EFFECT OF CHIRALITY ON THE PHASES IN THIN-FILM ANTIFERROELECTRIC LIQUID CRYSTALS

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EFFECT OF CHIRALITY ON THE PHASES IN THIN-FILM ANTIFERROELECTRIC LIQUID CRYSTALS

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Kajian Tentang Fasa-fasa Dalam Filem Nipis Hablur Cecair Antiferoelektrik

Abstrak

Teori diskrit fenomenologi Landau telah digunakan untuk menyiasat kesan khiral (*chiral*) ke atas hablur cecair filem nipis smectic tergantung bebas antiferroelektrik. Sistem smectic yang terdiri daripada tiga dan empat lapisan hablur cecair smectic telah dipilih untuk mewakili sistem berlapisan ganjil dan genap. Teori diskrit ini menjumlahkan tenaga bebas bagi setiap lapisan yang berinteraksi di dalam sesuatu sistem smectic. Interaksi-interaksi tersebut dibahagikan kepada dua bahagian, iaitu interaksi di dalam lapisan dan interaksi antara lapisan. Interaksi antara lapisan diambil kira sehingga jiran terdekat seterusnya (*NNN*) manakala interaksi khiral hanya diambil kira sehingga jiran terdekat (*NN*) sahaja.

Kajian ini telah dibahagikan kepada dua bahagian. Bahagian pertama mempertimbangkan kesan khiral terhadap kestabilan struktur SmA^* berorthoganal. Kestabilan sistem telah dianalisis melalui teori Landau-Khalatnikov. Keputusan kami menunjukkan bahawa kesan khiral meningkatkan suhu peralihan fasa SmA^* berorthoganal ke struktur menyerong yang berada pada suhu lebih rendah.

Bahagian kedua kajian ini dijalankan untuk menyelidik kesan khiral ke atas struktur menyerong di bawah fasa SmA^*. Kesan khiral menyebabkan struktur yang pada asalnya menyerong secara sesatah berputar kepada struktur SmC_α^* yang tidak sesatah. Dengan kata lain, kesan khiral meningkatkan suhu peralihan antara struktur menyerong

sesatah dan SmC_{α}^{*} tidak sesatah. Walaubagaimanapun, sempadan antara kedua-dua struktur ini menjadi kabur apabila nilai khiral bertambah, ini mengakibatkan peralihan antara kedua-dua struktur ini menjadi semakin berterusan. Sekiranya sesuatu struktur telah pun berada dalam keadaan tidak sesatah sebelum kesan khiral diambil kira, maka pengaruh khiral ke atas struktur tersebut adalah kecil. Analisis bahagian ini telah dilakukan berdasarkan teori Landau-Khalatnikov, ujian pembezaan terbitan kali kedua dan penghampiran Newton.

STUDIES OF PHASES IN THIN-FILM ANTIFERROELECTRIC LIQUID CRYSTALS

Abstract

The discrete phenomenological Landau theory is employed to investigate the effect of chirality on the freely suspended antiferroelectric smectic thin film liquid crystals. Smectic systems which consist of three- and four- layered smectic liquid crystals are chosen to represent odd and even layers system. This discrete model considers the interaction energy of the smectic system as a sum of energy of each interacting layer. Interactions are divided into two parts, the interaction within layer and interactions between layers. Interactions between layers are considered only up to next nearest neighbours while chiral interaction is considered to be significant between nearest neighbour only.

The studies has two parts. First part of the studies concerns the effect of chirality on the stability of the orthogonal SmA^* structure. Stability of system is analyzed through the Landau-Khalatnikov theory. Our results have shown that chirality increases the transition temperature of the orthogonal SmA^* to the tilted structures at the lower temperature.

The second part of the studies is performed to investigate the effect of chirality on the tilted structures below SmA^*. Chirality causes structures that are initially tilted uniplanar to wound into non-uniplanar SmC^*_α structures. In the other way of saying, chirality increases the transition temperature between the tilted uniplanar and non-

uniplanar SmC_{α}^{*}. However the boundary of phase transition between these two structures is blurred as chirality increases, causing the transition of these two structures to be more and more continuous. If the structures are already non-uniplanar even before chirality is added, then chirality has little influence on the structures. The analysis at this part of the study is performed through the Landau-Khalatnikov theory, the second derivative test and Newtonian approximation.

Chapter 1 General Introduction

1.1 Preview

The story of liquid crystals (LCs) started roughly more than a century ago. Since then, many great minds and efforts had been dedicated to this field of studies to unveil its mysteries. Here we only highlight some ground breaking discoveries toward the area that is related to our work (i.e. studies regarding chiral smectic phases).

In 1975, R. Meyer who was at that time working at Harvard University predicted the existence of ferroelectricity in a chiral smectic C phase. His prediction was based on a symmetrical argument of the molecular shape. Then he and co-workers synthesized the first of such a material and hence confirmed his prediction. Since this discovery, the research on ferroelectrtic LC has attracted many attentions. The simplified argument behind his prediction will be discussed in chapter 2. Indenbom and Pikin (V. L. Indenbom and S. A. Pikin, 1978) introduced a two-dimensional order parameter, $\vec{\xi}$ to describe the transition from chiral smectic A (SmA*) to chiral smectic C phases (SmC*). This order parameter had been used extensively in many papers (that discuss the transition within the smectic phases) due to its simplicity and relevance in describing the orientation of the LC molecules to the observable physical property - polarisation. The details of this order parameter are presented in chapter 3. The potential application of the ferroelectric LC was realized by both N. A. Clark and S. T. Lagerwall that later invented the Surface Stabilized Ferroelectric Liquid Crystal Display (SSFLCD) in 1980 (S. A. Clark and S. T. Lagerwall, 1980). This application is discussed in chapter 2. Shortly after the confirmation of the existence of antiferroelectricity in LC, Orihara and

Ishibashi (H. Orihara and Y. Ishibashi, 1990) proposed the first continuum theoretical model of smectic antiferroelectric LC. Then Čepič and Žekš (M. Čepič and B. Žekš, 1995) and Roy and Madhusudana (A. Roy and N. V. Madhusudana, 1996) independently developed their discrete models of antiferroelectric smectic liquid crystal. We will look into the details of these models in chapter 3.

LCs is no longer a jargon to the modern society nowadays. For the general public, it is commonly related with display elements that are in general called Liquid Crystals Displays (LCD). Indeed, LCD has deeply penetrated into the life of urban residents. According to the report (LCD market: Technology Directions and Market Analysis) by a market research and consulting firm – The Information Network, global shipments of Thin Film Transistor LCD (TFT-LCD) panel had increased from 528.3 million units in 2009 to 663.7 million units in 2010. The figure is expected to reach 1.3 billion by 2013. LCD are widely used in almost every optical related aspect such as televisions, computer screens, pocket calculators, thermometers, windows and even on military tanks.

While LCs might seem to be linked with high technology products, it is actually a common phase in the complex world of nature. From gene delivery (Safinya *et al*, 2006) to cell membrane forming (Singer and Nicolson, 1972), LCs play an essential role in forming our lives. Such versatile and novel roles of LCs in various fields made it a very interesting material to be explored. There are a number of phases in LCs depending on the types of materials and way of formations. Some of the common examples are nematic, cholestoric nematic, smectic, Twisted-Grain-Boundary (TGB), Blue phase and etc.

1.2 Study Motivation

The existence of antiferroelectric smectic LCs had been confirmed just about two decades ago, hence there are many mysteries yet to be unveiled. Smectics LCs were synthesized long before their conformation and they were treated as ferroelectric LCs probably due to the general pespective that "molecules in liquid crystal tend to align parallel to each other" (Takezoe *et al.*, 2010). It was around 1989 that the antiferroelectricity in LCs was confirmed by experiments. Since then, many antiferroelectric LCs have been produced. The antiferroelectricity in smectic is a result of alternating arrangement of the inclined polar molecules in adjacent layers. This kind of arrangement induces alternating spontaneous polarization. These spontaneous polarizations within the layers are perpendicular to the tilting plane of the molecules. As pointed out by Robert Meyer in 1974 through symmetry argument, chirality is the precondition for the existence of these spontaneous polarizations as it breaks the mirror symmetry of the molecules. Hence, it is interesting to study how chirality affects the antiferroelectric LCs where the spontaneous polarizations vary abruptly through out the smectic system. The smectic system we have chosen is the freely-suspended thin film. Some advantages of this freely-suspended thin film are the precise measurement of physical quantities and the ease to determine of the number of smectic layers.

1.3 Thesis Overview

This thesis is divided into two main parts, the part on literature review and another part on the theoretical results from our calculations. The former is in chapters 2 and 3, while the latter part ranges from chapters 4 to 6.

In chapter 2, we discuss the brief history on LCs, various types of LCs phases known and finally LCD. While in chapter 3, we discuss briefly on some theoretical works of LCs and also the freely-suspended smectic thin film. Chapter 4 covers the study of the effect of chirality on the SmA^* analysis. The effect of chirality on the phase transition and structures of the tilted phases below the SmA^* are presented in chapter 5. The main focus of our studies is on three- and four-layered smectic systems which represent odd and even numbers of smectic layers. Two layered-system was not chosen because of its lack of next nearest interaction. If system of more than 4 layers was chosen, then its behaviours will be closer to those of bulk. Finally, we discuss possible future work as we conclude our findings.

Chapter 2 Introduction to Liquid Crystals

2.1 Brief History on Discovery of Liquid Crystals

The Austrian chemist, Friedrich Reinitzer discovered the strange behaviour of Liquid Crystals (LCs) in 1888. At that time, he was at the University of Prague, working at the Institute of Plant Physiology. While trying to determine the correct formula and molecular weight of cholesterol benzoate, he noticed that it seemed to have two distinct melting temperatures. Upon heating, the solid crystal cholesterol benzoate melted at 145.5 ^{o}C, and then became a cloudy liquid. This cloudy liquid persisted until 178.5 ^{o}C, where it turned into a clear transparent liquid. After further purification Reinitzer realized that the cholesterol benzoate behaviour did not change. Reinitzer sought the help of an expert in crystal optics, the German physicist, Otto Lehmann. Later, Lehmann found more than 100 substances with the similar behaviour. He was convinced that there exists a new phase of matter and he coined the term "Liquid Crystals" as LCs have the important characteristics of both liquid and crystal. There is directional order within LCs and yet they flow like liquids. The idea of matter exists in LC phase was initially challenged as some scientists thought that it may be only a mixture of crystal and liquid phases. Between 1910 and 1930, there were conclusive experimental results and early theories that supported the existence of LC phase. Finally LC phase is accepted as a phase of matter in addition to the three phases that are commonly known. In 1991, French physicist Pierre-Gilles de Gennes was awarded the Nobel Prize in Physics for his contribution in research on LCs and polymers. (Official nobel prize website, 2011)

2.2 Types of Liquid Crystals

A solid crystal phase is characterized by the periodic repetitive positional order of its constituents (ions or molecules). On the other hand, isotropic liquid molecules are random in their distribution. Crystal and liquid are different in the degree of ordering of the constituents. If we were to look at different spots on the crystal, the structures at these spots are most probably not identical unless these spots are periodically spaced. In liquid, the structures at different spots are the same regardless of their difference in position. Liquid crystal as its name suggests, has structure between the solid phase and liquid phase.

Depending on the ways of formation and degrees of freedom, LC phase can be divided into a few phases. There are two ways of forming LC phase, either by changing its concentration in solvent or changing the temperature. For concentration induced LCs, they are termed lyotropic LCs while for temperature induced LCs, we called them thermotropic LCs. Figure 2.1 below shows an example of lyotropic LC that is made up by phospholipids, a main ingredient of cell membrane. The head site with nitrogen, oxygen and phosphorus atoms attached is polar (hence hydrophilic) while its long carbon chain tail is non-polar (hence hydrophobic)

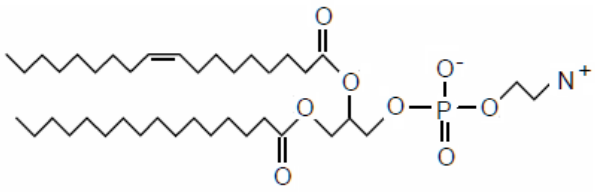

Figure 2.1 A phospholipid molecule with its polar head and its non-polar tail. (Oswald *et al.,* 2005)

When the concentration of phospholipids in low in the solvent (water), some of these molecules will adsorbed at the water – air surface while some of them is dissolved

in the water. When the concentration is high, phospholipids that dissolved in water tend to form a bilayer lyotropic LC structure as shown in Figure 2.2 with the polar head attracted to water and the long carbon chain tail shy away from the water.

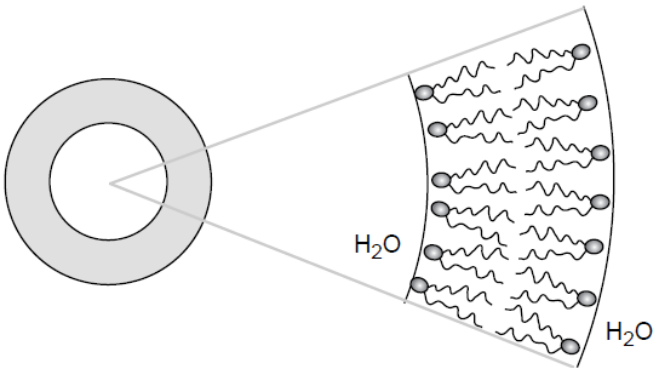

Figure 2.2 The lyotropic LC formed by mixing phospholipids with water. This lyotropic LC has a bilayer structure that is formed by two layers of phospholipids, with their heads attached to water at the two boundaries of water - phospholipids. (Oswald *et al.,* 2005)

On the other hand, temperature determines the phase of a thermotropic LC as shown in Figure 2.3 where orientational order is plotted against temperature of various phases.

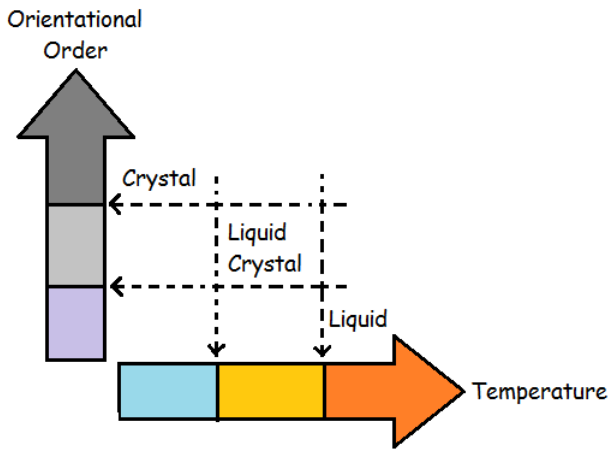

Figure 2.3 When temperature decreases, orientational order of thermotropic LC increases and it becoming more crystal-like. When temperature increases, orinetational order decreases and it is more liquid-like.

Thermotropic LC which exists in the temperature range of crystal and liquid has an orientational order between the corresponding order of crystal and liquid. Depending

on the degree of orientational order, thermotropic LC is further classified into a few phases that we are going to discuss in section 2.3. In order to form thermotropic LC, the shape of the constituent molecules is important. In general, there are three main types of suitable candidates. They are rod-like, disc-like and lath-like molecules. Figure 2.4 shows the shapes of these molecules.

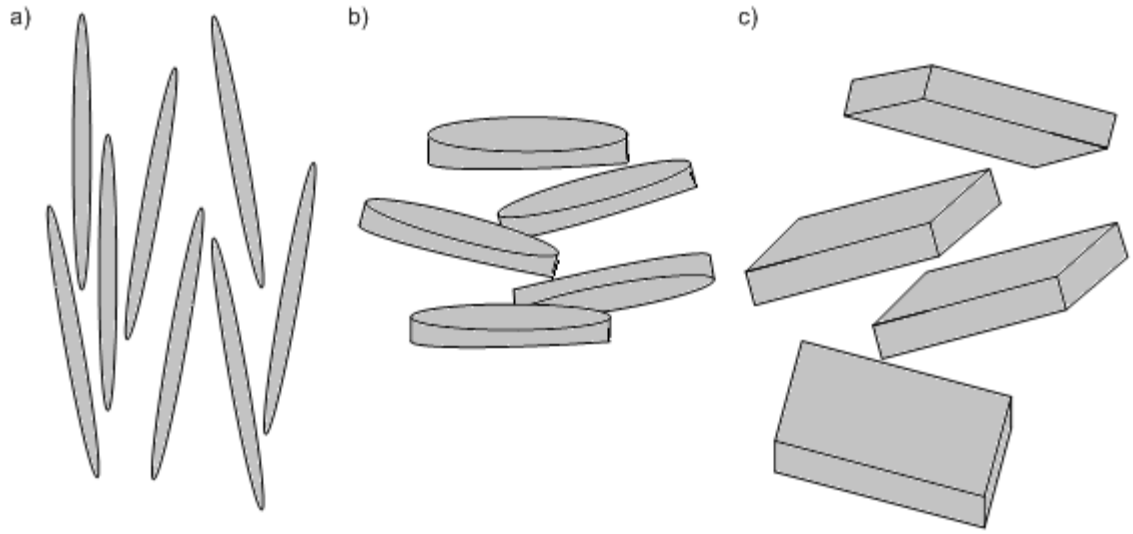

Figure 2.4 The main shapes of molecules that can form liquid crystals phase
a Rod-like **b** disc-like **c** lath-like

The similarity between these three types of molecules is associated with their shapes that are anisotropic so that certain orientational orders are more likely to occur. Our attention is on the LCs that are constituted of rod-like ($D_{\infty h}$ symmetry) molecules. Rod-like molecules are long chain molecules with two aromatic ring with rigid tail or molecules with at least five aromatic rings attached side by side. Aromatic rings are attached to this long chain to create polarization within the molecules so that they can be influenced by external electric field. The optical axes of rod-like molecules are their long axes. In next section, we are going to look at the details of thermotropic LC.

2.3 Thermotropic Liquid Crystals

As has been mentioned previously, thermotropic LCs are substances that undergo phase change due to temperature change. As temperature increases, molecules of a crystal phase substance are subjected to thermal fluctuation and hence the overall orientational order of these molecules decreases. At a certain critical temperature, the substance will be able to flow in a particular direction yet its molecules still preserve certain degree of orientational order. At this stage, the substance is already at LC phase. Depending on the structures and functional groups of the molecules, the substance may possess one or a few LC phases. A simple example of substance that possess only one LC phase is 4-heptyl-4'-cyanobiphenyl or in short 7CB. Figure 2.5 shows the molecular structure of this molecule and its corresponding phases at a few temperatures. It is a crystal solid at temperature higher than 28.5 ^{o}C, a nematic LC between 28.5 ^{o}C – 42.0 ^{o}C and an isotropic liquid above 42.0 ^{o}C. The molecule of 7CB has a polar cyano biphenyl part at one end and a non-polar alkyl chain, making the electron density distribution to be non-uniform. Figure 2.6 show this milky white nematic LC.

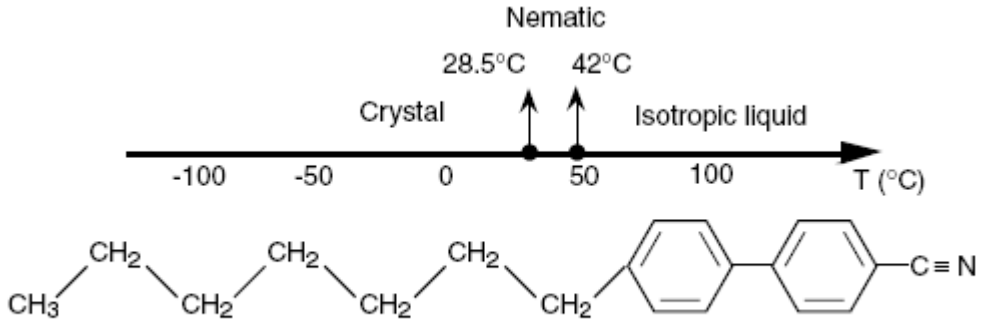

Figure 2.5 7CB which becomes a nematic LC between temperature range of 28.5^{o}C – 42.0^{o}C. (Oswald *et al.,* 2005)

Figure 2.6 The 7CB liquid crystals (http://www.tradekool.com/selling-leads/1874380/4-pentyl-4-cyanobiphenyl.html)

In rod-like thermotropic LCs, a unit vector $\hat{n}$ (called director) is assigned to show the average alignment direction of the elongated molecular axes of the rod-like molecules. The two ends of these molecules are normally not identical. Hence we could choose one end to be the head and the other end to be the tail of the molecules. If $\hat{n}$ is used to represent a molecule, the states of $\hat{n}$ and $-\hat{n}$ are however physically identical as there are same numbers of molecules pointing in the direction of $\hat{n}$ and $-\hat{n}$ at any particular moment. Figure 2.7 show the director of molecules in the one of the LC phase, i.e. nematic phase. The director represents the average directions of the molecules.

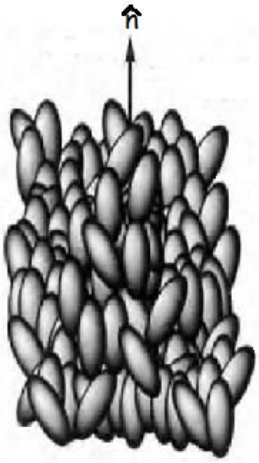

Figure 2.7 Alignments of molecules that are pointing parallel to the unit vector, $\hat{n}$. (D. Demus *et al.,* 1998)

2.3.1 Chirality in Thermotropic Liquid Crystals

Chirality refers to a situation where a mirror image of an object cannot superimpose with the object itself. The word chirality originated from the Greek word which means “hand”. This choice of word is due to the fact that one of the examples that possess chirality property is our hand. Our left and right hands are identical in the sense that both have five different fingers of different length correspondingly and yet both cannot match each other when we try to put one on the other. They are the mirror images for each other. In my study of thermotropic LC, the word chirality means a system that is constituted of chiral molecules. Figure 2.8 illustrates the schematic diagram of chiral molecules.

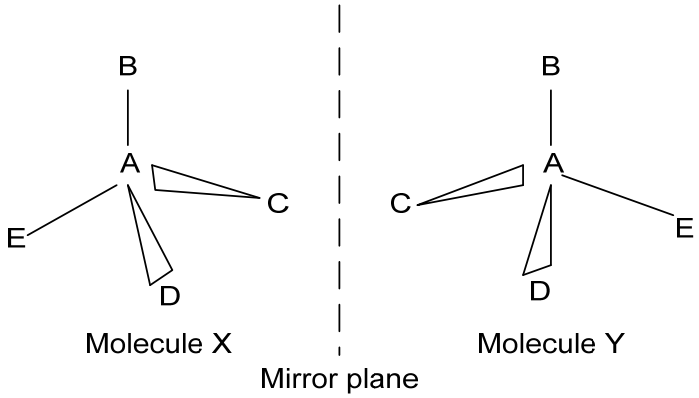

Figure 2.8 Molecules X and Y are both chiral molecules as though they are the mirror image for each other; they cannot superimpose one and another. Atoms A, B and E are on the paper plane, while C extends into the plane and D is out of the plane.

Chiral molecules with different structures are called enantiomers. The physical properties (melting point, boiling point etc) of enantiomers are identical. But biologically, one enantiomer may be beneficial to our body while the other one may be harmful. When chirality is present in LC (as a result of unequal number of two types of enantiomers in a mixture or the presence of only one type of enantiomer), a right or left

handed helix structure would formed where the director n̂ twists along a certain direction. Right and left handed helix is defined according to right hand and left hand screw directions. One example of chiral molecule that would form LC phase is MHPOBC (methyl heptyloxcarbonyl phenyl octyloxy biphenyl carboxylate) as shown in figure 2.9.

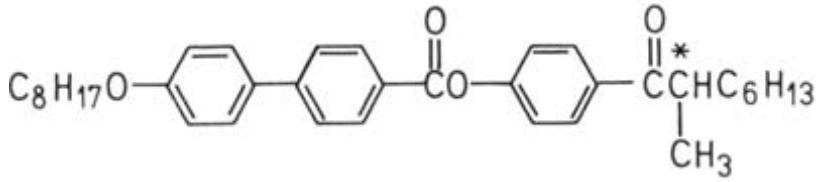

Figure 2.9 A chiral MHPOBC molecule that cannot superimpose with its mirror image. A carbon atom on the right denoted by a "*" is the chiral center, that is attached to four different ligands. These ligands are not lying in the same plane and hence causing the molecule to be chiral. (I. Muševič *et al.*, 2000)

2.3.2 Nematic Phase

The name nematic means thread-like (νημα) in Greek, and it was coined by George Friedel as a result of the thread-like texture of this phase. Figure 2.10a) shows the texture of the nematic phase. Nematic is usually the first phase in LCs after cooling from the isotropic liquid. If the isotropic liquid was formed by rod-like molecules, then one can guess that the next phase with a lower symmetry is characterized by structure where these molecules are aligned parallelly. There is no long range positional order but only long range orientational order in this phase. It differs from the isotropic phase only by having this orientational order. Figure 2.10b) shows the structure of this phase. From the figure, the long axes of the molecules are on average pointing toward the same direction. Molecules are free to rotate around their long axes. The distribution of the center of mass of these molecules on the other hand is random.

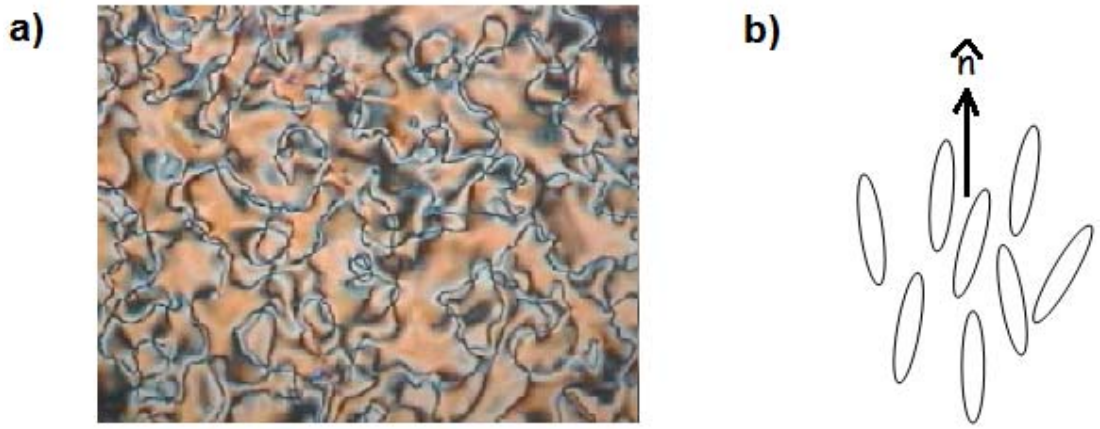

Figure 2.10 a) The thread-like nematic observed under crossed polarizers in polarizing microscope. Threads appear as molecules of different domains align parallel to each other at domains boundaries, causing optical axes of molecules to align in the same manner. When optical axes are parallel to the direction of either polarizers, minimum amount of polarized light passes and so threads (dark regions) appear. (Ingo Dierking, 2003) **b)** Arrangement of molecules in the nematic liquid crystal structure.

The orientational order of the nematic phase is measured as the degree of which its molecules align with the director, $\hat{n}$. This dimensionless order is defined as (D. Demus *et al.,* 1998)

$$S = \frac{1}{2}\left\langle 3cos^2\theta - 1 \right\rangle \tag{2.1}$$

where θ is the angle between the long axis of individual molecule and the director. The bracket < > indicates that the value of the order is taken as the average over large number of molecules. The value of this order is 1 for ideal nematic LC and 0 for isotropic liquid. For a realistic nematic LC, the typical value of S is between 0.4 to 0.7.

The nematic phase is uniaxial, which means that it has only one optical axis. This optical axis is parallel to the director. Light ray entering at acute angle with respect to optical axis shows birefringence effect. The properties of nematic LC is altered when chirality element present and phase changes into chiral nematic.

2.3.3 Chiral Nematic Phase

Chiral nematic LC is also named as cholesteric due to historical reason that during the early days it was derived from cholesterol molecule. Although nowadays it can be derived from other means as well, the name cholesteric is still preserved and it is interchangeable with chiral nematic. Chiral nematic is nothing but a special case of nematic LC. Whenever the molecules in the nematic phase are composed of chiral molecules of one handedness, a helical structure as in Figure 2.11 will be observed.

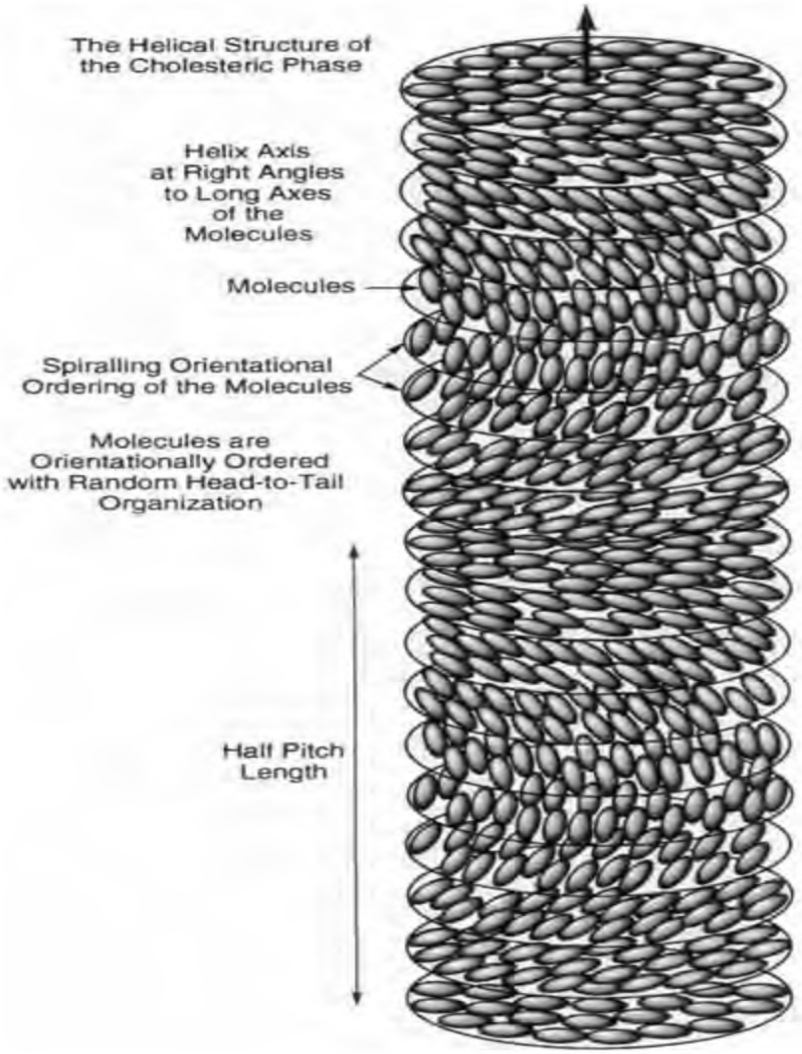

Figure 2.11 Chiral nematic phase with its helical structure. The spatial difference repeated itself every one half of its pitch, which is π/p as the director is up and down identical. (D. Demus *et al.,* 1998)

The layers in Figure 2.11 are fictitious, drawn only to exaggerate the phase difference along the direction of wave vector, *p*. The distance that the molecular orientation repeats itself (identical orientations) after 360 degree along the direction of *p* is called pitch.

In this phase, the molecules twist in a direction perpendicular to the direction of director. This twisting is a result of the tendency of chiral molecules to arrange themselves at an angle with the other nearby molecules. Unlike the previous nematic phase, chiral nematic phase is biaxial.

2.3.4 Smectic Phase

Upon further decreasing the temperature from the nematic phase, the molecules might self-organized into layered structures called the smectic LC. Translational symmetry is thus broken along the direction of director. The name smectic comes from the Greek word, "σμεγμα" which means soap. The name is given as its structure is similar to that of soap. Smectic LC has a creamy texture, unlike the fluid-like nematic. Smectic LC is a general name that refers to LC which has the layered structures. Within the layers, orientations of molecules may differ form one and another. Smectic LC is further break down into various phases depending on these orientations.

2.3.4.1 Orthogonal Smectic Phase (Smectic A)

The simplest structure in smectic is the orthogonal smectic phase or specially known as smectic A (SmA). The molecules are aligned on average, perpendicular to the layers plane. Within each layer, there is no positional order. Hence, molecules are free to

flow within the layers as in liquid phase. Figure 2.12 shows the schematic structure of a SmA phase.

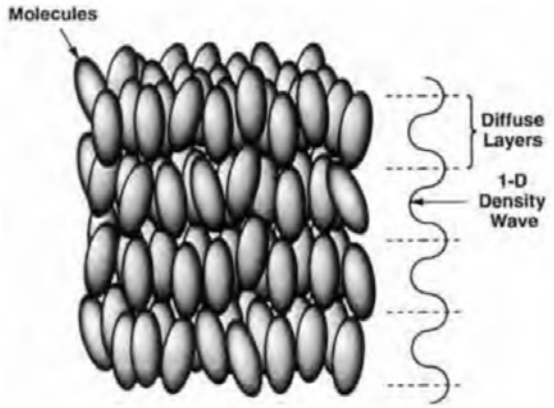

Figure 2.12 Smectic A liquid crystal structure. (D. Demus *et al.,* 1998)

As can be seen from Figure 2.12 the layers of SmA are not so ordered. Molecules are permitted to diffuse through layers. Sinusoidal wave density is applied to describe the distribution of the center of mass of molecules in SmA LC along the direction parallel to the director, with the peak of the wave corresponding to the middle of layer while the crest referring to the boundary of layer.

However, the layered property of this structure can be clearly observed. If a millimeter-sized SmA LC is dropped on a glass slide, a terrace structure but not a hemispherical shape is observed, unlike that of an isotropic liquid and nematic LC. This indicates the layered structure, which is shown in Figure 2.13. The terrace structure in Figure 2.13 corresponds to the differences in the number of layers within the free dropped SmA LC. Each region of flat horizontal surface is the region that contains the same number of LC layer. Regions of different thickness have different number of LC layers.

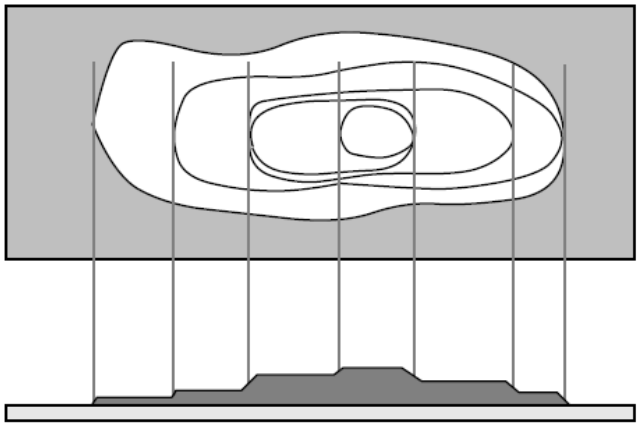

Figure 2.13 The terrace structure of a small drop of SmA LC viewed from the top and from the side. (Oswald *et al.,* 2006)

Another property of the SmA LC is the formation of focal conic or the fan-shaped texture when sandwiched between substrates viewed under polarizing microscope. The texture is a result of the parallel alignment of molecules (and hence optical axes) from different local focal domains as shown in figure 2.14. Formation of focal domains in smectic LC is common as it only involves the bending of smectic layers that needs a small amount of energy due to the small value of bending modulus.

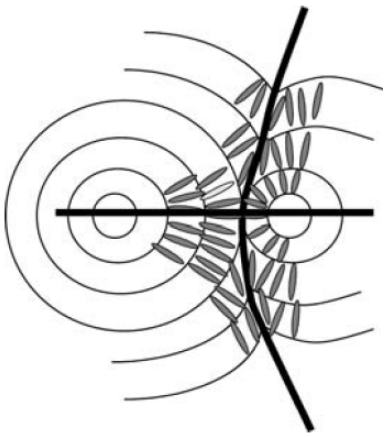

Figure 2.14 Dark lines indicate the direction of parallel alignment of molecules (optical axes) from different focal domains. (Ingo Dierking, 2003)

There are two types of textures depending on the arrangement the substrates and the focal domains in figure 2.14. If the substrates are parallel to the paper plane in figure

2.14, the texture seen under a polarizing microscope would correspond to figure 2.15 where regions of bright areas are separated by dark lines as in figure 2.14. The reason for the appearance of dark lines is same as that for the appearance of threads in the previously explained nematic phase.

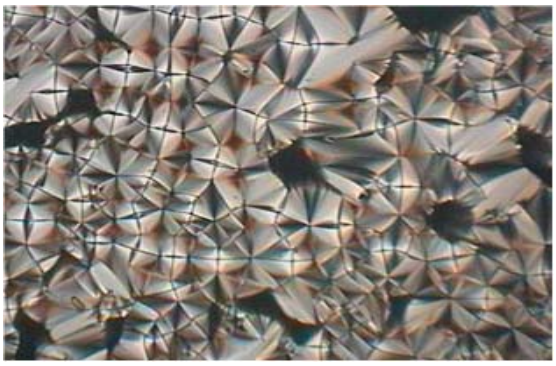

Figure 2.15 The focal conic texture of smectic A viewed under the polarizing microscope. (Ingo Dierking, 2003)

On the other hand, if the substrates are perpendicular to the paper plane, then a polygonal texture as shown in figure 2.16 is observed.

Figure 2.16 A polygonal texture of SmA (Ingo Dierking, 2003)

2.3.4.2 Tilted Smectic

The next phase after SmA is the tilted smectic structure. This phase is achieved by further lowering of temperature and it has lower symmetry compared to SmA. There is an additional orientational order where the molecules within a layer are tilted at an

angle θ with respect to the layer's normal. When all the molecules of all layers tilt in the same direction, the tilted smectic structure is known as the synclinic smectic C (SmC), where "syn" means same and "clinic" means tilted. Figure 2.17 shows the general structure of a SmC phase.

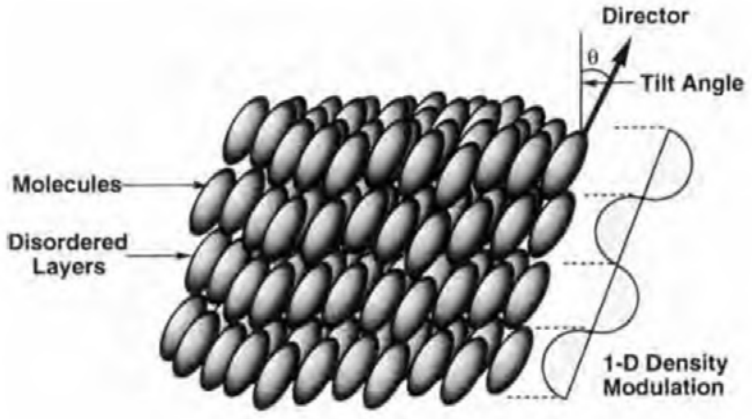

Figure 2.17 The general structure of synclinic Smectic C (SmC). (D. Demus *et al* 1998)

Though the molecules that made up this phase may be polar in nature, the overall phase does not contain spontaneous polarization. This is the consequence of symmetry argument. Symmetry operations allowed in this phase are the mirror symmetry in a plane which contains the layer's normal and the director, i.e. the tilt plane and a C_2 symmetry with rotation axis perpendicular to the mirror plane. These two symmetry operations will eliminate all possible spontaneous polarization. The explanation is as followed.

Suppose that the molecules of the synclinic smectic C is achiral molecules which carry a permanent dipole moment as shown in Figure 2.18a. Polarization of molecule is assumed to be resolved into three mutually perpendicular directions, one of them directed into the paper plane and the other two are perpendicular to the former. As mirror symmetry on the tilt plane is allowed for this achiral molecule, polarization

perpendicular to the tilt plane is hence removed. Polarizations on the other two perpendicular directions are removed by the C_2 rotation symmetry. Hence, ferroelectricity does not exist in this phase.

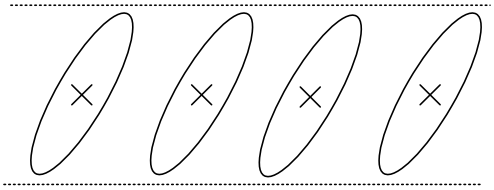

Figure 2.18a SmC made up of achiral molecules. Dotted lines represent the imaginary layers of smectic phase.

On the other hand if the molecules are chiral as shown in Figure 2.18b, polarization perpendicular to the tilt plane persisted as mirror symmetry is not permitted as the molecule is chiral. Only the C_2 rotation symmetry on the short molecular axis removes the two polarizations perpendicular to the tilt plane. Hence synclinic smectic C phase made up of chiral molecules is ferroelectric in nature by having spontaneous polarization that is perpendicular to the tilt plane.

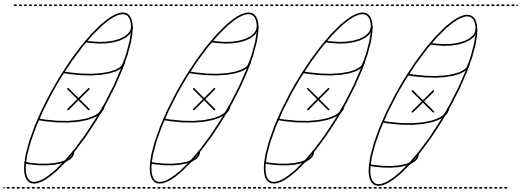

Figure 2.18b SmC* made up of chiral screw molecules. Polarization perpendicular to the tilt plane persisted as mirror symmetry on the tilt plane is prohibited due to the chiral molecules.

R.B. Meyer was the person who gives the idea that in order to create a ferroelectric LC, smectic C phase that is composed of chiral molecules will be the suitable candidate. Upon his discovery, chirality became an important subject in smectic LC.

Phases made up of chiral molecules are denoted by an asterisk *. As in the discussion above, smectic C phase made up of achiral molecules is denoted as SmC while those constituted of chiral molecules is called SmC*. Chirality tends to introduce a helical structure, causing the molecules to wind a bit, layer by layer, around in the direction of the layer's normal.

Besides the synclinic phase, there is another phase called anticlinic smectic C (SmC_A) where "anti" means oppose and "clinic" means tilted. Hence, in this phase the molecules in adjacent layers tilt in alternative directions. Figure 2.19 shows the general structure of this phase.

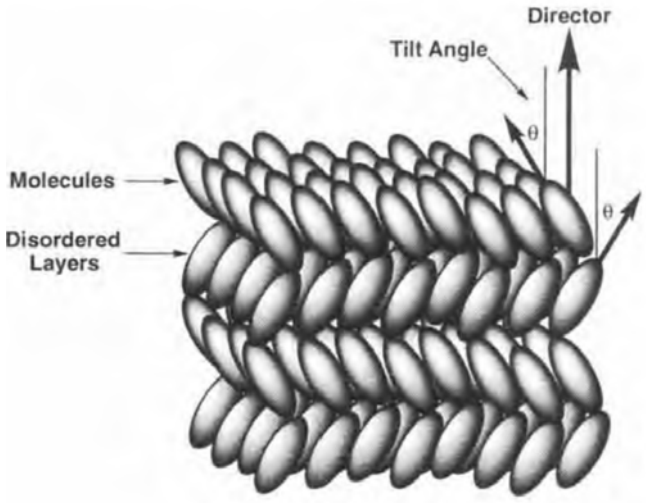

Figure 2.19 The general structure of anticlinic smectic C (SmC_A). (D. Demus *et al.,* 1998)

If the phase is composed of chiral molecules, then spontaneous polarization within each layer is again permitted, but overall they cancel out each other as they are in opposite directions to their neighbours. This phase is hence antiferroelectric in nature. Again chirality will induce helical structure in this phase and since molecules tilt alternately, a double helix is formed. The readers may wonder what is the difference between ferroelectricity and antiferroelectricity? Figures 2.20a and 2.20b show the

polarization versus external electric field applied for these two phases. For ferroelectric phase, there are two stable non-zero valued polarization when no electric field is applied while for antiferroelectric phase, there is only one zero-valued polarization as polarizations from each layer cancel off each other.

Figure 2.20 The polarization versus electric field applied for (Lagerwall, 1999)
a A ferroelectric phase **b** An antiferroelectric phase

There is another phase which has additional order where there is a constant phase difference between the projections of the directors in the adjacent layers. We called it the chiral smectic C alpha (SmC^*_α), where α denotes the value of the phase difference. The pitch is usually short, extended over a few to few tenths of layers only. Figure 2.21a and b shows the side and top views of this phase.

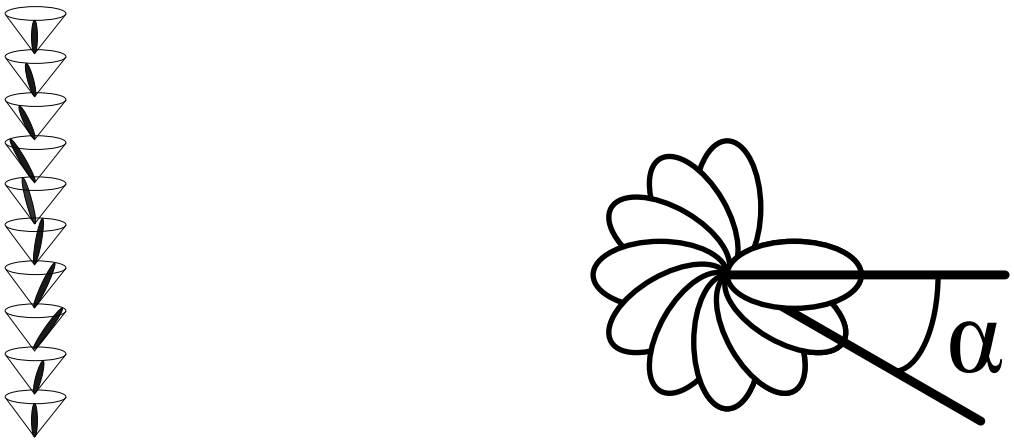

Figure 2.21a Side view of the SmC^*_α structure **b** Bird-eye view o the SmC^*_α structure

2.4 Applications of Liquid Crystals

The ability of LC to interact with light wave open up a door for us to manipulate its optical ability. They are good candidate for display elements because of their light weight and fast response to switching electric field. The simplest display which utilizes LC is called "Twisted Nematic" (TN). TN is usually used in small portable devices such as pocket calculators and wrist-watches. Advantages of TN are low operating voltage, low power consumption, long operating life-time and low cost. A comprehensive description of this technology can be referred to G. W. Gray *et al.*, paper published on Journal of Material Chemistry (Gray *et al.,* 1999). Figure 2.22 shows the schematic Figure of a TN display structure.

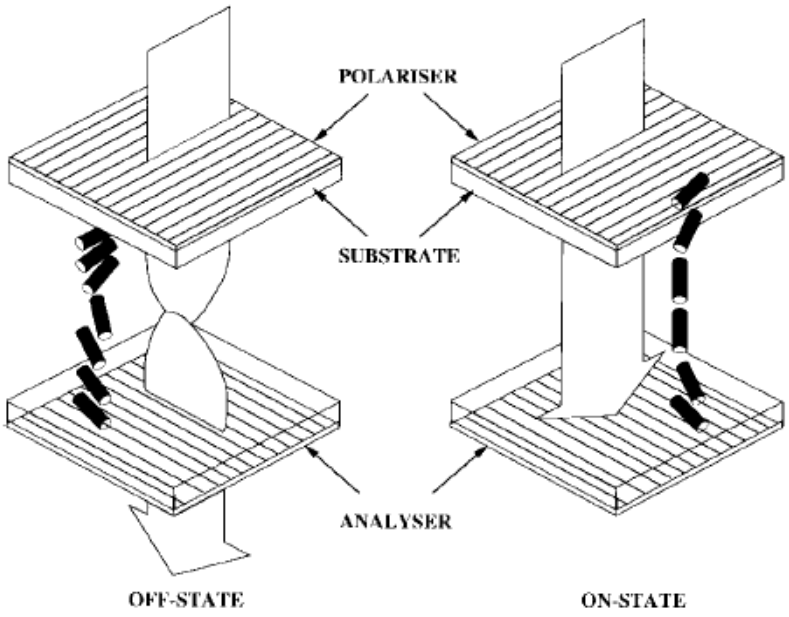

Figure 2.22 Schematic representation of a TN display. Electric field is used to control the alignment of the molecules, thus the states of light. (Gray *et al.*, 1999)

Nematic LC is filled into a closed thin cell (typically 5-10μm), sandwiched with two thin transparent substrates. Substrates are treated chemically such that the LC molecules in contact to them will align in parallel to the direction treated. The procedure is called surface treatment. Placing the substrates in 90 degree direction to each other

causes the director of the nematic LC to twist accordingly as well. Light ray that passed the polarizer interact with the molecules and twists its polarization plane by 90 degree to reach polarizer at the other end of the cell. Voltage is applied across the substrates to control the alignment of molecules, and hence the optical state. In the case where no voltage is applied, the polarised light passed through both polarizers. The state is called bright off-state. However when a certain threshold voltage is exceeded, the molecules (except those in contact with the substrates) are then align in a direction parallel to the applied voltage. The polarization plane of the light is no longer twisted by the molecules and so it cannot pass through the second polarizer. The state is called dark on-state. Of course the polarizers could be placed parallel to each other instead to give a bright on-state and dark off-state. With the principle described, we get pixels of dark and bright states by attaching cells together. Figure 2.23 shows a TN display unit to indicate number. It appears in dark and bright only. Coloured TN display can be created by placing red, green and blue filters after the polarizer to give combination of colours. However, typical TN LC is not suitable to be used in video display as its response time of 0.1-1s is still exceeding video rate of minimal 24 Hz.

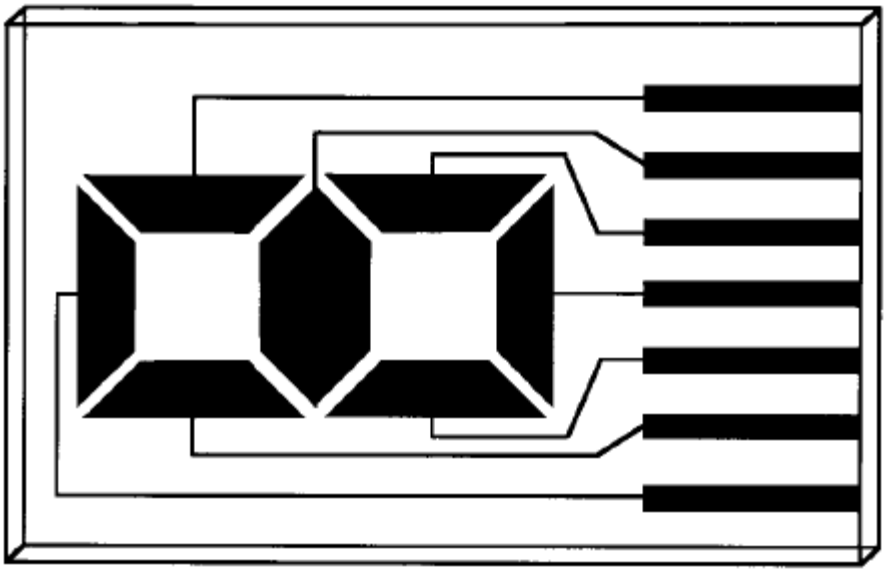

Figure 2.23 Schematic representation of a simple TN display unit. Each segment is connected to individual electrode to control the state. (Gray *et al.,* 1999)

The story of using ferroelectric smectic LC as a display element started during the 8th International Liquid Crystal Conference held at Kyoto, Japan on 1980. N. A. Clark and S. T. Lagerwall reported experimentally confirmed bistable switching. They named such a structure as Surface-Stabilised Ferroelectric Liquid Crystal (SSFLC). SSFLC is actually SmC* LC sandwiched between two anchoring treated thin substrates. The alignment of this smectic LC is such that the layers are perpendicular to the substrates. It is called "book shelf" structure. When the thickness of this structured LC is less than some critically value, helix of SmC* disappears and molecules will tilt in either one of the two energetically equivalent directions. Thus the structure will then possess macroscopic polarization pointing in either one direction. Figure 2.24 shows the effect of external electric field on the polarisation. There are two stable states which correspond to the two opposite directions electric field.