two or more aromatic rings. Thus the lowest energy will be obtained when the long axis of the molecule (optical axis) is parallel to the field.

The diamagnetic susceptibility tensor ( $\chi$ ) is defined as

$$\vec{M} = \chi \vec{H} \quad (1.17)$$

where  $\vec{M}$  is the magnetisation induced by the field  $\vec{H}$ .  $\chi = \chi_{\parallel}$  or  $\chi_{\perp}$  when A is parallel or perpendicular to the field direction. For reasons described above, in nematics with aromatic molecules  $\chi_a (= \chi_{\parallel} - \chi_{\perp})$  is positive.  $|\chi|$  is of the order of  $10^{-7}$  cgs units/gram.

## 1.6 Relation between Macroscopic Properties and the Orientational Order Parameter

We follow the derivation by Priestley [17] to relate a macroscopic physical property to the orientational order parameter using the diamagnetic susceptibility **as** an example. However, in principle any other macroscopic property for *eg* refractive index or dielectric response could also be used. Consider the general relationship between magnetic moment  $\vec{M}$  and magnetic field  $\vec{H}$

$$M_\alpha = \chi_{\alpha\beta} H_\beta; \quad \alpha, \beta = x, y, z \quad (1.18)$$

where  $\chi_{\alpha\beta}$  represents the  $\alpha\beta$ -component of the diamagnetic susceptibility tensor  $\chi$  and for static fields  $\chi_{\alpha\beta} = \chi_{\beta\alpha}$ . In Equation 1.18 the summation convention over repeated indices is implied. For the uniaxial nematic phase we can write  $\chi$  in the diagonal form **as**

$$\chi = \begin{pmatrix} \chi_\perp & 0 & 0 \\ 0 & \chi_\perp & 0 \\ 0 & 0 & \chi_\parallel \end{pmatrix}. \quad (1.19)$$

$\chi$  itself is not an order parameter because it does not vanish in the isotropic phase, but has a finite value. If we extract the anisotropic part of  $\chi$ , *viz.*  $\chi^a$  defined as

$$\chi^a = \chi_{\alpha\beta} - \frac{1}{3} \chi_{\gamma\gamma} \delta_{\alpha\beta} \quad (1.20)$$

which does vanish in the isotropic phase, we can define a suitable order parameter  $Q_{\alpha\beta}$  **as**

$$Q_{\alpha\beta} = G \chi^a \quad (1.21)$$

where  $G$  is a constant. Usually,  $G$  is chosen so that when the director is along  $z$  then  $Q_{zz} = 1$  in the fully aligned state. Considering the director  $A$  to be along the  $\hat{z}$  direction we can show that

$$Q_{zz} = \frac{\chi_\parallel - \bar{\chi}}{(\chi_\parallel - \bar{\chi})_{Q_{zz}=1}} \quad (1.22)$$

where  $\bar{\chi} = \frac{\chi_\parallel + 2\chi_\perp}{3}$ . The orientational order parameter ( $S$ ) **as** described in Section 1.3 is related to  $Q_{\alpha\beta}$  by the following relation [4]

$$Q_{\alpha\beta} = S \frac{(3n_\alpha n_\beta - 1)}{2} \quad (1.23)$$

where the term in brackets depends on the orientation of the macroscopic director. Thus, when  $A$  is along the  $\hat{z}$  direction we get

$$\begin{aligned} Q_{zz} &= S \\ &= \frac{\chi_\parallel - \chi_\perp}{(\chi_\parallel - \chi_\perp)_{S=1}} \\ &= \frac{\chi_\parallel - \chi_\perp}{\Delta\chi_o}. \end{aligned} \quad (1.24)$$

In terms of the principal dielectric constants, a similar relation is given by

$$S = \frac{\epsilon_\parallel - \epsilon_\perp}{\Delta\epsilon_o} \quad (1.25)$$

where  $\Delta\epsilon_o$  is the dielectric anisotropy for  $S = 1$ . However this relation is only an approximate one in view of the discussion in Section 1.5.2.

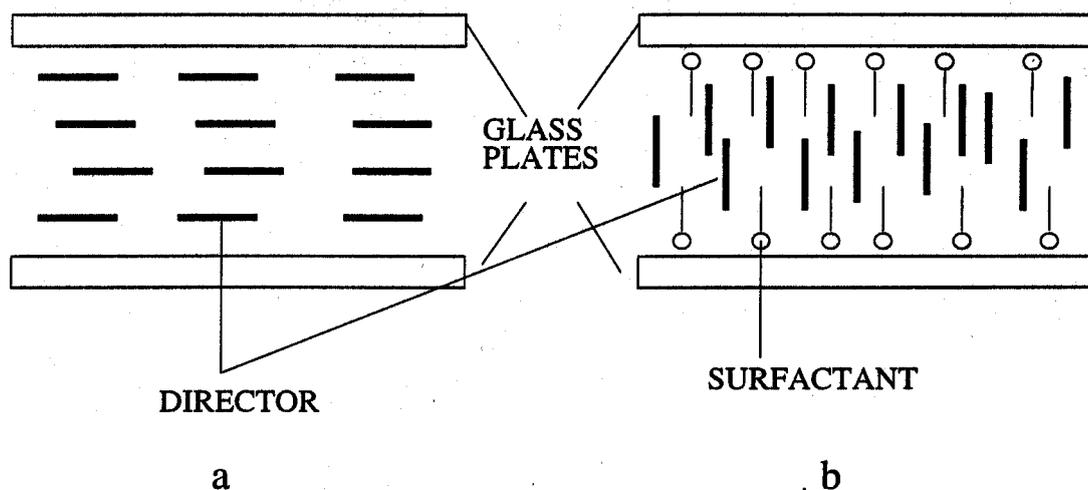


Figure 1.4: Schematic diagram of the homogeneous (a) and homeotropic (b) alignment of the director in a liquid crystal cell.

## 1.7 Alignment of Liquid Crystals

In an unaligned liquid crystalline medium the director  $A$  varies gradually from point to point. But in conducting certain experiments it is necessary that the director is oriented in a specific direction with respect to the bounding plates. If the director is oriented parallel to the glass plates it is called homogeneous alignment [18]. A glass plate coated with a thin layer of polyimide and rubbed in a specific direction gives rise to a homogeneous alignment of the director in the direction of the rubbing (Figure 1.4a). Another method adopted to obtain homogeneous alignment is by evaporating SiO in vacuum onto the glass plate at a **grazing** angle of  $30^\circ$  [19]. The molecules sit in the grooves created by the rubbing on the surfaces or those formed by the shadowing effect in the SiO coated plates to give a planar alignment.

If the director is oriented perpendicular to the glass plate it is called homeotropic alignment. A glass plate coated with a surfactant which has long chain molecules such as **ODSE** (octydecyl triethyl silane) or octadeconal gives rise to a homeotropic alignment. The long chained molecules are amphiphilic in nature having a polar group and an aliphatic chain. The polar end group is attracted to the surface of the glass plate and the long aliphatic chain interacts with the **alkyl** chain of the liquid crystal thus giving rise to perpendicular orientation of the director with respect to the glass plate (Figure 1.4b). A review on different alignment techniques is given by Cognard [20].