Surface Effects on Phases Transitions in Smectic Membranes

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Dedication

Dedicated to my wife Aolin Xie and my parents, Ruiyun Xu and Weixue Pan.
Abstract

In liquid crystal materials, frustration between competing interactions and thermal fluctuation results in the observation of many different phases (up to 5) in a relatively narrow temperature window (usually about 30K). Identifying the interactions as well as finding out the nature of those interactions that stabilize those phases is a very important and interesting question. In this thesis, we study the interlayer interactions in smectic liquid crystal materials through the study of surface effects on the phase transition in smectic liquid crystal films.

Elevated surface interactions in liquid crystal materials result in surface transitions higher in temperature than the bulk transitions. In the free standing film geometry employed in our research, the nature of the surface order (surface transition temperature, number of surface layers, surface critical exponent, etc.) are intrinsic properties of the system.

With the surfaces ordered before the rest of the sample, the interior transitions take place under the effective field created by the ordered surfaces. By studying the effects of this surface field on the interior transitions, as well as the interactions between surface layers and interior layers, and the interactions between the surface layers, we are able to obtain valuable information about the nature of the interlayer interactions in smectic liquid crystal materials. Our results also provide new insights into the nature of the surface transitions in the ordered surface region of the phase diagram.
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Chapter 1

Phase Transitions and Surface Effects in Liquid Crystals

Liquid crystal materials are important technological materials widely used in displays. On the other hand, they are also interesting systems for the study of frustration and intermolecular interactions. In this chapter a brief introduction is given on liquid crystal materials and surface effects in liquid crystals.

1.1 Phase Transitions and Various Structures in Liquid Crystals

1.1.1 Partially Ordered Systems - Liquid Crystal Materials

Liquid crystals are indispensable for modern day life. The wide application of this type of materials in display technology is rooted in two fundamental properties of liquid crystals: 1, fluidity and 2, electro-optical anisotropy [1]. These features come from the fact that liquid crystal materials have a degree of order in between the isotropic liquids which have continuous translational and rotational symmetry, and the crystalline solids which show discrete translational and rotational symmetry [2, 3]. This is also the reason sometimes liquid crystal materials are referred to as partially ordered systems.

Figure 1.1 shows the structures of the isotropic liquid and two common liquid crystal phases: the nematic phase as well as the smectic-A (SmA) phase. These phases are
Figure 1.1: Schematic illustration of the structure of (a) the isotropic liquid phase, (b) the nematic liquid crystal phase and (c) the SmA liquid crystal phase. Anisotropic molecules are presented as ellipsoids for their elongated shape.

usually observed in the order of: isotropic - nematic - SmA in the materials upon cooling, revealing their increasing degrees of order. Shape anisotropy of the constituting molecules is a necessary condition for the material to have a liquid crystal phase. For most materials we study, the molecules are elongated organic compounds having a shape resembling a rod, thus we use ellipsoids to represent the molecules in Fig. 1.1.

In the nematic phase, liquid crystal molecules have long range orientational order. This means the molecular axes of the molecules have a preferred orientation. At the same time, the positions of the molecules are randomly distributed as the situation observed in liquids. In the smectic phases, liquid crystal materials develop layered structures. In the SmA phase, the molecular axes are arranged parallel to the layer normal direction. Due to the Landau-Peierls instability, genuine long range positional order is forbidden in one dimension \[4, 5\]. Thus the positional order of the smectic layers along the layer normal direction is quasi-long ranged. This is the main reason why even with the intense x-ray beam at synchrotron facilities, researchers can usually only observe up to the third order peaks (003) of the layer Bragg diffraction.
1.1.2 Antiferroelectric Liquid Crystals and Smectic-$C^*$ Variant Phases

A group of smectic liquid crystal materials named antiferroelectric liquid crystals (AFLC) was first discovered around 1989 [6, 7, 8, 9]. In the chiral (optically pure) compounds of those materials, several new smectic phases were discovered below the SmA phase. In all these new phases, molecules in the smectic layers are tilted away from the layer normal. Within each layer, the tilt direction is constant if no defect is present. Different phases are distinguished by their different arrangements of the tilt direction along the layer normal. Those different structures show different properties in symmetries, electrooptical responses as well as unit cell sizes. They are referred to as the smectic-$C^*$ variant phases (SmC for the tilted phases, the * denotes chiral phases).

Figure 1.2 illustrates the different tilt structures of the six SmC$^*$ variant phases discovered so far. The smectic-$C^*_\alpha$ (SmC$^*_\alpha$), SmC$^*$, and smectic-$C^*_A$ (SmC$^*_A$) phases have helical structures with the helical pitch on the order of 10, 100 and 2 layers. The smectic-$C^*_{d3}$ (SmC$^*_{d3}$), smectic-$C^*_{d4}$ (SmC$^*_{d4}$), and smectic-$C^*_{d6}$ (SmC$^*_{d6}$) phases have distorted clock structure with unit cell sizes of 3, 4 and 6 layers. Due to the chirality of the molecules, all these structures have a long helix superstructure imposed on top of the unit cell structures. Since each molecular layer has a thickness of about 3nm, the SmC$^*_\alpha$ phase is optically uniaxial, while all other phases are biaxial in film geometries.

The usual sequence of the appearance of these phases upon cooling is: isotropic - SmA - SmC$^*_\alpha$ - SmC$^*$ - SmC$^*_{d4}$ - SmC$^*_{d3}$ - SmC$^*_A$ - crystal. One or several phases may be missing depending on the particular sample studied. The SmC$^*_{d6}$ phase only appears in very special mixtures.

Due to their different symmetry properties, phase transitions between different phases in AFLC are usually first order. However, the SmA - SmC$^*_\alpha$ and SmA - SmC$^*$ transitions are usually continuous, while the SmC$^*_\alpha$ - SmC$^*$ transitions are of the liquid - gas type with a critical point ending a line of first order transition due to their essentially identical symmetry. The research presented in this thesis is mainly focused on the study of AFLC materials.
Figure 1.2: Schematic illustration of the tilt structures of SmC* variant phases. Both side view (top) and top view (bottom) are shown. Arrows represent the tilt directions of the molecules within each smectic layer. Shown in the figure are: (a) the SmC*\textsubscript{\alpha} phase, (b) the SmC* phase, (c) the SmC*\textsubscript{d4} phase, (d) the SmC*\textsubscript{d3} phase, (e) the SmC*\textsubscript{d6} phase and (f) the SmC*\textsubscript{\Lambda} phase. For clarity, the super-imposed long helical structure is not shown for the SmC*\textsubscript{d4}, SmC*\textsubscript{d3} or SmC*\textsubscript{d6} phases.

1.1.3 Current Understanding of SmC* Variant Phases

Since their discovery, SmC* variant phases have been the topics of tremendous research efforts. However, till now, our understanding of these phases is still limited. One long lasting and yet unsolved question is: why do these materials exhibit so many different phases in such a narrow temperature window (usually about 30K), and what kind of interactions are responsible for these many structures?

Many theoretical models have been constructed trying to solve this mystery. Among them few are microscopic, while most rely on a phenomenological approach [10, 11, 12, 13, 14, 15, 16, 17]. Within the different theoretical models, some explain the existence of the SmC* variant phases with the competition of different short range interlayer interactions (although in most models, interaction upto third nearest neighbour interlayer interaction is included, we still classify these as short range interactions); while in others, long range interlayer interactions are argued to be a key ingredient. However,
since most models do not provide any experimentally measurable prediction other than the phase diagram or the unit cell sizes as a function of some model parameters, it is very difficult to determine the applicability or the validity of these models. Moreover, only few such models are able to produce all the 6 observed SmC$^\ast$ variant phases in the calculated phase diagram. So far, only models described in Ref. [15, 16], Ref. [11] and a modified version of the model in Ref. [14] can produce all the 6 SmC$^\ast$ variant phases. Thus, those theoretical models provide limited assistance in our understanding of the physics of AFLC materials.

On the other hand, experimental efforts on studying the AFLC materials have mostly been focused on the material response under external fields, and the phase behaviors in mixture systems. Although this type of study provides some useful information, it is of limited use regarding the understanding of the interlayer interactions that leads to the formation of the SmC$^\ast$ variant phases. So far to our knowledge, the only experimental attempts on studying the interlayer interactions in AFLC materials came from the study of the helical pitches of the SmC$^\ast_{\alpha}$ phase [18]. Utilizing a one-dimensional $J_1 - J_2$ model (details of the model are explained in Ch. 6), the temperature evolution of the phenomenological coefficients of the nearest neighbor (NN) and the next nearest neighbor (NNN) interlayer interactions can be obtained through fitting.

Although limited understanding of the SmC$^\ast$ variant phases has been achieved, it is generally agreed that the frustration between the NN interlayer interaction and some other forms of interlayer interactions provides the mechanism of the formation of those phases. The fact that the distorted phases (SmC$^\ast_{d4}$ and SmC$^\ast_{d3}$) usually appear between the SmC$^\ast$ and SmC$^\ast_{A}$ phase, where the NN interlayer interaction is believed to change sign thus having a small magnitude, provides support for this argument. Also, the appearance of the SmC$^\ast$ variant phases in the binary mixtures of compounds showing the simple SmC$^\ast$ phase and the SmC$^\ast_{A}$ phase respectively provides further evidence.

1.2 Surface Effects in Liquid Crystals

1.2.1 Surface Effects and Surface Orders in Liquid Crystals

Surface effects and finite size effects are unavoidable in experiments. Since real systems are always finite and thus have boundaries. Finite size effects are known to shift the
magnetic ordering temperatures of thin films and cause rounding of the transitions [19]. Surface effects, on the other hand, have richer variety of consequences in different systems [20].

In the study of phase transitions, surface effects have been shown to produce its own class of critical behavior at the surfaces. In most solid state systems, surface induced disorder (also called surface melting) is observed as reduced values of the order parameter at the surface region in the ordered phase. This is due to the reduced values of interactions or reduced coordination number at the surfaces. However, in soft materials, surface induced order (also called surface freezing) is commonly observed. In smectic liquid crystals with layered structures, surface tension at the free surfaces elevates the surface interaction, resulting in a surface transition several degrees higher in temperature than the bulk transition [4].

Surface effects other than the surface induced order are also observed in liquid crystal systems. The layer by layer melting behavior [21] and the surface induced reduction of twisting power (details in Ch. 6) are examples of such phenomena. However, in many cases, it is difficult to attribute one phenomenon to just the surface effects or the finite size effects, as both tend to show more pronounced effects as the sample size reduces.

1.2.2 Why Study Surface Effects?

As discussed above, in smectic liquid crystal films, surface order is usually established through a surface transition several degrees higher in temperature than the bulk transition, when the rest of the sample orders. With the established surface order, the interior layers of the film go through phase transitions under an effective field from the surfaces (called extraordinary transition). By controlling the thickness of the films we study, we control the distance between the two surfaces as well as the ratio of the surface layers in the sample. Thus for smectic liquid crystal films where samples with desired thickness can be prepared, we can control the level of the surface effects, and we expect stronger surface effects to be observed in thinner films due to the increased surface to interior ratio.

Depending on the different structures of the surface layers and the interior layers, as well as the number of surface layers and the film thickness, the surface field will have different effects on the structure and/or the stability of the phases of the interior layers.
By studying those surface effects on the interior phases and/or structures, valuable information about the interaction between the surface layers and interior layers can be obtained. Depending on the constructive or destructive effect of the surface - interior interaction on various SmC* variant phases, we gain new insights into the nature of those phases. Also, the study on surface effects and on surface - surface interaction forms a first experimental attempt on elucidating the nature of the interlayer interactions in AFLC materials, thus will provide a solid paradigm for future theoretical or experimental studies.

In this thesis, chapter 2 describes the experimental technique employed for the research. Chapter 3 to chapter 6 describe our study on the surface effects in AFLC free standing films, including the surface induced ordering effect and the surface transitions, the surface - surface interaction across disordered interior layers, and the surface induced reduction of twisting power in the helical structures. Chapter 7 reports our study on the thickness dependent phase behavior of one AFLC compound. Chapter 8 concludes the thesis.
Chapter 2

Experimental Techniques

In this chapter, the set up and the principle of null transmission ellipsometry are described in detail. It is the experimental probe employed for all the experiments reported in this thesis. The free standing film geometry is also explained, which is a key element for the study of surface effects in smectic liquid crystal materials.

2.1 Free Standing Film Geometry

The layered structures of smectic liquid crystals enable us to prepare free standing films of this type of materials. This is the sample geometry utilized for all the experimental studies reported in this thesis. To prepare a smectic free standing film, cover glasses with circular film holes in the center are used as film plates. Bulk sample in the smectic liquid crystal phase is pasted around the edge of the hole. Thus when a spreader slides across the film hole, a free standing film is created.

After the film is spread, surface tension will tend to keep the thickness uniform across the film. Usually by keeping the freshly spread film in the SmA phase for about one to two hours, a film with uniform thickness can be obtained. The uniformity of the film thickness can easily be checked by viewing the sample under a microscope, as different thicknesses will show different characteristic reflection color under white light illumination.

Figure 2.1 shows the picture of a freshly prepared smectic free standing film. Regions with different thickness can be clearly identified by their distinct color.
Figure 2.1: Picture of a freshly spread smectic free standing film taken under a microscope. Region with different thickness shows different color. Due to surface tension, thinner parts appear in the central region of the film.

There are several advantages of the free standing film geometry. First, without substrates the surface properties observed during the experiments are intrinsic properties of the material studied. Second, we can have a precise knowledge of the thickness of the sample. Films with thickness from up to several thousand molecular layers down to a 2-layer film can all be easily prepared and studied (each layer has a thickness of about 3nm, 1-layer film is not stable). Third, the smectic layers in the film are parallel to the film plate, thus provides us with a well-defined experimental coordinate frames for the study. Since this thesis focuses on the surface effects in smectic liquid crystals, free standing film provides an ideal geometry for the experiments.
Figure 2.2: If linearly polarized light transmits through the film, it will be converted to an elliptically polarized light. By properly aligning the fast axis of the quarter wave plate with the major axis of the elliptically polarized light, it can be converted back to linearly polarized light. Then the analyzer will be able to find a null condition at the photo diode. The orientation of the quarter wave plate and the analyzer at the null situation can be used to find the phase change and ellipticity caused by the sample. In this conceptual set up of the experiment, the rotating elements are the quarter wave plate and the analyzer.

2.2 Null Transmission Ellipsometry

2.2.1 How Does Ellipsometry Work?

The experimental probe employed for the research presented in this thesis is our in-house null transmission ellipsometry (NTE) [22]. Ellipsometry probes the optical properties of thin dielectric films through recording the change of the polarization state of the laser beam upon reflecting from or transmitting through the sample. The change of the laser’s polarization state is the result of the interactions between the electromagnetic wave and the sample’s dielectric tensor. Thus the structural information of the sample can be obtained by analysing the recorded data with the relevant theoretical models.

Figure 2.2 shows the conceptual set up of a transmission ellipsometry. A linearly polarized monochromatic incident light is obtained from a laser and a polarizer (labelled Polarizer in the figure). Upon transmitting through the sample, the polarization state
of the laser beam is modified and becomes elliptically polarized [23].

Two parameters are needed to fully characterize the polarization state of an elliptically polarized light, the ellipticity (ratio of the major and minor axes) as well as the phase difference between the two components of the field vector in a particular reference frame. By aligning the the fast axis of the quarter wave plate with major axis of the elliptically polarized transmission light, a linearly polarized light is obtained again. This can be checked by a second polarizer (Analyzer). When oriented perpendicular to the polarization axis of the light transmitted through the quarter wave plate, a null situation is achieved at the photo diode. At this moment, the orientation of the quarter wave plate and the analyzer can be used to find the phase difference and the ellipticity of the light transmitted through the sample. Thus, the angular positions of the quarter wave plate and the analyzer at the null condition contain information about the optical properties of the sample, which is directly related to its structure.

2.2.2 Experimental Set up of Null Transmission Ellipsometry

Although the conceptual set up shown in Fig. 2.2 is more straight forward in explaining the principles of ellipsometry, in real experiments it is much easier to set up the experiments in a reversed order, as shown in Fig. 2.3. From the light source (a He-Ne intensity stabilized laser, with output wavelength $\lambda = 632.8\text{nm}$), we first have the polarizer and the quarter wave plate, followed by the sample, then we have the analyzer and the photo diode. The laser is fixed at a 45° incident angle of the film plate and chopped by an optical chopper for the lock-in detection of the photo current at the photo diode. Here instead of rotating the quarter wave plate and the analyzer as shown in the conceptual set up, we fix the orientation of the quarter wave plate and rotate the two polarizers mounted on stepper motor rotation stages (Polarizer and Analyzer). The rotation stages allow a 0.02° precision of the orientation of the two polarizers, producing data with extremely high precision and accuracy. The rotation of the Polarizer produces an elliptically polarized incident light at the film, with a particular phase difference between the $p$ and $s$ components of the light that upon transmitting through the sample, a linearly polarized light will be obtained. Then the rotation of the Analyzer will achieve a null situation at the photo diode, only then the orientations of the Polarizer ($\phi_P$) and Analyzer ($\phi_A$) will be recorded.
Figure 2.3: The actual set up of NTE in our lab. In this set up of the experiment, the rotating elements are the polarizer and the analyzer.

For our experimental set up, the two ellipsometric parameters $\Delta$ and $\Phi$ have a simple relation with the recorded quantities:

$$\Phi = \phi_A; \Delta = 90^\circ - 2\phi_P$$

(2.1)

Here $\Delta$ measures the phase difference between the $p$ and $s$ components of the incident light necessary to create a linearly polarized transmission light. $\Phi$ yields the orientation of the polarization axis of the transmitted light.

To study the phase transitions of smectic liquid crystals, the film plate is enclosed in a temperature controlled oven with a stability of about $\pm 15$ mK. He or Ar gas is used as exchange gas to reduce the chemical degradation of the sample.

2.3 Information from Null Transmission Ellipsometry

Since AFLC materials have chiral molecules, in the SmC* variant phases, each layer has a net electric polarization. Thus when the film has a finite polarization, we can align the whole structure with an external in-plane DC electric field. The set up used for the external field is illustrated in Fig. 2.4. Around the film hole, we attach 8 evenly spaced electrodes onto the film plate, by applying a set of voltages to the electrodes according
Figure 2.4: Schematic illustration of the film plate used in NTE. The red cylinder represents the laser beam. Large blue arrow shows the direction of the external field created by the voltages on the electrodes. Orange blocks represent the electrodes, while molecules are shown as yellow ellipsoids with green arrows representing their polarization vectors. Elements in this figure are not to scale.

To \( V_i = V_0 \cos[(i-1)45^\circ - \alpha] \), with \( i \) being the index of the electrode, we can create a uniform electric field across the sample, with a strength \( E = V_0/r \), \( r \) being the radius of the film hole. The direction of the electric field is given by \( \alpha \), which is measured from the projection of the wave vector \( k \) of the laser beam onto the film plate. The rate we change the electric field is on the order of \( (V/mm)/\text{min} \), much slower than the response time of the material. Thus in all our measurements, the samples are in equilibrium with the applied field. Also, the strength of the applied field is just strong enough to align the sample without inducing any structural change or field induced transition. One exception would be the case reported in Ch.5, where the applied field causes a field induced transition in the relative direction of the two surfaces. To cause any structural change or field induced transition, a field strength 3 orders of magnitude stronger than the one we use would be required. Our applied field typically has a value of several V/cm.

As explained in Ch.1, different SmC* variant phases have different symmetries. The symmetry information of the sample can be studied by recording the optical parameters
from NTE as a function of electric field orientation $\alpha$ when keeping the temperature constant (we call this a rotation data set). Shown in Fig. 2.5 are two simulated rotation curves from a 12-layer film with the SmC$_{d3}^*$ and the SmC$_{d4}^*$ structure, respectively (For similar real data set, see Fig. 7.2 on page 76). The simulation results are obtained from a 4×4 matrix method [24, 25].

Upon examining the simulation, we see that in Fig. 2.5 (a), there’s a mirror symmetry axis at $\alpha = 90^\circ$, shown as a dashed line in the figure. (Note, the symmetry axis at $\alpha = 270^\circ$ is the same axis.) This reflects the structural symmetry of the SmC$_{d3}^*$ phase as illustrated in Fig. 2.5 (b), where the mirror symmetry axis is also shown as a dashed line. On the other hand, for the SmC$_{d4}^*$ phase shown in Fig. 2.5 (c) and (d), we observed two mirror symmetry axes perpendicular to each other in the data. This clearly shows the higher degree of symmetry of the SmC$_{d4}^*$ phase compared to the SmC$_{d3}^*$ phase, as illustrated from the structural models shown in the figure.
Depending on the different symmetries of the different structures, we will see rotation data with distinct characteristic features, thus allowing us to identify the corresponding phase at a particular temperature. Sometimes, more information of the structure can be obtained by fitting the data to a model composed of a series of dielectric slabs. But the large numbers of fitting parameters involved (each layer contribute two parameters, magnitude and direction of the tilt, thus a N-layer film has 2N parameters) leave room for a large set of degenerate solutions, making ellipsometry less deterministic in structural elucidation.

Complete knowledge of the structure is obtained from NTE when a rotation data set is recorded over the temperature range of the sample we are interested in. However, this is a time consuming process. Usually when the purpose is only to identify the phase sequence or the transition temperatures of a known phase sequence we can record data at fixed electric field orientation when changing the temperature of the system over the temperature window of interest (we call this a set of T ramp data). By recoding and comparing data at $\alpha = 90^\circ$ and $\alpha = 270^\circ$, we will have enough information for the purpose of phase identification, provided we know what kinds of SmC* variant phases are involved.

2.4 Thickness Measurement from Null Transmission Ellipsometry

Smectic liquid crystals have layered structures, thus free standing films of smectic liquid crystals have thickness quantized in integer numbers of molecular layers N. Surface tension usually prevents thickness fluctuations once a uniform film is obtained. Since this thesis focuses on the study of surface effects in free standing films of smectic liquid crystals, a precise knowledge of the thickness of the sample studied is of vital importance.

For NTE, this information can be obtained by studying the films in the temperature window of the SmA phase. In this temperature window, all the layers have the same thickness (about the same as the molecule length), and the sample is optically uniaxial. This results in a constant value of ellipsometric parameters $\Delta$ and $\Phi$, independent of the field orientation $\alpha$. Now $\Delta$ and $\Phi$ are functions of index of refraction of the material ($n_e$, $n_o$) and film thickness only. Since the film thickness is quantized into $Nd$, if we plot
Figure 2.6: The experimental data together with fitting from a $4 \times 4$ matrix method in the thickness measurement of free standing films of compound 10OHFBBB1M7.

$\Delta$ vs $\Phi$ for the data collected in the SmA window from different films, the data set will show discrete points over the parameter space.

By measuring $\Delta$ and $\Phi$ from films with different thickness and fitting to a $4 \times 4$ matrix method, we can obtain a series of $\Delta$ and $\Phi$ values as a function of $N$, with $n_e$, $n_o$ and $d$ being fitting parameters. In the $4 \times 4$ matrix method, the film is modeled as a $N$-layer uniaxial slab with indices of refraction being $n_e$, $n_o$ and layer thickness being $d$. The best fit determines the values of the parameters $n_e$, $n_o$ and $d$ to a high degree of precision and produces a series of $\Delta$ and $\Phi$ values as a function of $N$, which can be used to compare to the measured values in the SmA phase window to obtain the thickness of the film studied.

A sample data set and corresponding fitting results are shown in Fig. 2.6. The data are obtained from compound 10OHFBBB1M7.
Chapter 3

Surface Tilt Transition in Smectic Liquid Crystal Films

In this chapter, the surface tilt order and its surface transition in smectic liquid crystal films are described in detail. The mean field phase diagram of a semi-infinite Ising square lattice is introduced and serves as the theoretical background for the following discussion. The surface critical behavior of the surface transition is compared with the corresponding bulk transition and discussed in the framework of lower dimensional phase transitions.

3.1 Surface Transition

3.1.1 Mean Field Phase Diagram

As discussed in Ch. 1, surface effects produce rich phenomena and the study of those effects provides important insight on the physical properties of a system. However, it is usually quite difficult to separate surface effects from finite size effects in most experiments, as both effects show more pronounced results when the system sizes decrease. Thus the semi-infinite model serves as an ideal system for the theoretical understanding of surface effects without the complication brought in through finite size effects.

Shown in Fig. 3.1 is the schematic structure of the cross section of a semi-infinite Ising square lattice. The lattice occupies half space and the surface of the lattice resides
Figure 3.1: Schematic illustration of a semi-infinite Ising square lattice. Finite size effects are irrelevant for this model. The surface of this lattice is at $z = 0$. In the lattice, the surface interaction differs from other nearest neighbor interactions.

at the $z = 0$ plane. In this model, only ferromagnetic nearest neighbour (NN) interaction is considered. All the NN bonds have interaction strength $J$, except for spins at the surface layer, where a surface interaction strength $J_S$ is found. Since for this model, linear sizes along all dimensions are infinite, finite size effects are irrelevant. Thus we are left with surface effects only.

Mean field calculation of this model reveals a phase diagram as shown in Fig. 3.2 [20]. The topology of this phase diagram is correct whenever the surface can support independent order. In this phase diagram, three different types of surface behaviors are observed as a function of the surface enhancement $J_S/J$.

For $J_S/J$ smaller than the critical value, the surface and bulk order at the same temperature $T_C$ (the ordinary transition). The order parameter (magnetization density $m(z)$) decreases upon approaching the surface (surface disorder), and the local magnetization density $m(z)$ is expected to decrease faster near the surface upon heating which correspond to a larger local critical exponent $\beta_1$ as compared to the bulk exponent $\beta$.

Upon increasing $J_S/J$ beyond the critical point (which is a multicritical point where the special transition is observed), we reach the surface order region, where the surface orders at a higher temperature ($T_S$, the surface transition temperature). For comparison, the bulk still orders at $T_C$. The transition at $T_C$ in the presence of an ordered
Figure 3.2: Mean field phase diagram of the semi-infinite Ising model as a function of temperature and surface enhancement $J_S/J$. The critical surface enhancement $J_{SC}/J$ has a value around 1.5 depending on the model and method of calculation.

surface is called the extraordinary transition.

3.1.2 Surface Transition

In the surface order region, where surface orders at a higher temperature ($T_S$) than the bulk transition temperature $T_C$, the order parameter $m(z)$ increases upon approaching the surface, as shown in Fig. 3.3. For $T_C < T < T_S$, deep in the bulk the order parameter remains 0. However, since the surface is already ordered, near the surface $m(z)$ has a finite value. And for $T < T_S$ (including below the bulk transition temperature), $m(z)$ decreases into the bulk value exponentially as a function of the distance from the surface, with a characteristic length of the decay determined by the corresponding bulk correlation length at the temperature.

Since the surface transition is observed with enhanced surface interaction, it is expected to show a $d-1$ dimensional critical behavior for a $d$-dimensional bulk system. This can be understood with the following argument. When the NN interactions in the
surface layer \((J_S)\) is much stronger than the other interactions \(J\), the surface is effectively detached from the bulk and forms a \(d-1\) dimensional system. Thus the critical behavior of the surface transition is expected to be that of the corresponding \(d-1\) dimensional behavior of the bulk universality class [26, 27].

For the local order parameter \(m_1\) at the surface layer, and the surface order parameter (also called the excess magnetization) \(m_S = \int (m(z) - m(\infty))dz\), we expect \(m_1 \propto (-\tau)^{\beta_1}\), and \(m_S \propto (-\tau)^{\beta_S}\), where \(\tau = T - T_S\) is the reduced temperature of the surface transition, and \(\beta_1\) and \(\beta_S\) are the local and excess/surface exponent of the order parameter.

For the surface transition in 3-d systems, theory suggests we should have \(\beta_1 = \beta_S = \beta_{2d}\), as explained above.
3.2 Surface Tilt Transition

3.2.1 Surface Tilt Transition

In most soft material systems, surface enhanced order is observed. This effect is especially common in liquid crystal systems [4]. For materials exhibiting a SmA to tilted smectic phase transition, the most common surface order is observed as a SmA - SmC type tilt transition at the free surfaces of the material several degrees above the bulk transition. For example, for materials exhibiting a SmA - SmC, SmA - SmC*, or SmA - SmC*α transition, a surface tilt order is almost always observed above the temperature at which the whole sample turns into the tilted phase. Figure 3.4 shows an example of surface tilt order. Shown is a 4-layer film with the two outermost layers tilted while the two inner layers are still in the SmA state. Depending on the temperature window of the SmA phase, the surface transition temperature is not always accessible for experiments on free standing films. If the SmA window is small and the surface enhancement is large, we might have a situation where the surface tilt transition temperature $T_S$ would be higher than the bulk isotropic liquid - SmA transition temperature. Under this situation $T_S$ is not accessible for experiments on free standing films since liquid structure does not support the formation of stable free standing films, and thus the film would fracture before reaching $T_S$.

For materials with a $T_S$ that is below the bulk isotropic liquid - SmA transition temperature, we can study the surface tilt transition in free standing films using NTE. For this transition, the tilt angle gives the order parameter amplitude, with $\theta_1 \propto (-\tau)^{\beta_1}$ and $\theta_S \propto (-\tau)^{\beta_S}$ expected for the surface transition.

3.2.2 Experimental Procedure

For a simple tilt transition in smectic liquid crystal films, where the structure is planar, the difference of the ellipsometric parameter $\Delta$ obtained with the molecules tilted towards and away from the incident laser beam is proportional to the total tilt of the film. For our NTE set up, the two situations correspond to $\alpha = 90^\circ$ and $\alpha = 270^\circ$, so we have $\Delta_{270} - \Delta_{90} \propto \sum_{i=1}^{N} \theta_i$ [28]. And for the surface tilt transition, where the interior tilt is 0, if the two surfaces tilt towards the same direction, we would have $\theta_S \propto \Delta_{270} - \Delta_{90}$ for $T_C < T < T_S$ [29].
Figure 3.4: Schematic illustration of the surface tilt order. Shown is a 4-layer film with the two outermost layers tilted (ordered), while the two inner layers are not tilted (disordered).

To study the surface transition behavior, especially for the measurement of the critical exponent, the stability of the sample is very important. For experiments with liquid crystal, there’s always a possibility of sample degradation during the course of the experiment due to the relatively high measuring temperatures. Such situation would reduce the transition temperature of the sample. To minimize this effect, we use noble gas as exchange gas. Also, during our study of the surface tilt transitions, we measure $\Delta_{270} - \Delta_{90}$ in a single cooling (sometimes heating) run by switching the applied field orientation between 90° and 270° every several minutes while changing temperature slowly (see the inset of Fig. 3.5). This way $\Delta_{270} - \Delta_{90}$ can be obtained from a single experimental run, which ensures high data quality.
3.3 Surface, Two Dimensional and Bulk Transition

The compound studied for the surface tilt transition is MHPBC. Both optically pure, R-MHPBC and its near racemic mixture with 50.5% S- and 49.5% R-, called racemic MHPBC for the remaining of the thesis, are studied. The chemical structure of MHPBC is shown on top of Fig. 3.5. MHPBC has a bulk phase sequence: Isotropic (109 °C) SmA (76 °C) SmC\(_{\alpha}\) (71 °C) SmC\(_{d4}\) (66 °C) SmC\(_{d3}\) (62 °C) SmC\(_{A}\). This compound has a very large SmA temperature window between the isotropic liquid phase and the SmC\(_{\alpha}\) (tilted helical structure) phase, enabling us to access the surface ordering temperature, thus allowing an experimental study of the surface transition.

The ellipsometric parameters \(\Delta\) and \(\Psi\) were measured from about 50 films with thickness ranging from 2 to 200 layers at 104.9 °C where there are no surface tilts present. Fitting of measured data was done using the 4×4 matrix method. By modeling each layer as a uniaxial slab with \(n_o\), \(n_e\), \(d\) being the principal indices of refraction and layer thickness, we were able to obtain values of \(n_o\), \(n_e\), \(d\) to be 1.481 ± 0.002, 1.626 ± 0.01, and 3.44 ± 0.05 nm, respectively. Afterwards, the same fitting method was used to determine the thickness of all films studied.

Shown in Fig. 3.5 is a sample data set from an 81-layer film of R-MHPBC. The inset shows the raw data set. As explained above, we recorded the data when switching the field orientation between 90° and 270° back and forth while changing temperature. The direction of \(E\) was switched every 150 sec between \(\alpha = 90°\) and \(\alpha = 270°\). The temperature ramping rate was set to be 40mK/min in the region 10K below the surface transition temperature \(T_s\) and 20mK/min above it. As the inset of Fig. 3.5 shows, data for \(\alpha = 90°\) between \(T_2\) and \(T_3\) was obtained by linear interpolation of the data over \(T_1\) and \(T_2\), as well as \(T_3\) and \(T_4\). With the result, we then averaged the 5 data points for each temperature window and obtained one data point in Fig. 3.5. With this procedure we were able to obtain a complete set of ramping data with \(\alpha = 90°\) and 270° from a single cooling run.

3.3.1 Surface Transition

The temperature evolution of the surface tilt from films with different thickness \(N\) is plotted in Fig. 3.6 (Fig. 3.7) for R-MHPBC (racemic MHPBC), together with the data
Figure 3.5: $\Delta$ and $\Psi$ as a function of temperature upon cooling from an 81-layer film of R-MHPBC. Inset shows raw data obtained from a cooling run while switching the direction of $E$. Each data point in this figure is then obtained by averaging the 5 data points of this temperature window. In the data, $T_S (T_b)$ marks the surface (bulk) tilt transition temperature, while $T_1' (T_2')$ marks the temperature where visible difference starts to develop between different films (between the data and the power law fitting). On the top is the chemical structure of MHPBC.

From 2-layer films (and 4-layer film for racemic MHPBC). The data are shown in the reduced temperature scale of the initial tilt transition of the film, for the thicker films it is the surface transition; however for the 2-layer and the 4-layer films, the whole film goes into the ordered phase. Note for the 4-layer film of racemic MHPBC, near the tilt transition temperature, the film is in an antiparallel structure, thus giving 0 for $\Delta_{270} - \Delta_{90}$.

It is clear from the data, that the tilt evolution of the surface transitions observed from free standing films of MHPBC (both R- and racemic ones) is independent of the film thickness for sufficiently thick films. This is a strong evidence that the transition
Figure 3.6: $\Delta_{270} - \Delta_{90}$ measured from films of R-MHPBC with different thickness. Data are shown in the reduced temperature scale.

observed is indeed a surface transition and the tilt is mostly localized in the outermost two layers on each surface. A comparison of the data from thicker films to the tilt transition data from the 2-layer film suggests that in this type of materials, the surface tilts can be mostly attributed to the outermost single layer. Here we assume that the behavior of the 2-layer film is representative of the behavior of the outermost layer in thicker films. This is a reasonable assumption given the fact that for smectic liquid crystals, intralayer interactions are much stronger than interlayer interactions.

Given the situation of the surface orders in MHPBC, it presents an ideal system for the study of surface transitions with enhanced surface order. And for the first time, we can check whether the theoretical predictions apply.

To gain quantitative knowledge of the surface transition behavior, a power law fitting was carried out for films with $N \geq 20$. The measured $\Delta_{270} - \Delta_{90}$ data were fitted to $\theta_S \propto (-\tau)^{\beta_S}$, with $\tau = T - T_S$ and both $T_S$ and $\beta_S$ are fitting parameters. The resolution of $\Delta_{270} - \Delta_{90}$ was found to be $\pm 0.007^\circ$ and was used as experimental uncertainty in the fitting. Shown in Fig. 3.8 (Fig. 3.9) are the $\log(\Delta_{270} - \Delta_{90})$ as a function of $\log(-\tau)$.
with the value of $T_S$ obtained from fitting. It is clear that the data for the surface transition from films with different thickness $N$ fall onto a single straight line, which is a good indication of the power law behavior. The best fit gives an exponent value $\beta_S = 0.26 \pm 0.01$ for the R-MHPBC films and $\beta_S = 0.28 \pm 0.01$ for the racemic MHPBC films.

### 3.3.2 Transition in 2-Layer Films

For the data shown in Fig. 3.6 and Fig. 3.7, it is clear that the temperature evolution of the tilt angle from the 2-layer films shows different behavior compared with the surface transition behavior from thicker films. It increases with an initially flatter slope than the thicker films. For R-MHPBC (see Fig. 3.6), the 2-layer film data quickly reach the same magnitude as thicker films before its structure turns antiparallel. For the 2-layer film of racemic MHPBC shown in Fig. 3.7, it popped at about 2K below the transition temperature.

For the 2-layer film, there are no interior layers. Thus a two dimensional behavior is
Figure 3.8: Log-log plot of $\Delta_{270} - \Delta_{90}$ measured from films of R-MHPBC with different thickness. Transition temperatures used in the plot are obtained from fitting. Error bars are shown only for the first and last data point of each film.

expected for the tilt transition, i.e., we should have $\theta_{2LR} \propto (-\tau)^{\beta_{2LR}}$, where $\beta_{2LR} = \beta_{2d}$ for the universality class of the transition (XY) [30].

We carried out a power law fitting for the data of the 2-layer films similar to the ones described above. In Fig. 3.8 and Fig. 3.9, we plotted the log($\Delta_{270} - \Delta_{90}$) as a function of log(-$\tau$) with the value of the transition temperature obtained from the best fit. The data points also fall onto a straight line with a slope steeper than the surface transitions. This indicates a power law behavior for the two dimensional transition with an exponent larger than the surface transition values. Indeed the best fits give $\beta_{2LR} = 0.40 \pm 0.02$ for the R-MHPBC film and $\beta_{2LR} = 0.39 \pm 0.01$ for the racemic MHPBC film.
3.3.3 Comparison with Bulk Transition

To form a comprehensive understanding of the surface and two dimensional transition behavior observed from free standing films of MHPBC, we carried out tilt angle measurement on thick sample for the bulk tilt transition using x-ray diffraction. Since smectic liquid crystals have layered structures, along the layer normal direction a one dimensional periodic structure is formed. X-ray diffraction can be used to probe this periodic structure and the position of the Bragg reflection peaks can be used to find the periodicity of the structure, i.e., the layer spacing. At the tilt transition, the molecules will tilt away from the layer normal direction, leading to a reduced value of the layer spacing, following $d(T) = d_0 \cos(\theta(T))$, where $d_0$ is the layer spacing at the transition temperature and roughly equals to the molecular length, and $\theta(T)$ is the tilt angle at temperature T. This way the temperature evolution of the tilt angle can be calculated from the temperature evolution of the layer spacing.

Shown in Fig. 3.10 is the temperature evolution of the layer spacing obtained from
the positions of the Bragg peaks in x-ray diffractions. The experiment was carried out at beam line X-19A at National Synchrotron Light Source, Brookhaven National Laboratory. A two stage oven is used for temperature control, in which a thick free standing film of R-MHPBC was prepared [31]. From the image under an optical microscope and its reflective color, the thickness of the film studied was estimated to be well above 1000 layers. Thus it should show bulk properties for the study of the tilt transition.

In Fig. 3.11, we plotted the $\theta(T)$ data in the reduced temperature scale of the bulk transition calculated from the $d(T)$ data. Close to $T_C$, data were taken in 30mK steps to ensure an accurate determination of the transition temperature. $\theta(T)$ is expected to show power law behavior $\theta(T) \propto (T_C - T)^\beta$ with $\beta$ being the critical exponent. A log-log plot of the data with $T_C = 74.40^\circ C$ is shown in Fig. 3.12. The data fall onto a linear curve in the log-log plot indicating a power law behavior as expected. A linear fit gives a slope $\beta = 0.35 \pm 0.01$, agrees very well with the expected 3D XY type critical behavior ($\beta_{3d,XY} = 0.347$). Note due to the first order nature of the phase transitions between SmC* variant phases, small discontinuities of the layer spacing were observed.
Figure 3.11: $\theta(T)$ data calculated from the $d(T)$ data of MHPBC film. Only data between 70°C and $T_C$ were used.

at those transitions. Thus only data within the SmC*$^\alpha$ phase were used.

### 3.4 What Did We Learn?

In Fig. 3.13 we summarized the values of the critical exponent $\beta$ obtained from the surface tilt transition, two dimensional tilt transition and the bulk tilt transition, together with values from various theoretical models. The order parameter of this transition has both an amplitude and a phase: $\theta = \theta e^{i\phi}$ (phase $\phi$ corresponds to the azimuthal orientation/direction of the tilt). Also, the interaction responsible for the tilt transition is believed to be short ranged. Thus the critical behavior of this transition is expected to belong to the XY universality class.

As shown in Fig. 3.13, for XY model we should have $\beta_{2d,XY} = 0.23$ for finite-sized systems and $\beta_{3d,XY} = 0.347$. Comparing with our experimental results we find that the bulk critical exponent $\beta$ agrees with the 3D XY value. However, the results obtained from the 2-layer films show very different value from the expected 2D XY prediction.
For the critical behavior of the surface transitions in the surface order region, theory predicts $\beta_1 = \beta_S = \beta_{2d}$. However, we have $\beta_S = 0.27$ and $\beta_{2d} = 0.39$, in contradiction to the theoretical prediction of the surface transition.

From our results, we find that although the bulk critical exponent of the tilt transition found in MHPBC matches the prediction of 3D XY model pretty well, the corresponding results for the surface transition and two dimensional transition differ from the theoretical calculations. This suggests that the surface critical behavior is more complicated than expected for the surface order region of the phase diagram.

For free standing films of smectic liquid crystals, experiments reveal that near the surface, the interlayer interactions are also elevated and the enhanced interaction might not be restricted to the thin region of several surface ordered layers. Details about the interlayer interaction near the surface region are given in Ch. 6 and Ch. 7. This together with the fact that intralayer interaction is much stronger than the interlayer interaction might lead to non-universal behavior for the surface transition. However, the unexpectedly large value of the critical exponent from the two dimensional samples
Figure 3.13: Summary of the values of critical exponent $\beta$ obtained from the surface tilt transition, two dimensional tilt transition and the bulk tilt transition, together with values obtained from various spin models.

is still beyond our understanding.

Due to the fact that almost all solid state systems belong to the surface disorder region and almost all theories agree that the surface transition in the surface order region should simply show $d-1$ dimensional critical behavior, surface transition has never been studied in detail either theoretically or experimentally. Our experiments revealed that the previous naive understanding for the surface transition is inadequate, and calls for further theoretical and/or computational study in the future.
Chapter 4

Surface and Bulk Biaxial Transitions in Smectic Liquid Crystal Films

In this chapter our experimental results on the study of the uniaxial to biaxial SmA transition in free standing films of a bent core liquid crystal material is reported. Surface induced biaxial order as well as surface biaxial transition were studied. Critical exponents of the surface transition were obtained and compared to the corresponding values of the interior transition. The results were discussed in the general framework of phase transition in lower dimensions [33].

4.1 Biaxial SmA Phase in Bent Core Liquid Crystals

Since the discovery of polar switching behavior in an achiral bent core liquid crystal [34], a considerable amount of research interests have been attracted to this type of material. Due to the bent shape of the molecules (see Fig. 4.1, and Fig. 4.2 for chemical structure and schematic illustration of bent core liquid crystal), mirror symmetry is intrinsically broken along the bow direction of the molecules (x’ direction in Fig. 4.2(a)). Thus, unlike the situation for liquid crystals with rod like molecules, polar order can be established in bent core materials even when the constituting molecules are achiral. During
recent years, several new liquid crystal phases were discovered in the bent core materials [35, 36]. Since those bent core phases usually exhibit high spontaneous polarization density, they are potentially good candidates for fast responding electro-optical devices.

Although the study of bent core liquid crystals has been a heated area, most researches were focused on elucidating the structures of the various bent core phases. Relatively little work studied the phase transition behavior between those phases, which is a very important and interesting question in its own right [37, 38].

In this chapter we study the uniaxial (SmA_u) to biaxial smectic-A (SmA_b) transition of one bent core liquid crystal. The liquid crystal material chosen for this study is bent core compound UD180. Its molecular structure is shown at the top of Fig. 4.1. Phase sequence of UD180 is isotropic -(146°C)- SmA_u -(98°C)- SmA_b -(88°C)- B2. The SmA_u
phase is a uniaxial SmA phase, in which the molecules within each layer are oriented randomly. The Sm$_A_b$ phase is a biaxial SmA phase, in which the molecules develop long range in-plane orientation order, thus each layer becomes biaxial. Due to its antiparallel arrangement, the Sm$_A_b$ phase of UD180 is found to be antiferroelectric. Figure 4.1(a) and (b) illustrate the structure of Sm$_A_u$ and antiferroelectric Sm$_A_b$ phase. The B$_2$ phase is antiferroelectric with molecules tilted away from the layer normal. B$_2$ phases of bent core materials have four different stable structures.

### 4.2 Order Parameter of the Transition

For the study of phase transition, a proper definition of an order parameter that can be measured experimentally is always the starting point. The Sm$_A_u$-Sm$_A_b$ transition is a process in which, with lowering temperature, the molecules develop a preferred average direction for the molecular orientation in the layer plane. Thus it is a uniaxial to biaxial transition as well as a non-polar to polar transition. As discussed above, mirror symmetry is intrinsically broken in bent core molecules. Shown in Fig. 4.2(a) is a schematic illustration of a bent core molecule in its molecular frame. The mirror symmetry along x' axis as observed in achiral rod like or discotic molecules, is broken due to the bend of the two arms (the degree of the bend is defined with the green cone in the figure). Thus, although the molecule itself is achiral, it is biaxial and polar, even when the molecules are not tilted. The polarization is parallel to the bend direction (x' axis). The ellipsoid of index of refraction for a cluster of bent core molecules is illustrated in Fig. 2(b). Three principal axes are along the x', y' and z' directions. Since for the study of the biaxial SmA transition, we are concerned with transition between two nontilted phases, z' axis of the molecular frame is parallel to the z axis of the laboratory frame (along the layer normal direction).

Since this transition is a process mainly in plane, we need to take a close look in the layer plane in order to identify the order parameter of this transition. Shown in Fig. 4.2(c) is a local index of refraction ellipse in the layer plane of the laboratory frame. The direction of the x axis is defined by the direction of the applied aligning field $E$, which defines the preferred average direction of the molecular polarization as well as the molecular bend direction. The local molecular frame x’y’ is at an angle $\varphi$ away from the
Figure 4.2: Schematic illustration of (a) a bent core molecule in its molecular frame, the green cone defines the bend angle, (b) the local index of refraction ellipsoid, (c) the in-plane index of refraction ellipse in the laboratory frame, orange arrows represent the principal axes, $\varphi$ is the angle between one of the principal axes of the ellipse and the $x$ axis, (d) local polarization density in the laboratory frame, red arrow represents the polarization vector.

Thus, the local polarization and in plane principal axes of index of refraction ($\hat{n}$) are also $\varphi$ away from the $x$ axis. Since the molecules are intrinsically polar and biaxial, we can write ($\hat{n}_{x'y'}$) as

\[
(\hat{n}_{x'y'}) = \begin{pmatrix} n_{o1} & 0 \\ 0 & n_{o2} \end{pmatrix}
\]

due to the molecular biaxiality. In order to obtain the total biaxiality ($\langle n_x - n_y \rangle$) of the sample, we need to average over the whole film (here $\langle \rangle$ indicates thermal averaging). So we have

\[
(\hat{n}_{xy}) = \hat{R}^T(\varphi)(\hat{n}_{x'y'})\hat{R}(\varphi)
\] (4.1)
where \( \hat{R}(\varphi) \) is the rotation matrix in two dimensions. From the algebra, we obtain \( \langle n_x-n_y \rangle = (n_{o1}-n_{o2})\langle \cos(2\varphi) \rangle \), while \( \langle P_x \rangle = P_0\langle \cos\varphi \rangle \), \( P_0 \) stands for the local polarization density. Thus, for the Sm\( A_u \)-Sm\( A_b \) transition of bent core molecules, spontaneous polarization density \( \langle P \rangle \) is the primary order parameter, while the biaxiality measured in \( \langle n_x-n_y \rangle \) is the secondary order parameter. Since UD180 is antiferroelectric in the Sm\( A_b \) phase, \( \langle P \rangle \) stands for the sub-lattice polarization.

As discussed in Ref. [37], when setting the aligning field \( E \) to \( \alpha = 0^\circ \) or \( 90^\circ \) direction in the Sm\( A_b \) phase, the film will have its principal axes of in-plane index of refraction parallel or perpendicular to the projection of the laser beam. The difference of ellipsometric parameter \( \Delta \) obtained under these two orientations is proportional to the total biaxiality of the film, i.e., we will have,

\[
\Delta_0 - \Delta_{90} \propto \langle n_x - n_y \rangle
\]

Thus by studying the temperature dependence of \( \Delta_0-\Delta_{90} \) for free standing films of UD180 through the Sm\( A_u \)-Sm\( A_b \) transition, we will be able to obtain the critical behavior of the biaxiality of the sample, which is a secondary order parameter of this transition.

### 4.3 Surface vs. Interior Biaxial Transition

Various films with different thickness were prepared in the ellipsometer in the Sm\( A_u \) phase. Following the same procedure as described in Ch.2, we used a \( 4 \times 4 \) matrix method to obtain values of the principal indices of refraction and layer spacing in the Sm\( A_u \) phase to be \( n_o = 1.549\pm0.006 \), \( n_e = 1.73\pm0.01 \), and \( d = 4.2\pm0.1 \) nm. Those values were later used in the fitting to determine the thickness of the films studied.

Free standing films of UD180 with thickness ranging from 5 to more than 300 molecular layers were studied. Biaxiality as a function of temperature was obtained by subtracting \( \Delta \) acquired in two successive cooling runs with \( \alpha = 0^\circ \) and \( 90^\circ \), respectively. Note, for bent core liquid crystal materials, the viscosity is very high, so that when the electric field direction is changed in the polar phases, including the Sm\( A_b \) and the B\( 2 \) phase, the response time of the sample is on the order of 10min, thus we cannot perform the same ramp and switch procedure described in the previous chapter. Cooling rate
Figure 4.3: Biaxiality measured in $\Delta_0-\Delta_{90}$ for a 9-layer film (black square) and a 65-layer film (blue triangle) is plotted in the reduced temperature scale of the surface transition. Lines are the fitting results discussed in detail in the text. Vertical axis is shown in log scale in order to present data clearly for both the surface and the interior transition. $T_C$ is at $11.5 \pm 0.1^\circ C$ and $12.93 \pm 0.01^\circ C$ below $T_S$ for the 9- and 65-layer film, respectively. Black arrow around $23^\circ C$ below the $T_S$ of the 65-layer film marks the transition into the $B_2$ phase.

was set to 60mK/min. Data from a 9-layer film and a 65-layer film are shown in Fig. 4.3.

In free standing films of UD180, surfaces establish polar biaxial order at a higher temperature ($T_S$) than the temperature at which the whole film goes into the new phase ($T_C$). For this material, the large temperature window of the Sm$A_u$ phase allows us to reach $T_S$ experimentally. As shown in Fig. 4.3, at $T_S$, both films develop a small biaxiality which evolves with temperature rapidly. This marks the onset of a continuous surface biaxial transition. The surface biaxiality data were fitted to a power law, $A' (T_S - T)^{\tilde{\beta}'}$. $A'$, $T_S$ and $\tilde{\beta}'$ are all treated as fitting parameters. Only data within about 7°C of $T_S$ were used in the fitting.
Contribution from the interior biaxial transition below $T_C$ was obtained by subtracting the surface fitting equation extrapolated over the whole temperature range from the total biaxiality of the film. As shown in Fig. 4.3, the sudden increase of biaxiality at about 12°C below $T_S$ marks the interior biaxial transition. From Fig. 4.3, it is clear that the surface biaxiality from samples with different thickness shows almost identical behavior, while the interior biaxiality of the 65-layer film is about one order of magnitude larger than the 9-layer film. This observation provides strong evidence that the transition at higher temperature is a surface phenomenon, while at lower transition temperature, the whole film orders.

The interior biaxiality was also fitted to a power law, $A(T_C - T)^\tilde{\beta}$, with $A$, $T_C$ and $\tilde{\beta}$ being fitting parameters. The fitting results for the 9-layer and the 65-layer film are shown in Fig. 3 as solid lines. Log scale is used for the vertical axis so that data from the surface transition can be visible. Note that just above $T_C$, there are obvious deviations from the power law behavior of the surface biaxial transition, these are probably due to the pre-transitional behavior of the interior transition, or due to the effective field created by the biaxial polar surface layers. At 23°C below $T_S$, another large increase was observed in the biaxiality from the 65-layer film, which marks the onset of the $B_2$ phase. In the 9-layer film and a 5-layer film we studied, the $B_2$ phase was suppressed.

A least square fitting process was used. The resolution of the biaxiality measured from NTE was found to be $\pm 0.008^\circ$ (this quantity used as experimental uncertainty during the fitting). The resulting parameters $\tilde{\beta}'$ and $\tilde{\beta}$, for the surface and interior biaxial transition, are plotted in Fig. 4.4 as a function of film thickness. Note for the 5-layer film, no separate interior transition was observed; while for the 16-layer film, a defect formed during the data collection prevented us from getting a reasonable fitting for the interior transition; the surface biaxiality data for films thicker than 100 layers are noisier than thinner ones, thus we have a big error bar for the surface exponent of the 141-layer film and the value for the 330-layer film is not available.

The averaged value for the bulk exponent $\tilde{\beta}$ is $0.70 \pm 0.03$, while the surface exponent $\tilde{\beta}'$ (excluding the 141-layer film result) is $0.58 \pm 0.05$. Theory suggests that for $d < 4$, we have $\tilde{\beta} > 2\beta$, with $\beta$ ($\tilde{\beta}$) being the critical exponent for the primary (secondary) order parameter [39]. Although the order parameter symmetry suggests this transition is of the XY type, with the measured $\tilde{\beta}$ value as well as the ones reported in some previous
Figure 4.4: Critical exponents of the biaxiality for the surface transition (black square) and the interior transition (red dot) as a function of film thickness N. Results from N = 5-, 9-, 16-, 65-, 141- and 330-layers are presented. Dashed and dotted lines mark twice the value of exponent $\beta$ for 2D XY (effective exponent for finite sized systems) and 3D XY models.

experiments [37, 38], it is unlikely that this transition is of the 3D XY class (in Ref. [38], $\langle n_x - n_y \rangle$ was mistakenly treated as the primary order parameter). The reason might be because of the shape of bent core molecules, intralayer interaction is expected to be much stronger than interlayer ones, thus making the system more toward 2D instead of 3D XY.

On the other hand, the surface exponent $\tilde{\beta}'$ is found to be always smaller than $\tilde{\beta}$. This can be understood in the framework of surface transition. In this situation, theory suggests the enhanced surface interaction will make the surfaces show lower dimensionality than the bulk (as discussed in detail in Ch. 3). A direct comparison of $\beta$ and $\beta'$ of the primary order parameter would be preferable, however, it is not always achievable in experiments and remains to be obtained. Although there’s no numerical results of the exponents of the secondary order parameter available for comparison,
smaller exponent value of the surface transition ($\tilde{\beta}'$) does suggest lower dimensional behavior.

### 4.4 What Did We Learn and What Else Can We Learn?

In this chapter, we studied another example of the surface induced order and surface transition phenomena, namely, the surface biaxial transition of bent core liquid crystal materials. We investigated the critical behavior of the surface biaxial transition (expects 2D behavior) and compared it to the corresponding situation observed for the interior layers, which is supposed to show bulk properties (3D) in the thick film limit (e.g., the 330-layer film). The comparison of the results, together with some previously published measurements, suggests that the uniaxial to biaxial SmA transition is unlikely to be of the 3D XY class. However, the results are consistent with the theories on the study of surface transition.

Before concluding this chapter, the importance of studying the Sm$_A$$_u$-Sm$_A$$_b$ transition needs to be discussed from another aspect. In recent years, de Vries type Sm$_A$ materials have attracted a lot of attention. For this type of materials, very little layer spacing change (less than 1%) is observed through the SmA-SmC transition, when a large biaxiality is developed in the sample. This property is very attractive for making smectic liquid crystal devices, for it would avoid the defects developed when the layer spacing changes in conventional SmA - SmC transition. In the diffuse cone model of the de Vries material, molecules are suggested to be pre-tilted with a random distribution of tilt directions. In the de Vries type SmA - SmC transition, a preferred direction of the tilt is developed, thus the sample becomes biaxial and shows apparent tilt with minimum layer spacing change.

However, although proposed a long time ago, there’s still no direct experimental evidence for the diffuse cone model [9]. And without a model physical system, theoretical advances of de Vries type SmA-SmC transition have been limited.

In the diffuse cone model, the rod-like molecules are tilted in the SmA phase with uniform azimuthal distribution. At the transition to the SmC phase, a preferred azimuthal orientation develops with almost no change in the molecular tilt angle, thus producing minimal layer contraction. However, this is exactly what happens at the
SmA\textsubscript{u}-SmA\textsubscript{b} transition of a bent core material; if we view one single layer of bent core SmA material as two layers of tilted rod-like molecules (see the part enclosed in the light grey box in Fig. 4.1). The tilt angle of the molecules is thus defined by the bend of the two arms (the green cone in Fig. 4.2(a)). As shown for UD180, at the SmA\textsubscript{u}-SmA\textsubscript{b} transition, there’s no layer spacing variation. Recent study on a de Vries type SmA material even showed qualitatively similar behavior under applied field as a non-tilted smectic bent core material [40, 41]. All the above discussion suggests that bent core materials with SmA\textsubscript{u}-SmA\textsubscript{b} transition can be used as a model system to study the de Vries type SmA-SmC transition, and will probably bring new insights into this topic.

For summary, in this chapter, our study on the SmA\textsubscript{u}-SmA\textsubscript{b} transition of free standing films of the bent core material UD180 is reported. Biaxiality is identified as the secondary order parameter of this transition. Both surface and bulk exponents of the biaxiality were obtained. The significances of the results are discussed in the aspects of 1) the nature of the SmA\textsubscript{u}-SmA\textsubscript{b} transition of bent core material; 2) the experimental realization of surface transition and comparison of the surface and bulk critical exponents; 3) the potential of using this type of materials as a model system for studying the de Vries type SmA phase.
Chapter 5

Surface - Surface Interaction in Liquid Crystal Films

In this chapter we study the surface - surface interaction in smectic liquid crystal films. Following the study of the surface order described in the last two chapters, we investigate the temperature (T), external field (E) phase diagram of films with different thickness in the temperature window $T_C < T < T_S$. In this temperature window, surface layers are ordered while the interior layers are disordered. From the field induced transitions observed in the experiments, we are able to obtain information regarding the nature of the surface - surface interaction, thus gain valuable insight into the interlayer interactions in AFLC materials.

5.1 Field Induced Surface Transition

5.1.1 What Can We Learn from Field Induced Surface Transitions?

The study of surface order and surface tilt transition is described in detail in Ch. 3. For free standing films of smectic liquid crystals, surface layers will order at a higher temperature than the interior layers. Thus in the temperature window $T_C < T < T_S$, tilted surface layers are observed while the interior layers are not tilted. This makes the surface layers ferroelectric while the interior layers remain paraelectric. Under this condition the surface layers can be aligned and their structure can be changed with
applied external field, which is the topic of this chapter.

It has been a long unsolved question whether long range interlayer interactions could exist in smectic liquid crystals. Another question is whether such interactions, if existing at all, would be a necessary ingredient for the formation of SmC* variant phases. However, direct measurement of interlayer interactions would be an extremely challenging task, if possible at all, especially when facing the interaction beyond the nearest neighbouring layers. Under this condition, the study of surface - surface interaction through field induce transition of the surface arrangement would be able to provide valuable information regarding the questions raised above.

The applied in-plane field we use is too weak to cause any structural change within each surface on the top or bottom of the film. However, for films with appropriate thickness, it is possible to achieve a field induced transition regarding the relative orientations of the two surfaces. This situation is possible only if there is indeed an interaction between the two surfaces, otherwise the two surfaces would always be aligned with the electric field direction and a field induced transition would not be observed at all.

The thickness range in which we do see a field induced transition of the relative surface arrangement gives us the range of the surface - surface interaction. And the ground state of the surface - surface arrangement without applied field provides the sign of the surface - surface interaction. However, if the ground state is parallel/synclinic, we would not be able to see any field induced transition either. With those information available from the study of field induced transition of surface arrangements, this study will provide a unique and solid approach for understanding the nature of the interlayer interaction in AFLC materials.

5.1.2 Data of Field Induced Surface Transition

The materials we choose for this study are R- and racemic MHPBC (details see Ch. 3). From the study presented in Ch. 3 we found that MHPBC films show a simple surface tilt order below $T_S$, with $T_S$ below the isotropic - SmA transition temperature, making it experimentally accessible. Also, $T_S$ is sufficiently higher than bulk $T_C$ (about 20K), which allows the surface tilt to saturate before going to the lower temperature phase. Moreover, the thickness of the surface ordered layers is relatively small, one at each surface. All these unique properties make MHPBC an excellent candidate for the
Figure 5.1: Sample scan data from an 11-layer film of R-MHPBC at 1.25K below $T_S$. Free standing films were prepared and studied in our NTE. Eight evenly spaced electrodes around the film hole allow us to create an uniform in-plane electric field across the film. The field strength is determined by the applied voltage and the diameter of the film hole (4mm). Ellipsometric parameter $\Delta$ was acquired as a function of temperature ($T$) and transverse electric voltage ($V$) for films with different thickness ($N$). Electric field was oriented perpendicular to the laser beam. A sample V scan is presented in Fig. 5.1. Note, $V > 0$ corresponds to $\alpha = 270^\circ$ while $V < 0$ corresponds to $\alpha = 90^\circ$.

The data set in Fig. 5.1 is obtained from an 11-layer film of R-MHPBC at 1.25K below $T_S$. We obtained all our V scans with a voltage sweep rate of 0.1V per minute. From the data, two field induced transitions are observed upon changing the applied electric voltage. This indicates that the two surfaces of the film switch from being antiparallel at low voltage to being parallel above the threshold as illustrated in Fig. 5.2. The relative arrangements of the surfaces are apparent from the fact that below the threshold voltages, the data $\Delta$ is the same for $V > 0$ and $V < 0$; while above the threshold voltages, a finite difference between the two orientations develops. The difference in $\Delta$ is proportional to the total surface tilt angle at the temperature the measurements were
Figure 5.2: Schematic illustration of the two surface arrangements observed in the voltage scan. For low field values (left) the two surfaces are antiparallel while for higher field values (right) they are in a parallel arrangement.

taken. The fact that field induced transitions are observed demonstrates the existence of the surface - surface interaction as discussed above. From the scan, two characteristic field values can be identified, $V_L$ and $V_H$ ($|V_L| < |V_H|$), corresponding to the lower and upper switching field due to the first order nature of this field induced transition. Since the behavior of the film is symmetric for $V > 0$ and $V < 0$, most scans were performed only with $V < 0$ for the higher sensitivity in this orientation due to our NTE set up.

5.2 Comparison with Magnetic Phenomena

The voltage scan data presented in Fig. 5.1 show an intriguing resemblance to the re-magnetization curve obtained for ferromagnetic (FM) layers separated by a non-magnetic spacer with an antiferromagnetic (AFM) coupling between the two FM layers [42]. Thus, the switching behavior of the ferroelectric surface layers with paraelectric interior layers can be viewed as a liquid crystal counterpart of the well-known phenomenon interlayer exchange coupling (IEC) in magnetism. The similarities between these two systems are obvious. Both systems involve ferro-electric/magnetic layers separated by
non-ordered spacers. Upon changing external field, different relative arrangements between the two surfaces can be achieved. Although for the case of AFLC films, the spacer layers and surface layers are the same material, the elevated surface tilt transition studied in Ch. 3 makes this comparison valid. Thus, just like from the re-magnetization curves of IEC systems researchers can obtain the sign and magnitude of the interaction between the two FM layers, we should be able to obtain those information for the interaction between surface layers of AFLC films following a similar approach. On the other hand, the similarities between the two systems do not go beyond the phenomenological level. The microscopic mechanism for the coupling between the two surfaces is obviously different in these two systems. For IEC systems, researchers now understand that the coupling is mediated by the conduction electrons of the spacer layer; while for the AFLC films, as discussed above the nature of the interactions between different layers remains a long lasting question.

5.3 Surface - Surface Interaction

5.3.1 Temperature Dependence

To study the temperature dependence of the surface - surface interaction, we performed voltage scans at different temperatures in the surface ordered temperature window of the films. The data shown in Fig. 5.3 were obtained from the 11-layer film of R-MHPBC as a function of temperature. Plotted in T-T\textsubscript{S} scale, Fig. 5.3(b) presents \(\Delta_{270} - \Delta_{90}\) measured in the parallel configuration of the two surface layers. Thus they can be viewed as the average tilt angle of each surface. We measured this value immediately after each voltage scan for each temperature point. From the data, it is clear that the surface tilt transition is continuous with \(\Delta_{270} - \Delta_{90} \propto (-\tau)^{\beta}\) with \(\tau\) being the reduced temperature, \(\beta \simeq 0.27\) from our previous study. Figure 5.3(a) shows the V-T phase diagram, with threshold voltage \(V_L, V_H\) and their average \(V_C\) as a function of temperature. All the threshold voltage values increase sharply upon approaching \(T_S\) from below. The two spinodal lines \(V_L\) and \(V_H\) merge as temperature increases, the difference between them disappears within 0.5K of \(T_S\). Although the V scans still show step-like switching behavior, we cannot determine whether there is a tricritical point below \(T_S\) along the transition line due to our limited experimental resolution.
Figure 5.3: (a) V-T phase diagram and (b) the surface tilt value measured as a function of the reduced temperature of the surface transition from the 11-layer film of R-MHPBC. In the V-T phase diagram, both the upper, lower switching field and their average value are shown. For \( T < T_S \), below \( V_C \) two surfaces are in an antiparallel arrangement, while above \( V_C \) they are in a parallel arrangement. For \( T > T_S \), the whole film is disordered (non-tilted and paraelectric). Arrow marks the temperature when the hysteresis between the upper and lower switching field goes to 0.

We would like to form a better understanding of the obtained phase diagram, especially about the \( T \) dependence of the switching voltage \( V_C \). The two-layer Ising model is a good choice for modeling our system qualitatively. Thus we model the two surfaces of AFLC films as two layers of Ising spins on a square lattice as shown in Fig. 5.4(a), with all spins aligned in plane. Since for \( V = 0 \) the surfaces are in an anti-parallel configuration, the interaction between the layers is therefore antiferroelectric.

The Hamiltonian for such system can be expressed as:

\[
\mathcal{H} = J \sum_{\langle ij \rangle} s_i^1 s_j^1 + J \sum_{\langle ij \rangle} s_i^2 s_j^2 + K \sum_i s_i^1 s_i^2 - h \sum_i (s_i^1 + s_i^2) \quad (5.1)
\]

with \( s_i^1 \) being the spin on site \( i \), layer 1, \( J < 0 \) being the coefficient for the FM intralayer nearest neighbour interaction and \( K > 0 \) being the coefficient for the AFM
Figure 5.4: (a) Structure of the two-layer Ising model and (b) the expected phase diagram.

interlayer interaction, h being the external field. For temperature independent J and K, we would expect an h-T phase diagram as illustrated in Fig. 5.4(b), with the value of the switching field between the antiparallel and parallel states decreasing upon approaching transition temperature at h = 0. However, this is clearly not the case for our system, as shown in Fig. 5.3(a). This can happen only if K itself (assuming J is temperature independent), as a function of T, increases sharply upon approaching transition temperature from below. A hand-waving argument would suggest K increases faster than $(\cdot \tau)^{-\beta}$ for the situation observed. This point will be discussed in more detail in the next subsection.
5.3.2 Thickness Dependence

We present in Fig. 5.5 (Fig. 5.6) the switching voltage $V_C$ as a function of temperature for films with different thickness $N$ of R- (racemic) MHPBC. By studying films with different thickness, we effectively control the distance between the two surfaces of the film, thus allowing the study of distance dependence of the interaction. Films with thickness from 10 to about 20 layers were studied. Films thicker than 20 layers would either yield a switching field too low to be measured accurately; or in the case of a sufficiently thick film, result in no interaction between the two surfaces at all. On the other hand, films thinner than 10 layers would require a field value higher than what we can achieve in our setup. Thus the range of thickness best suited for the study is about 10 to 20 layers.

In Fig. 5.5 (Fig. 5.6), we show the data from R-MHPBC (racemic MHPBC) films. Switching voltages from all the films increase upon approaching $T_S$ from below, while $V_C$ decreases at a given temperature with increasing film thickness, i.e., increasing the distance between the two surfaces. Hysteresis between the two spinodal lines $V_L(T)$
and \( V_H(T) \) all show similar trend as described in Fig. 5.3. The several data points with large deviations for the 20-layer R-MHPBC and 12-layer racemic MHPBC films were probably due to the formation of domain walls during the voltage scan.

Since the surface tilt in \( \Delta_{270} - \Delta_{90} \) and the \( V_C \) were measured together, we can look at their relation by plotting one quantity as a function of the other. Shown in Fig. 5.7 (Fig. 5.8) are the data from R- (racemic) MHPBC films with different thickness. Only data within about 5K of \( T_S \) are shown (excluding some points with very high \( V_C \)). In this region, as clear from the log - log plot shown in Fig. 5.7 and Fig. 5.8, a power-law behavior seems to be able to describe the relation between \( V_C \) and \( \theta_S \).

A fitting to the power-law function gives a relation \( V_C \propto \theta_S^\gamma \) with \( \gamma = -2.1 \pm 0.3 \), from data from all the 7 films studied. This confirms our argument in the last section that \( V_C \) increases much faster than \((\tau)^{-\beta}\). Also, since for the ferroelectric smectic liquid crystal we have spontaneous polarization density \( P \propto \theta \), which leads to \( V_C \propto \theta_S^{-2.1} \propto P^{-2.1} \). This power-law relation should be helpful in creating an understanding of the microscopic mechanism for this surface - surface interaction.

Figure 5.6: Switching voltage measured from racemic MHPBC films with thickness \( N = 12, 16, 18 \) and \( 20 \) -layers.
Figure 5.7: Switching voltage as a function of tilt angle plotted in log - log scale for R-MHPBC films, only data in the range in which a power-law like behavior is observed are shown.

In Fig. 5.9 we plotted $V_{C}(N,T)$ with $\Delta_{270} - \Delta_{90}$ being 0.1, 0.12, 0.14 and 0.16 for R-MHPBC and $\Delta_{270} - \Delta_{90}$ being 0.12, 0.14 and 0.16 for racemic MHPBC in log-log scale as a function of distance $d$ between the center of the two surfaces. Clearly, $V_C$ as a function of $d$ decreases faster than power law, and has a cut-off value of about 40 layers for R-MHPBC films and about 25 layers for racemic films. Thus the interaction between the two surfaces of AFLC films of MHPBC does not seem to be of the long-range nature. For reference, the dotted line in the figure has a distance dependence of $d^{-2.5}$.

From Fig. 5.9, we can see that around $d = 15$ layers, the behavior of $V_C$ as a function of $d$ follows the dashed line $d^{-2.5}$ pretty well. If we extrapolate the dashed line back to $d = 1$ layer, we obtain $V_C \simeq 0.5kV$, which correspond to an E value of about 2.5V/µm for nearest neighbours. This is a reasonable number for AFLC materials to produce a field induced antiferroelectric to ferroelectric transition in the bulk. However, upon increasing $d$, $V_C$ decreases faster at larger $d$, especially for racemic MHPBC films.
This leads us to the conclusion that although the interlayer interaction between two surfaces of AFLC films is not short ranged, it is not truly long ranged. Thus we call it quasi-long range interaction.

### 5.4 What Did We Learn?

With the experimental results presented above, we set out to explore the physical implications of our results. To form a better understanding of the surface-surface interaction we wrote down the phenomenological free energy involved in the field induced transition.

\[
F = J_s \xi_1 \cdot \xi_2 - a \mathbf{E} \cdot (\mathbf{P}_1 + \mathbf{P}_2) + b (\xi_1 \times \xi_2)^2
\]  

(5.2)

In the free energy expression, the \(J_s \xi_1 \cdot \xi_2\) term is the surface-surface interaction, with \(J_S > 0\) since the ground state structure is antiparallel; the \(-a \mathbf{E} \cdot (\mathbf{P}_1 + \mathbf{P}_2)\) term describes the dipole-field interaction due to the ferroelectricity of the tilted surface.
Figure 5.9: Distance dependence of the switching voltage $V_C$ for R- and racemic MH-PBC films with different values of $\Delta_{270} - \Delta_{90}$ plotted in log-log scale. The dashed line shows a power-law behavior with power $-2.5$.

layers, $a > 0$ being the coefficient; while the $b(\xi_1 \times \xi_2)^2$ term provides the anisotropy energy needed to allow an antiparallel-parallel transition instead of continuous rotation of the two surface layers.

At the transition $E_C (V_C)$, the free energy of the two arrangements are equal, thus we have $J_S = 2aPE_C \propto PV_C$. Since we already have $V_C \propto \theta_S^{-2.1}$ near $T_S$, this leads to $J_S \propto \theta_S^{-1.1}$ near $T_S$. Thus the interaction strength, although we cannot measure it close enough to $T_S$, seems to diverge at the surface transition temperature.

A satisfactory explanation of the T dependence would require an understanding of the microscopic origin of the interactions being measured, which unfortunately we do not have at the moment. However, it is quite unlikely that dipole-dipole interaction would be the major force here; for otherwise we would see a decrease in $V_C$ as tilt angle/polarization decreases upon increasing T. On the other hand, smectic layer fluctuations have been demonstrated to be able to produce long range interlayer interactions [15, 16, 17]. We suspect surface fluctuation plays an important role in forming
the interaction we measured. But the existing theory does not explain the fact that the interlayer interaction prefers anti-parallel arrangement between the two surfaces nor can it explain other aspects of the results.

Before relating our results on the surface - surface interaction to discussion about the nature of interlayer interactions in AFLC materials, we need to answer one question: is the interaction between two layers affected by them being at the surface? In other words, for the situation shown in the left and right halves of Fig. 5.10, are the interactions between layer A and layer B the same? We answer this question by first pointing out that the interaction we measure is not the Casimir-like interaction caused by surface fluctuations or surface potential. This type of interaction would indeed result in unique repulsive or attractive interaction between the two surfaces [57]. However, this is clearly not what has been reported in this chapter. Secondly, as long as the interaction involved can be expressed as pair interactions that involves only the two layers concerned, it should make no difference whether the two layers studied are at the surfaces or in a bulk material. Since the majority of the phenomenological models rely on effective interaction terms that are pair-wise additive, our results on the surface - surface interaction should at least be able to describe the qualitative behavior of the general interlayer interaction in AFLC materials.

Finally, we are surprised to see that $V_C$ for racemic MHPBC films has almost the same value as $V_C$ for R-MHPBC at same $T - T_S$ around $d \approx 10 - 15$ layers, although for racemic films $V_C$ decays faster as a function of $d$. Since for racemic films, enantiomeric excess is very small (1% of that of R-MHPBC), these results suggest that there exist some kind of clustering and correlation between molecules of the same chirality in the two surfaces of the racemic films. If there were no clustering or correlation, we would expect $V_C$ of racemic films to be very different from that of R-MHPBC films. We would like to point out again that the interaction we measure is of the antiferroelectric type that favors the antiparallel arrangement between the two surface layers. Thus it is not the fluctuation induced attraction/repulsion; and we observed no oscillations in $V_C$ as a function of $d$ in our limited data set. For MHPBC, we know that just below the bulk $T_C$ the nearest neighbour interlayer interaction is ferroelectric and the next nearest neighbour interlayer interaction is antiferroelectric. If the interlayer interaction between the interior layers follow similar behavior as the one we observed between two
surfaces layers (i.e. antiferroelectric quasi-long range interaction), then we can form a new phenomenological understanding of the SmC* variant phases. Those novel phases are the result of competition between ferroelectric (or antiferroelectric, depending on the temperature) nearest neighbour interlayer interaction and antiferroelectric quasi-long range interlayer interaction. Although we still have no clue about the microscopic mechanism of the interlayer interaction in AFLC materials, our experiment provides important new insight into the behavior of the interlayer interaction of AFLC films beyond the nearest neighbour, and also provides a new direction for the phenomenological understanding of the system. Several pieces of published work have reported the studies of FM systems frustrated by long range AF interaction and have shown such systems do produce structures similar to SmC* variant phases [43]. However, a detailed molecular dynamics study of the situation and a complete phase diagram for AFLC materials with the parameters derived from our work would be in order.
Chapter 6

Surface Effects on the Helical Structures in Liquid Crystal Films

In this chapter, we study the temperature evolution of the helical structure of the Sm\(C^*_\alpha\) phase with NTE. Free standing films with thickness ranging from 31 to more than 400 layers were prepared and studied. The experimental results show a reduced twisting power in thin films. A simple model was constructed to explain the results. Surface effects were found to be the key reason for this phenomenon. Our findings are consistent with the theoretical studies of helically ordered magnetic films.

6.1 Helical Structure in Smectic Liquid Crystal Films

6.1.1 Structure of the Sm\(C^*_\alpha\) Phase

In the Sm\(C^*_\alpha\) phase, molecules are tilted away from the layer normal. Within each layer, the tilt directions are uniform if no defects are present, while along the layer normal direction, the tilt direction of each layer is arranged in a helix with pitch on the order of a few layers. A schematic illustration of the helical structure is shown in Fig. 6.1. Since the layer spacing of smectic liquid crystals is around 3nm, the unit cell of the Sm\(C^*_\alpha\) phase has a size of about 30nm. Thus this phase is optically uniaxial, since optical wave
Figure 6.1: Schematic illustration of the helical structure of the SmC$^\ast$ phase. Red arrows represent tilt directions of the layers.

length is much larger than the size of the unit cells.

6.1.2 The $J_1 - J_2$ Model

The formation of the helical structure along the layer normal direction can be understood in a simple model involving only nearest and next nearest neighbor interlayer interactions. The relevant free energy is:

$$F = J_1 \sum_{i=1}^{n} \xi_i \cdot \xi_{i+1} + J_2 \sum_{i=1}^{n} \xi_i \cdot \xi_{i+2}$$  \hspace{1cm} (6.1)

Here $J_1$ is the nearest neighbour (NN) interlayer interaction. $J_1$ can be either ferroelectric or antiferroelectric. $J_2$ is the antiferroelectric next nearest neighbour (NNN)
interlayer interaction. $\xi_i$ is a unit vector describing the tilt direction of the $i$th layer, and is allowed to rotate in plane. The frustration between the NN and the NNN interlayer interaction will produce a helical structure, with an angle $\phi$ between neighbouring layers given by:

$$\cos(\phi) = -\frac{J_1}{4J_2}$$

with $-1 \leq \frac{J_1}{4J_2} \leq 1$. Although quite simple, this model is a starting point for understanding the behavior of the SmC$^*$ phase, and has been used to illustrate the temperature evolution of the interlayer interactions in the AFLC materials [18].

6.1.3 Magnetic Helical Structure

Some magnetic materials like Ho, show a similar helical structure to the SmC$^*$ phase. Ho has an hcp structure in single crystals and epitaxial films. Below its magnetic ordering temperature, the magnetic moments on the lattice point to the same direction within the a-b plane, while along the c-axis they arrange in a helical structure. This magnetic structure is very similar to the helical structure found in AFLC liquid crystal films [45, 44].

Studies show the formation of the helical structure in Ho films can also be viewed as the result of competition between the nearest and next nearest neighbor interlayer interactions, thus can also be understood in the $J_1 - J_2$ model described above. This interesting similarity suggests similar behavior can be expected from both systems, and also that the information obtained from one system can facilitate the understanding of the other one.

6.1.4 What Are We Looking For?

Some recent computation studies of the helically ordered magnetic films suggest that contrast to the bulk structure in which constant rotation angle is found between moments in neighboring layers across the sample, in films, near the surface reduced value of the rotation angle is observed [45, 46, 47]. This points to a possible surface induced reduction of twisting power. With the similarity discussed above between the helical structures in magnetic films and liquid crystal films, a possible similar situation can be expected in liquid crystal films.
Inspired by those studies of helically ordered magnetic films, in this chapter we study the evolution of the Sm\(C^*\)\(\alpha\) structure in free standing films with thickness ranging from 31 layers to more than 400. Our data show that as the film thickness decreases, the effective pitch of the helical structure increases, and a *buffer region* with reduced twisting power was discovered next to the surface region. Although similar results were reported in the computational studies of the helically ordered magnetic films, to the best of our knowledge, no experiments have been able to demonstrate this effect. Thus our results can also be viewed as experimental confirmation of the computation results on helical magnetic films.

### 6.2 Surface Induced Reduction of Twisting Power

#### 6.2.1 Experimental Results

The material used for this study is AFLC compound 10OTBBB1M7 (C10). Bulk C10 shows a Sm\(A\) to Sm\(C^*\)\(\alpha\) transition at 124°C \(T_C\). C10 was chosen for this study because we have detailed knowledge about the temperature evolution of the Sm\(C^*\)\(\alpha\) pitch in bulk samples from previous resonant x-ray diffraction (RXRD) experiments, providing a reference for the results in thin films.

Ellipsometric parameter \(\Delta_{90}\) \(\left(\Delta_{270}\right)\) was acquired from our null transmission ellipsometer (NTE) as a function of temperature \(T\) with a weak in-plane external DC field \(E\) set to 90° \(\left(270°\right)\) from the incident laser direction.

More than 40 films with different thicknesses were prepared in the ellipsometer in the Sm\(A\) phase. Following the procedure described earlier in Ch. 2, optical parameters measured from those films at 129°C were used in a \(4 \times 4\) matrix method to obtain values of the principal indices of refraction and layer spacing in the Sm\(A\) phase to be 
\[
\begin{align*}
n_o &= 1.490 \pm 0.005, \\
n_e &= 1.64 \pm 0.01, \\
d &= 3.89 \pm 0.02 \text{ nm}
\end{align*}
\]
Those values are later used in the same fitting procedure to determine the thickness of the films studied.

Figure 6.2 shows the temperature evolution of the parameter \(\Delta_{90}\) obtained in cooling from films with thickness \(N = 41, 112, 184\) and 322 layers. For this study cooling rates from 10mK/min to 50mK/min were used. In the Sm\(A\) window \(T - T_C > 0\), the parameter \(\Delta_{90}\) is almost temperature independent; while in the Sm\(C^*\)\(\alpha\) window \(T - T_C < 0\), \(\Delta_{90}\) shows oscillations, characteristic of the Sm\(C^*\)\(\alpha\) phase in free standing films.
Figure 6.2: $\Delta_{90}(T)$ from films with different N. The data are shown in the reduced temperature scale of the SmA-SmC*_α transition. On the top is the chemical structure of C10.

Also, it is evident from the figure that thicker films show more oscillations.

Before proceed to data analysis, we need to understand the mechanism of the oscillations in $\Delta_{90}$. As discussed in the previous chapters, surface enhanced order usually produces a surface transition several degrees higher than the bulk transition for smectic liquid crystals. For the case of the SmA-SmC*_α transition in free standing films, several surface layers will be already tilted at $T_C$. However, in the SmC*_α phase, those biaxial surface layers are not part of the optically uniaxial helical structure of SmC*_α. As the pitch of the helix evolves with temperature, the two biaxial surfaces rotate at the same time, producing the observed oscillations. A complete oscillation is observed when the
Figure 6.3: Current understanding of the helical structure of the SmC∗α phase in free standing films. Yellow region represents the surface ordered biaxial layers, while the blue region represents the bulk like layers.

The number of turns in the structure changes by one [48, 49].

Since surface layers do not contribute to the formation of the helical structure in the SmC∗α phase, determination of the number of surface layers is a vital step. Figure 6.4(a) shows in log-log scale the $\Delta_{270}-\Delta_{90}$ measured at 129°C (5°C above $T_C$) from films with $N$ ranging from 2 to more than 400 layers. It has been shown that for planar structures, $\Delta_{270}-\Delta_{90}$ is proportional to the total tilt angle of the film. In Fig. 6.4 (a) two distinct behaviors can be identified. For $N < 6$, an almost linear increase of $\Delta_{270}-\Delta_{90}$ is observed as $N$ increases; while for $N > 6$, $\Delta_{270}-\Delta_{90}$ is almost constant. This feature clearly indicates that the surface order can be accounted for with a surface layer number $N_S = 3$. Thus for the SmC∗α structures in free standing films of C10, there are 3 biaxial surface layers at each air - liquid crystal interface, with $N_{in} = N - 2N_S$ layers.
Figure 6.4: (a) $\Delta_{270} - \Delta_{90}$ ($\Delta_+ - \Delta_-$) measured at $T = 129^\circ\text{C}$ from films with thickness $N$ ranging from 2 to more than 400 layers plotted in log-log scale. (b) Temperatures of the oscillation minima in the SmC$^*_a$ window of the 452-layer film. (c) cartoon (top) of the SmC$^*_a$ structure in the bulk with pitch = 8 layers and top view (bottom) of the proposed structure of the buffer region, numbers are the layer index from the surface region.

in the interior of the film. Biaxiality due to the incomplete helix in the interior is small compared to the one from the surface layers.

Figure 6.4(b) shows the temperatures of the minima of the oscillations in $\Delta_{90}$ from a 452-layer film over the SmC$^*_a$ window. The temperature of each minimum was obtained by a parabola fitting of the data near the minimum. The temperatures of the minimum locations can be described very well with a linear function. Thus the oscillation frequency over the temperature window concerned is constant. This agrees with the results from the RXRD data. So the oscillation behavior can be well-described by the average frequency in temperature.

Figure 6.5 shows the $\text{Freq.}_{Norm.}/N_{in}'$ as a function of $N_{in}'$ for films with $N$ ranging from 31 to 452 layers ($N_{in}' = N_{in} - 1$, since between $N$ layers there are $N-1$ rotation angles). Note the 31-layer film is the thinnest film studied, for it showed just more than
Figure 6.5: Data (symbol) and fitting with the linear model (solid line) and exponential model (dash line) of the Freq.\_Norm.\_in/N′\_in plotted as a function of N′\_in. Frequency is normalized with the bulk value.

half oscillation. Frequency of the oscillation was obtained from the temperature and number of oscillations between the first and last discernible minimum. Freq.\_Norm. was acquired by dividing frequency of the oscillation with the corresponding value of the bulk sample (Freq.\_Norm. = Frequency/Frequency\_bulk) (In our RXRD experiments, we found bulk C10 shows a pitch evolution almost linear in temperature in the SmC∗ \_α window, with pitch equals to 8.15 layers at 122.77°C and 5.81 layers at 119.2°C). Position of each minimum is again obtained from parabola fitting.

Since the number of oscillations is given by the change of turns in the helix, frequency is proportional to the temperature derivative of (N′\_in/P(T)), with P(T) being the pitch at temperature T. As a result, Freq.\_Norm./N′\_in is proportional to 1/P_{eff}^2, where the effective pitch P_{eff} is the average number of layers in one complete turn of the helix. From Fig. 6.5, surprisingly, a decrease in the Freq.\_Norm./N′\_in is observed as film thickness decreases. This observation is unexpected based on the previous understanding of the SmC∗ \_α structure (Fig. 6.3), which would result in a constant average twisting power over
Figure 6.6: Structure of the model used in the text. Shown in open symbols are the rotation angle $\phi$ between two neighbouring layers of the linear model for films with $N_{in}$ greater (square) and smaller (circle) than $2a$, with size of the buffer region $a = 6$ in the figure. Solid red triangle shows the $\phi$ profile of the exponential model with $\zeta = 3$.

the thickness studied. The decrease in $\text{Freq.}_{\text{Norm.}}/N_{in}'$ suggests an increase of effective pitch, i.e., a reduced twisting power of the helix in thin films. Since this effect is more pronounced in thin films, we expect surface effects and/or finite size effects to be the reason.

6.2.2 Structural Model and Fitting

To obtain further understanding and quantitative knowledge of the results, we first constructed a simple linear structural model. The model used is illustrated in Fig. 6.6 in open symbols. In our model, we assume that at each surface, there are $N_S = 3$ surface layers that do not contribute to the formation of the helix; next to the surface layers, we have $N_S' = a$ layers of buffer region with rotation angle $\phi_a(i)$ smaller than the bulk value. The remaining part of the film ($b$ layers, if $N > 2N_S + 2N_S'$) is assumed to have the bulk structure. In the buffer region, $\phi_a(i)$ is assumed to increase linearly from 0 to
the bulk value $\phi_b$ as a function of the distance from the surface $(i)$, so we have $< \phi_a > = \phi_b/2$. A cartoon of the structure of the buffer region is shown in Fig. 6.4 (c) and Fig. 6.7. Thus, the total rotation angle of the film is found to be:

$$\phi_{total} = \begin{cases} 
(N'_{in} - a)\phi_b & \text{if } N_{in} \geq 2a \\
(N'_{in}/2)^2 \phi_b/a & \text{if } N_{in} < 2a
\end{cases}$$

The $Freq.\_\text{Norm.}/N'_{in}$ is then given by:

$$Freq.\_\text{Norm.}/N'_{in} = \begin{cases} 
(N'_{in} - a)/N'_{in} & \text{if } N_{in} \geq 2a \\
N'_{in}/4a & \text{if } N_{in} < 2a
\end{cases}$$

Note, frequency is given by $\Delta \phi_{total}/(2\pi \Delta T)$, and we have $\Delta \phi_b/(2\pi \Delta T)$ being the
Figure 6.8: Data (symbol) and fitting (line) of the frequency of the oscillation.

bulk value used as reference for the normalization (Frequency_{bulk}). ΔT is the temperature range of the SmC_{α} phase. Thus, for films thicker than 2(N_{S} + N'_{S}), we have the Freq./N'_{in} decreases slowly as N'_{in} decreases; while for thinner films, the Freq./N'_{in} is proportional to N'_{in}. The data can be described very well with the above equations as shown in Fig. 6.5. The best fit shown in Fig. 6.5 in solid line gives N'_{S} = 6 layers for the data. Note in all our discussion, we assumed N > 2N_{S}.

We can also fit the data to an exponential structural model, with the rotation angle profile φ(i) given by φ_{b}*(1 - exp(-i/ζ)), where i is distance from the surface region, and ζ is a characteristic length of the model. This model is illustrated in Fig. 6.6 with solid symbols. Here we have

\[ \text{Freq.}\text{Norm.}/N'_{in} = 1 - \frac{2}{N'_{in}} \left( \frac{1 - e^{N'_{in}/2ζ}}{1 - e^{i/ζ}} \right) \]  

The experimental results can also be well-described by this model, which produces almost identical behavior as the linear model. The best fit shown in Fig. 6.5 in dash line gives ζ = 3 layers. However, as shown in Fig. 6.6, the linear model gives a more straightforward estimate of the size of the buffer region.
Our data were also analyzed with a different method. We studied the dependence of the oscillation frequency on N. The relation between those two quantities can be described with a linear function, with the interception on the thickness axis $N_0 = 13$ layers. This result is consistent with the previous result from fitting the data in Fig. 6.5 with the linear model. Since in our model we have $\langle \phi_a \rangle = \phi_b/2$, if we treat the whole film as only consisting of surface region that does not contribute to the helix and interior region that is bulk like, the two buffer region (2$N'_S$ with $\langle \phi_a \rangle$) will contribute the same $\phi_{total}$ as $N'_S$ layers with $\phi_b$, thus we will have an effective total surface thickness $2N_{Seff} = 2N_S + N'_S = N_0$, namely, we should have $2N_{Seff} = (6 + 6)$ layers $\approx N_0$. The excellent agreement of the results from two different methods suggests that the structural model we used is a very good representation of the system.

### 6.3 What Did We Learn?

In a recent paper \[44\], we demonstrated that the finite size effects on the stability of both the SmC$^\ast_\alpha$ phase in AFLC and the helically ordered magnetic films can be understood with the same $J_1 - J_2$ model. And due to the fact that near the surfaces, there are fewer NNN interlayer bonds than NN interlayer bonds, we have a reduced weight of the AFM type NNN interlayer interaction as compared to the FM type NN interlayer interaction. As a result, near the surfaces the rotation angle $\phi$ between the magnetic moments in neighbouring layers (for the SmC$^\ast_\alpha$ case, $\phi$ is the angle between the tilt direction of molecules in neighbouring layers) is smaller compared to the interior value. In other words, near the surface region there is a tendency towards FM alignment, and the closer to the surface, the smaller $\phi$ will be.

The above discussion provides a brief reasoning of our model. While this structure was suggested in several computational studies of the helically ordered magnetic thin films, at this moment there is no direct experimental evidence available. With the demonstrated similarities between the SmC$^\ast_\alpha$ phase and the helically ordered magnetic films, our study constitutes an experimental confirmation of the main computational results reported for the magnetic system.

It is interesting to see from our results that the buffer region is larger than the surface region, we have $N'_S = 2N_S$. This suggests a strong surface induced aligning
field in liquid crystal free standing films. The aligning field in this region is probably produced by the planar biaxial surface layers. The mechanism of this surface field and its long effective range is beyond our work and calls for future theoretical studies.

Also, the satisfactory fitting results to the smooth function shown in both Fig. 6.5 and Fig. 6.8 suggest that the size of the buffer region remain constant for the different film thickness studied. If the size of the buffer region changes with film thickness, we would observe fragmentation of the data curve in Fig. 6.5 or change of slope in Fig. 6.8. The absence of those situations shows a thickness dependent buffer region is very unlikely.

6.4 What Else Can We Learn?

To gain further and more quantitative understanding of our results, we went back to the $J_1 - J_2$ model. Since our results show that the buffer region with reduced twisting power is found next to the biaxial surface region, it is very likely that this effect is due to the biaxial surfaces.

The usual way of forming a theoretical understanding of such results would be through providing some format of trial interaction or potential profile, and calculating the corresponding set of rotation angles $\phi_i$ that minimizes the free energy. By comparing the calculated results to the experimental results, we would be able to obtain some understanding of the potential mechanism of the formation of the buffer region.

Here, we follow a different path. Since from fitting our data to a structural model we already obtained a set of $\phi_i$ profiles, it would be much more straight forward to obtain a corresponding profile of interaction coefficient provided proper phenomenological terms in the free energy expression are included.

First we add the anisotropy energy to the $J_1 - J_2$ model. The free energy now reads:

$$F = J_1 \sum \xi_1 \cdot \xi_{i+1} + J_2 \sum \xi_1 \cdot \xi_{i+2} + \sum b_i (\xi_1 \times \xi_{i+1})^2$$

(6.4)

where the $b_i$ term is a position dependent anisotropy energy that provides the necessary tendency towards planar alignment. Thus the coefficient $b_i$ is expected to be large near the surface and goes to 0 in the interior of the film.
Figure 6.9: Calculated profile of \( b/J_2 \) for a film with 34 interior layers. The rotation angle profile is given by the models with \( a = 6 \) layers for the linear model and \( \zeta = 3 \) layers for the exponential model. \( J_1 = -2J_2 \) and \( \phi_b = 60^\circ \) is used for the calculation.

The above equation can be written as:

\[
F = J_1 \sum \cos(\phi_i) + J_2 \sum \cos(\phi_i + \phi_{i+1}) + \sum b_i(\sin(\phi_i))^2
\]  \hspace{1cm} (6.5)

For an N-layer film we have N-1 rotation angles \( \phi_i \), and for the ground state we expect to have \( \partial F/\partial \phi_i = 0 \) for all \( \phi_i \). Thus we would have N-1 equations for an N-layer system. For the \( J_1 - J_2 \) model, we already know that in bulk systems, \( \cos(\phi) = -J_1/4J_2 \).

From the equations, \( b_i/J_2 \) can be expressed as a function of \( \phi_{i-1}, \phi_i, \phi_{i+1} \) and \( J_1/J_2 \), which can all be obtained from the fitting to the structural model discussed in the previous sections.

Figure 6.9 shows the results of \( b_i/J_2 \) profile calculated from the \( \phi_i \) profile of a film with 34 interior layers, obtained from the linear model and exponential model with the parameter from experiments on C10. For the calculation, a bulk rotation angle of 60\(^\circ\) which corresponds to a \( J_1 = -2J_2 \) was used. From the results, \( b_i/J_2 \) goes to 0 in the center of the film as expected. This, together with the fact that \( b_i/J_2 \) has its maximum value near the surface region and decays when going into the interior of the film confirms
Figure 6.10: Calculated profile of $J_{11}/J_2$ for a film with 34 interior layers. The rotation angle profile is given by the models with $a = 6$ layers for the linear model and $\zeta = 3$ layers for the exponential model. $J_1 = -2J_2$ and $\phi_b = 60^\circ$ is used for the calculation.

our argument that the observed reduction of twisting power near the surface region is indeed a surface effect. From the calculated $b_i/J_2$ profile we found that range of this surface aligning potential is quite large. For the linear model it equals to the size of the buffer region. However, for the exponential model, the range of finite $b_i/J_2$ is much larger.

We also tried adding an enhanced NN interlayer interaction near the surface to the $J_1 - J_2$ model, so we would have:

$$F = J_1 \sum \xi_i \cdot \xi_{i+1} + J_2 \sum \xi_i \cdot \xi_{i+2} + \sum J_{11}(\xi_i \cdot \xi_{i+1})$$

(6.6)

and:

$$F = J_1 \sum \cos(\phi_i) + J_2 \sum \cos(\phi_i + \phi_{i+1}) + \sum J_{11}(\cos(\phi_i))$$

(6.7)

$J_{11}$ is a position dependent NN term that is expected to reach 0 deep in the center of the film, and it provides the necessary enhanced tendency towards parallel alignment near the surface region. Following the same procedure as described above, we obtained a $J_{11}/J_2$ profile as shown in Fig. 6.10.
From Fig. 6.10, we find that $J_{11}/J_2$ goes to 0 in the center of the film as expected. However, the large increase near the surface region and the large interaction range suggest a really strong aligning field near the surface. Note $J_{11} + J_1$ is the total NN interlayer interaction and since we have $J_1 = -2J_2$ for this calculation, a 100% (about 80%) increase is found in the calculated results for the linear (exponential) model near the surface.

With those calculations, we demonstrate that the reduced twisting power near the surface region is indeed due to a strong surface aligning field, which has a large effective range. The mechanism for this aligning field is not clear at this moment. From our calculation it might be related to the anisotropy in the elastic constant created by the biaxial surfaces.
Chapter 7

Surface Effects and Finite Size Effects on the Phase Behavior

In this chapter we study the thickness dependence of SmC* variant phases from free standing films of MHPBC. In this type of studies, both surface effects and finite size effects affect the phase stability of different SmC* variant phases. To the best of our knowledge, this is the first systematic study of thickness dependence of the stability of SmC* variant phases. Thus, we believe the results will provide new insight into our understanding of the nature of SmC* variant phases and the interactions responsible for their appearance [44].

7.1 The Thickness Dependent Phase Diagram

7.1.1 Finite Size Effect and Surface Effect

In real experimental systems, surface effects and finite size effects usually appear together, since all systems are finite and have boundaries. For theoretical studies, surface effects can be studied in semi-infinite systems to avoid finite size effects [26]. In the experimental studies of such topics, it is not always straightforward to decide if one phenomenon should be attributed to finite size effects or surface effects or maybe even to both effects.

In the previous several chapter, we studied different aspects of surface effects in
smectic liquid crystals. The general argument for attributing the observed phenomena to surface effects instead of finite size effects is their size (thickness) independent behavior. For example, in the study of surface order and surface transitions, the temperature evolution and surface transition temperature are generally thickness independent (details in Ch. 3 and Ch. 4); and for the surface induced reduction of twisting power in helical liquid crystal films, the size of the buffer region is thickness independent, thus the effective region of the surface aligning field is also thickness independent (Ch. 6). All those studies suggest that for experimental studies on thin films, surface effects usually are not affected by the change of the system size on the dimension perpendicular to the surface, provided the film thickness is greater than the surface region.

Finite size effects however, would show more pronounced results with decreasing system size. It has been shown to cause lowering of the transition temperature and rounding of the transition in the study of critical phenomena [19]. In the case of smectic liquid crystals, finite size effects have rarely been found to be relevant. One of the few examples of finite size effects is the lowering of the SmA-HexB transition temperature of 75OBC films thicker than 15-layers; for thinner films, surface effects result in an increased transition temperature [50]. Thus even for the same quantity, finite size effects and surface effects might be dominant in different thickness region, and show very different results.

Since our ultimate goal would be to find out the intermolecular interactions responsible for the SmC* variant phases, it would be interesting to see the effects of surface and finite size on the stability of different SmC* variant phases; i.e., study the thickness dependent phase diagram. On the one hand, through the effect of ordered surfaces on different SmC* variant phases we expect to be able to gain some insights into the major force stabilizing those phases; on the other hand, by observing the stability of these phases through different film thickness N, we will find some clue whether long range interaction is necessary for the formation of those phases.

7.1.2 Thickness Dependent Phase Diagram

The AFLC compound chosen for this study is again R-MHPBC. Its phase sequence found in bulk is isotropic (109°C)-SmA-(76°C)-SmC*A*(71°C)-SmC*4d-(66°C)-SmC*3d-(63°C)-SmC*4d. This compound was chosen for its simple surface structure as explained
Figure 7.1: $\Delta$ as a function of temperature upon cooling from films with thickness $N = 6, 10, \text{and } 34$ layers with $\alpha = 90^\circ$ (black squares) and $270^\circ$ (red dots). T0, T1, T2, T3, and T4 mark the transitions into Sm$C^{\ast}$, Sm$C_{\alpha}^{\ast}$, Sm$C_{d4}^{\ast}$, Sm$C_{d3}^{\ast}$, and Sm$C_{A}^{\ast}$ phase.

in earlier chapters. We know R-MHPBC has a surface tilt transition about 20K above the bulk tilt transition, which can be accounted for with one tilted surface layer. As comparison, C10 has surface $\approx$ 3 layers (Ch. 6), 12F1M7 has multiple surface transitions [51]. Thus using MHPBC allows us to minimize the complicated surface effects.

Figure 7.1 shows the ellipsometric parameter $\Delta$ as a function of temperature upon cooling from the Sm$A$ phase. The temperature ramp rate was 60mK/min. Data with $\mathbf{E}$ field orientation $\alpha = 90^\circ$ (black squares) and $\alpha = 270^\circ$ (red dots) are presented for films with thickness $N = 6, 10, \text{and } 34$ layers. In the figure, T0, T1, T2, T3, and T4 marks the transition into Sm$C^{\ast}$, Sm$C_{\alpha}^{\ast}$, Sm$C_{d4}^{\ast}$, Sm$C_{d3}^{\ast}$, and Sm$C_{A}^{\ast}$ phase. These phases have the following characteristic features for parameter $\Delta$. Above T0/T1, surface induced tilt produce a discernible difference between $\Delta_{90}$ and $\Delta_{270}(|\Delta_{270} - \Delta_{90}|_{\text{surf}})$. Between T1
Figure 7.2: $\Delta$ data (symbols) and fitting (lines) as a function of $\alpha$ from the 6 layer film at (a) $T = 80.3^\circ C$ (SmC* phase), (b) $T = 67.6^\circ C$ (SmC$_{d_4}^*$ phase), (c) $T = 65.7^\circ C$ (SmC$_{d_3}^*$ phase). (d) top views of structures for SmC$_{d_4}^*$ and SmC$_{d_3}^*$ phase. Arrows represent the tilt direction of each layer. Number denotes the layer index within the unit cell.

and T2, characteristic oscillation in $\Delta_{90}$ and $\Delta_{270}$ is the signature of SmC$_{a}^*$ phase. Due to the optically uniaxial structure of SmC$_{a}^*$ phase, $|\Delta_{270} - \Delta_{90}|_{SmC_{a}^*} \leq |\Delta_{270} - \Delta_{90}|_{Surf}$. For the data between T0 and T2 of the 6 layer film, $|\Delta_{270} - \Delta_{90}|_{T0toT2} > |\Delta_{270} - \Delta_{90}|_{Surf}$ indicates that it is the SmC* phase. For data between T2 and T3; and data below T4, $\Delta_{90}$ matches $\Delta_{270}$ as temperature changes, this indicates a 2-fold rotational symmetry in the structure. Thus the phases in these two regions are SmC$_{d_4}^*$ and SmC$_{a}^*$. For data between T3 and T4, a noticeable difference between $\Delta_{90}$ and $\Delta_{270}$ was observed since the films were in a ferrielectric phase (SmC$_{d_3}^*$). Because the transitions at T2, T3 and T4 are all first order transitions, variations in transition temperatures are observed between different runs, and are treated as uncertainties for the transition temperatures.

In order to study the symmetries and structures of the phases in more detail and to confirm the results obtained from the temperature ramp, data were taken as a function of E field orientation $\alpha$ at various temperatures for several films. Shown in Fig. 7.2(a),
7.2(b), and 7.2(c) are $\Delta$ as a function of $\alpha$ from the 6 layer film at temperatures $T = 80.3^\circ \text{C}, 67.6^\circ \text{C},$ and $65.7^\circ \text{C}$. The solid lines are fitting results using a $4 \times 4$ matrix method. Values of the principal indices of refraction and layer spacing used in the fitting are, $n_o = 1.481 \pm 0.002$, $n_e = 1.626 \pm 0.01$, and $d = 3.44 \pm 0.05 \text{ nm}$.

The structure used for the fitting in Fig. 7.2(a) is SmC* with an antiparallel arrangement between two outermost layers. The tilt angle profile from surface to interior is: $11^\circ \pm 2^\circ$ (1st and 6th layer), $9^\circ \pm 2^\circ$ (2nd and 5th layer), and $8^\circ \pm 2^\circ$ (3rd and 4th layer). For Fig. 7.2(b), the structure used is SmC$^{*}_{d4}$ with an antclinic surface(a top view of the SmC$^{*}_{d4}$ phase was shown in Fig. 7.2(d)). $\delta_2$ used for the fitting is $10^\circ \pm 2^\circ$, an overall helix with pitch = 72 layers was added to the structure for the fitting. The tilt angle profile used is: $18^\circ \pm 2^\circ$, $16^\circ \pm 2^\circ$, and $15^\circ \pm 2^\circ$. The tilt angle
profile used for Fig. 7.2(c) is: 20° ± 2°, 17° ± 2°, and 16° ± 2°. The structure used is SmC∗d3 with δ1 = 60° ± 10°. Surface with a synclinic arrangement (solid red line) or anticlinic arrangement (dashed blue line) gave equally good fitting result. Parameters δ1 and δ2 used for fitting the SmC∗d3 and SmC∗d4 structure are consistent with results from previous studies [52].

Free standing films of MHPBC with thicknesses ranging from 6 to 106 layers were studied. The resultant thickness dependent phase diagram obtained upon cooling from the SmA phase is shown in Fig. 7.3. To avoid complications due to even-odd effect, for N ≤ 60 layers, only films with even number of layers were chosen and studied. From the phase diagram, it is clear that all the transition temperatures show trends of increases upon decreasing N. T1 (transition into the SmC∗α phase) shows a slight increase until N < 10 layers, where the SmC∗α phase disappears and the SmC* is observed instead. Upon decreasing N, T2 (transition into the SmC∗d4 phase) increases dramatically, while T3 (transition into the SmC∗d3 phase) and T4 (transition into the SmC∗A phase) stay almost constant.

7.2 Results on the SmC∗α Phase

7.2.1 Phase Stability

Figure 7.4(a) shows the temperature window of the SmC∗α phase (∆T(SmC∗α)) as a function of N. ∆T(SmC∗α) shows an overall trend of decrease upon decreasing N till below the 10-layer film, where the SmC∗α phase completely disappears. The disappearing of the SmC∗α phase in thin films has been observed in two other compounds [54, 53]. However, in the 6-layer film of MHPBC, SmC* structure is observed below SmA.

7.2.2 Results on Helical Magnetic Films

A similar result was observed for the helical magnetic ordering temperatures (T_N) in Ho thin films [45]. E. Weschke et al. studied T_N as a function of film thickness by resonant magnetic soft x-ray and neutron diffraction. They found that T_N decreases with decreasing film thickness L, and reaches 0 below a film thickness L_0 (10 monolayers) which is of the order of bulk helix period P_0 (7 to 12 monolayers as a function of
Figure 7.4: (a) $\Delta T(\text{SmC}^*_\alpha)$ as a function of $N$. (b) free energy per layer of the SmC$^*_\alpha$ structure (black squares) and SmC$^*$ structure (red dots) as a function of film thickness calculated from the $J_1 - J_2$ model.

So far, the ferromagnetic structure in the films with $T_N$ equals 0 has not been observed experimentally. Due to the structural similarities between helically ordered magnetic films and liquid crystal films in the SmC$^*_\alpha$ phase, our results can be viewed as an experimental confirmation of the prediction made for magnetic systems. Although due to the finite size effect, the ordering temperature for magnetic thin films is predicted to decrease as film thickness decreases, this is not observed for AFLC films. The most important reason for this is that for AFLC films, surfaces are more ordered than
the interior, and stronger surface interactions prevent the ordering temperature from decreasing.

### 7.2.3 The $J_1 - J_2$ Model

The helical pitch of the Sm$C_\alpha^*$ structure of MHPBC was previously determined to be about 7 layers [55]. Taking into account the surface layers, the film thickness at which the Sm$C_\alpha^*$ phase disappears is of the order of the bulk helical pitch, below which the Sm$C^*$ structure is observed below SmA instead of Sm$C_\alpha^*$.

Here we employ the $J_1 - J_2$ model again to illustrate the properties of the system. Free energy of an N-layer helical structure can be written as

$$F = (N - 1)J_1 \cos \phi + (N - 2)J_2 \cos 2\phi \quad (7.1)$$

with $J_1$ and $J_2$ being the coupling constants between the nearest neighboring (NN) layers and next nearest neighboring (NNN) layers, and $\phi$ being the rotation angle between the tilt direction of adjacent layers. For the case of MHPBC, $J_1 = -2.5J_2$ gives a pitch value of 7 layers. Figure 7.4(b) shows the free energy per layer calculated with $J_1 = -2.5J_2$ for $\phi = 51.4^\circ$ (Sm$C_\alpha^*$, black squares) and $\phi = 0$ (Sm$C^*$, red dots). As shown in the figure, above a thickness of 6 layers, the Sm$C_\alpha^*$ structure has lower energy, while below 6 layers the Sm$C^*$ structure has lower energy, which is consistent with the experimental results. An intuitive explanation would be that in thin films the weight of $J_1$ would be more pronounced than $J_2$, since there are fewer n. n. n. bonds than n. n. bonds, so that a longer helix is favored.

### 7.3 Results on the Sm$C_{d4}^*$ Phase

Figure 7.5(a) shows the temperature window of the Sm$C_{d4}^*$ phase ($\Delta T(\text{Sm}C_{d4}^*)$) as a function of $N$. $\Delta T(\text{Sm}C_{d4}^*)$ increases dramatically as $N$ decreases, especially for $N < 20$ layers.

In order to understand the enhanced stability of Sm$C_{d4}^*$ phase in thin films, we studied the behavior of free energy per layer as a function of $N$. $|F|/N$ is an estimate of the average energy required to flip the orientation of a random layer in the structure, thus it is a rough calculation of the stability of the phase. Figure 7.5(b) shows a cartoon of
Figure 7.5: (a) $\Delta T(SmC^{*}_{d4})$ as a function of $N$ (black square) and free energy per layer calculated with Eq. (2) (red line). (b) Cartoon of a film with even number of layers in the $SmC^{*}_{d4}$ phase.

The $SmC^{*}_{d4}$ structure of a film with even number of layers $N$. Since the distortion angle $\delta_2$ of MHPBC is small ($10^\circ \pm 2^\circ$), a planar structure (Ising like) is a good approximation. The two outermost surface layers are assumed to be anticlinic with the neighboring layers as obtained from the fitting shown in Fig. 7.2(b).

Taking into account the fact that surface bonds are usually stronger than interior bonds, we write the coupling strength between the surface and the adjacent layer to be $-\gamma J_1$ (in the $SmC^{*}_{d4}$ phase $J_1 < 0$, so here a negative sign is needed to produce the anticlinic surface arrangement shown in Fig. 7.5(b)) and $\gamma J_2$ stands for the coupling strength between the surface and the NNN. Here $\gamma$ (a constant) represents the level of surface enhancement. Thus for the structure shown in Fig. 7.5(b), including a NN and NNN interaction, we have

$$F(SmC^{*}_{d4}) = F_{\text{interior}} + F_{\text{surf}}$$

with $F_{\text{interior}} = \sum_{i=2}^{N-2} J_1 \xi_i \cdot \xi_{i+1} + \sum_{i=2}^{N-3} J_2 \xi_i \cdot \xi_{i+2}$, and $F_{\text{surf}} = -2\gamma J_1 \xi_1 \cdot \xi_2 + \ldots$
Thus we have

\[ \frac{|F(SmC_{d4}^*)|}{N} = J_2 + \left[ 2\gamma(J_2 - J_1) - (4J_2 + J_1) \right]/N = a + b/N \]  

(7.2)

Here \( J_1 \) (\( J_2 \)) term stands for the interior NN (NNN) interaction. \( \xi_i \) represents the tilt direction of layer \( i \). \( a = J_2 \), and \( b = [2\gamma(J_2 - J_1) - (4J_2 + J_1)] \). The red line in Fig. 7.5(a) was obtained with \( a = 3.9 \pm 0.3 \) and \( b = 43 \pm 3 \). Using \( J_1 = -2.5J_2 \) as determined from the SmC\(_{A}^*\) structure, we obtain \( \gamma = 1.8 \). If however, we follow the constrains in the ANNNI model for the SmC\(_{d4}^*\) structure: \(-J_1 < 2J_2 \) [56], then we have \( \gamma > 2.2 \). The value of \( \gamma \) obtained is reasonable for the case of smectic liquid crystals (for example, see the results shown in section 6.4).

These results show that the dramatic increase of \( \Delta T(SmC_{d4}^*) \) in thin films is the result of enhanced coupling strength at the surface. Structure of the SmC\(_{d4}^*\) phase allows the bonds between the surface and the n. n. as well as the bonds between the surface and the n. n. n. to both contribute to the enhancement of stability of this phase, causing the effect to be more pronounced. For the case of SmC\(_{A}^*\) which also has an Ising like structure, these two interactions will work against each other, causing the effect to be less obvious. With \( J_1 = 2.5J_2 \) and \( \gamma = 2 \), we will get \( \Delta T(SmC_{A}^*) \) increases for about 26\% in decreasing \( N \) from 100 to 6 layers, which is much less compared to the situation of about 200\% for SmC\(_{d4}^*\). Since in SmC\(_{A}^*\), \( J_1 > 0 \), the \( \gamma J_1 \) term will not need a negative sign.

### 7.4 What Did We Learn?

We studied the thickness dependent phase diagram of free standing films of R-MHPBC. The SmC\(_{A}^*\) phase disappears below a film thickness of 10 layers, which is of the order of the bulk helix, and the SmC\(^*\) structure is observed in thinner films below SmA. This result is attributed to the reduced coordination number of the surface layers and is a finite size effect. Our result is also consistent with studies on helically ordered magnetic system.

Our results also show that the temperature window of the SmC\(_{d4}^*\) phase increases dramatically upon reducing the film thickness. Surface enhanced couplings are found to be the key reason. The ratio \( \gamma \) for the enhanced surface couplings with respect to
bulk ones is found to be around 2. This value matches the results calculated from the study of surface effects on the SmC* structure.

Of course our model of the results on the SmC* phase is very rough. To form a detailed understanding of the enhanced stability of the structure, in principle one would want to have a phenomenological model that is capable of resulting all the relevant phases and also need to be able to accommodate surface effects. However, the construction of such a model is beyond the scope of this thesis.

Here we also point out that from the results of the last chapter, we found that the surface layers will create an aligning field in the region close to the surface. This field might provide the anisotropy energy that favors the SmC* structure, thus resulting in the enhanced stability of this phase in thin films.
Chapter 8

Concluding Remarks

In this chapter a summary of the main results obtained in the previous chapters will be given.

In free standing films of smectic liquid crystals, enhanced interaction at the surface layers results in a surface transition at a higher temperature than the corresponding bulk transition. The ordered surfaces will then create a surface ordering potential or surface field. The surface field is found to enhance the stability of the SmC*$_{d4}$ phase in thin films, and it also reduces the value of rotation angles near the surfaces in the helical SmC*$_{a}$ phase.

The experimental results indicate that the surface potential has a range much larger than the immediate neighboring layers, creating a tendency towards parallel alignment close to the surface layers. The range of the surface aligning field found in the study of helical structures is comparable to the thickness below which a dramatic increase of the stability of the SmC*$_{d4}$ phase is observed. Thus we believe it gives a reasonable estimate of the range of surface potential, which is about 10 molecular layers.

Surface layers generate a potential and show its effects on interior layers over this range which is much larger than its own size (number of surface layers at each surface). However, without a clear understanding of its microscopic mechanism, it does not provide support for the existence of long range or quasi-long range interactions in bulk materials, i.e., the surface potential could be due to interactions caused by the increased surface tilt or similar factors that are absent in bulk materials.

With the ordered surface layers on top of disordered interior ones, we are able to
study the surface - surface interaction between the two surfaces of a free standing film. We found this interaction to be antiferroelectric and of quasi-long range. Although at this moment we do not have a good understanding of the mechanism of this interaction, the temperature and distance dependence seem to suggest they are not of the dipole - dipole origin. Also it is quite unlikely that the surface aligning potential is the reason for this interaction, for it does not explain the antiparallel ground state configuration.

It is an interesting question whether the surface - surface interaction we studied is representative of the interlayer interaction inside bulk materials. To be able to answer this we need to have a microscopic understanding of the interlayer interaction in AFLC materials, at least we need to know what type of interaction it is. However, as explained above, we expect the surface - surface interaction not to be mediated through the overlapping of the surface potential. Nonetheless we do expect whatever theoretical models that include interlayer interaction in AFLC materials to be able to explain the surface - surface interaction and its sign, distance dependence and maybe even its temperature dependence. Thus, our results can serve as a test for the various phenomenological model on this topic.

To conclude this thesis, we studied the surface effects of smectic AFLC materials in free standing film geometry, in the attempt to elucidate the nature of the interlayer interaction in this type of materials. In the process, various interesting and fascinating aspects of the surface effects are discovered and investigated. The studies of surface effects are shown to be very informative, even regarding the understanding of the bulk properties. Thus our results will provide insights and much needed systematic experimental studies on AFLC materials, and offer a solid test ground for any theories regarding this topic.
References


