We present detailed systematic studies of structural transformations in thin liquid crystal films with the smectic-C (SmC) to hexatic (HSmB) phase transition. For the first time all possible structures reported in the literature are observed for one material (5O.6) at the variation of temperature and thickness. In unusual modulated structures the equilibrium period of stripes is twice with respect to the domain size. We interpret these patterns in the framework of phenomenological Landau type theory, as equilibrium phenomena produced by a natural geometric frustration in a system having spontaneous splay distortion.

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I. INTRODUCTION

Spontaneous formations of spatial patterns arise in a wide variety of dynamic processes. Even more spectacularly they are observed in equilibrium situations involving, fluids, solids and liquid crystals. Especially remarkable are free standing smectic films where one can avoid (in other systems often dominating) influence of underlying substrates. These systems provide a realization of many models describing diverse apparently disparate physical phenomena (phase transitions, frustrations, ferro-electricity, magnetism), and an opportunity to study the crossover from two-dimensional to bulk behavior by drawing films of increasing thickness.

For liquid crystal materials with phase sequences in bulk samples HSmB (or crystalline CrB) → SmA the phase transformations in thin free-standing films are well studied at present time [1, 2]. At temperature $T_{S1}$ which is about $10^{\circ}C$ above the bulk transition point $T_C$ the phase transition occurs only in surface smectic layers. The interior layers remain in the SmA phase. Below $T_{S1}$ there are no phase transitions up to the temperature slightly above $T_C$. The next transition in nearest to surface layer occurs at the temperature $T_{S2}$ about $1^{\circ}C$ above $T_C$. Sequence of discrete layer-by-layer transitions on cooling may constitute from 2 to 5 transitions. In thick films the transition of the whole film into the low temperature phase occurs at $T \sim T_C$.

Few words on nomenclature of tilted hexatic smectics (usually labeled as SmF, SmI, SmL) may be helpful here. In the SmI phase the tilt direction is along of the local bonds, in the SmF phase it is halfway between two local bonds, while in SmL phases, the tilt direction lies along an intermediate angle. Transitions in the films of tilted smectics in which the high temperature bulk phase is SmC and the low temperature phase is tilted hexatic occur in an essentially different way [3, 4, 5, 6]. In this case no sequence of discrete layer-by-layer transitions is observed. After the surface transition into the hexatic structure, the transformation of the film structure on cooling continues in a broad temperature range. Several characteristic temperatures $T_i$ may be pointed at which qualitative changes of the film texture take place. Similar structure and texture transformations were observed in several smectic materials [3, 4, 5, 6]. So one may expect that these transformations have common physical nature and occur through a universal mechanism. However, up to now the mechanisms of these structural transformations and physics behind remain unclear.

Our motivations for presenting this paper are twofold. First, in section II, we present detailed systematic studies of structural transformations in thin liquid crystal films with SmC to hexatic phase transition. We go one step further with respect to the results known already (see, e.g., [3, 4, 5, 6]) investigating all possible structures in one material (5O.6) at the variation of temperature and thickness. Besides, in section III we rationalize and interpret our observations in the framework of simple phenomenological model which includes the minimal number of ingredients, i.e., it is just at the border between under-fitting models (those that do not explain the data well) and over-fitting models (those that fit the data too well by using too many parameters). Although our model is a toy model in the sense of caricaturizing some physical features, when properly interpreted, it can yield quite reasonable values for a variety of measured quantities. A more realistic model will not affect
much our conclusions, and transparency of treatment is worth a simplification. The conclusion section is used to briefly summarize our results and to augment their discussion.

II. OBSERVATIONS

The measurements were made on the Schiff’s-base compound 4-n-hexyl-N-[4-n-pentyloxy-benzilidene]-aniline (50 µm). The sequence of phase transitions in the bulk sample is SmA – (50.5°C) – SmC – (49.5°C) - HSmB. Below the HSmB in the bulk sample the transition to a tilted hexatic structure (SmF) takes place. Free-standing films were prepared by drawing the liquid crystal in a smectic phase across a circular 4mm hole in a thin glass plate. The experimental set-up enabled simultaneous optical observations and reflectivity measurements. The thickness of the film was determined by the reflected intensity from the film in the "backward" geometry [7]. Observations of film structure and phase transitions were made using polarized light reflected microscopy (PRLM) and depolarized light reflected microscopy (DRLM) [8]. The images were recorded by a CCD camera. The orientational order parameter \( P_2 = \frac{1}{2} \left( 3 \langle \cos^2 \alpha \rangle - 1 \right) \) [9] was determined by optical absorption measurements. At cooling \( P_2 \) changes from 0.75 to 0.8 in the SmA phase, is about 0.82 in SmC, and increases up to 0.92 in the hexatic phase.

We performed investigations of thin smectic films starting from thickness of 2 molecular layers. Figure 1 shows the temperatures of the transitions in the films. Similar symbols denote the temperatures of the transitions between the similar structures in the films of different thickness. The high temperature part of the phase diagram corresponds to the SmC structure. As it was established early [11] the temperature of the SmC-SmA phase transition in free-standing films is essentially shifted to higher temperature with respect to the bulk samples. Texture of the film is characterized by a smooth spatial variation of the \( c \)-director (Fig. 2a). The picture was taken in the part of the film with a point topological defect, which is typical just for SmC phase.

Upon cooling of the SmC film the first phase transition (filled circles, transition into the SmT₁ state, Fig. 1) leads to an abrupt change of the film texture (Fig. 2b). In liquid crystalline materials with the bulk hexatic phases the higher temperature transition is associated with the phase transition of the surface layers into the hexatic structure [1, 2]. In thick films the high temperature shift of the transition with respect to the phase transition temperature into the HSmB structure in the bulk sample is about 9°C. This value is approximately the same as for the HSmB–SmA transition [1, 2]. A different situation is observed for thin films. While for the SmA phase the shift of the transition in the 2-layer film with respect to thick films does not exceed 2°C, this shift in our case is essentially larger (more than 6°C). Below the transition the film consists from domains with different \( c \)-director orientations and sharp boundaries between them (Fig. 2b). Such a texture may be expected for tilted hexatic in which the \( c \)-director has a discrete set of orientations and correspondingly sharp boundary between domains. However, it is not typical for the SmC structure, which exists in the interior of the film. For the films with \( N > 5 \) the view of the films is mainly determined by the SmC structure of the film interior. Thus, we conclude that the SmC structure inside the film differs sufficiently from the conventional SmC structure. Sharp boundary between the domains suggests that not only in the surface layers (i.e., in the hexatic state) but also inside the film (i.e., in the SmC state) at the domain boundary the break of the \( c \)-director orientation occurs. The question arises about the nature of the boundary between domains inside the film. These peculiarities of the SmC structure inside the film become extremely essential after the next transition (open squares in Fig. 1).

At the next transition (into the SmT₂ state, Fig. 1, Fig. 3) the domains break up into narrow parallel stripes with alternating brightness and sharp boundaries. According to Refs. [3, 4] at this transition the surface layers transform into a so-called SmL phase in which the tilt plane is oriented in the hexatic structure at the angle 15° with respect to the direction of the hexatic bond orientation order. In this structure there are possible 12 equivalent (i.e., having the same energy) orientations of the tilt plane. Our optical measurements confirm that the difference in the \( c \)-director orientation in the neighboring stripes is about 30° (±5°) with two symmetric orientations of the \( c \)-director relative to the stripe boundary \( \varphi = \pm 15° \) (Fig. 4a-c). The direction of the hexatic bond orientational order does not change across the stripes (along x-axis), while the direction of tilt plane changes at the stripe boundary. Inside the film, in the SmC structure there is also a break in the \( c \)-director orientation. Contrary to this, a smooth change of stripe orientation along domains is connected with change of the direction of bond orientation order, meanwhile the orientation of the \( c \)-director relative to the bond orientational order is preserved. The inset in Fig. 3a clarifies the periodic stripe structure, in particular in the region of the contact between two stripe domains. The stripe period increases with decreasing temperature (Fig. 5). When upon cooling the stripe period achieves the value of about 13–15µm, the stripe width increases sharply and the structure becomes aperiodic. Open triangles in Fig. 1 show the temperatures of this transition.

In the SmT₃ region (Fig. 1) the film texture may be different (Fig. 3b,c and Fig. 6a) and in many
aspects is similar to the observed earlier in films of SmC material with hexatic phases [3, 4, 5, 6]. However
the transition temperatures between different textures are hardly reproducible. Moreover the low temperature
texture (Fig. 6a) as a rule transforms at heating directly into the state with periodic stripes (Fig. 3a). Due
to this reason in the phase diagram (Fig. 1) we point only the transition temperature between periodic stripe
and aperiodic structures (open triangles in Fig. 1). The domain structure, shown in Fig. 3b, is formed on
cooling from the narrow periodic stripes through their broadening. This picture (Fig. 3b) was obtained by
means of depolarized light reflection microscopy. The domain boundaries with the same brightness are oriented
at about 45° with respect to the polarizers. It manifests that orientations of the c-director in the neighboring
domains are symmetric with respect to the domain boundary. Measurements with crossed polarizes prove that the
c-director in domains is oriented at the angles ±15° with respect to the domain boundary. Therefore, the
structure of wide domains (Fig. 3b) is similar to the narrow periodic stripes (Fig. 3a). The honeycomb texture
(Fig. 3c) forms from the line domains (Fig. 3a) and exists only in a small temperature range (≤ 0.5°C). More
typical textures in the SmT2 state are domains with continuous change of the c-director orientation across the
domains (upper part of Fig. 6a) or large domains (lower part of Fig. 6a) also with a continuous variation of the
c-director orientation. In thin films this structure can be cooled to low temperatures (< 40°C). In thick films
(N > 10) a reversible phase transition is observed with formation of the texture shown in Fig. 6c. This texture
is typical for the tilted SmF phase. In the limit of very thick films (N > 100) crossed domains may be formed
(Fig. 6b) below the surface phase transition temperature. Two independent sets of domains are formed at both
film surfaces. Formation of these independent structures in the thick films may point that surface correlation
length ξS is less than about 50 smectic interlayer periods.

III. THEORETICAL INTERPRETATION

In order to provide a more complete account of the phenomena described in the previous section, it would
seem appropriate to discuss how the observed results can be consistently modeled theoretically. Without prior
knowledge of the actual structure, we shall assume the simplest model to answer the natural questions why
the phase transitions in materials with SmA and SmC phases are so different, and what kind of mechanisms
are responsible for the formation of the periodic stripe structure and its temperature dependence. From our
experimental observations a few conclusions about the following qualitative features of the film structures and
their transformations seem inescapable.

First, formation of the periodic stripes (Fig. 3a) is related to the structure of the surface layers. In the
higher temperature SmT1 state the c-director is oriented along one direction (Fig. 4a) in the middle between
apexes of the SmF phase hexagon. In the SmL phase the energy minimum splits and the c-director may
orient in two directions [3, 4] corresponding to two equivalent energy minima (±15° with respect to the initial
orientation, Fig. 4a,b). As it is known competing attractive and repulsive interactions generate domain patterns
in a wide variety of systems [10]. Formation of a periodic structure is a signature of instability that arises from
a competition between two antagonistic fields, and that, above some threshold, a modulated state has a lower
energy than the uniform one. In liquid crystals this scenario is often related with existence of electric polarization
and a certain competition between the long-range forces (namely electric and elastic ones). In the thin film
under consideration, the electric polarization may appear due to nonuniform profile of the order parameter
induced by the film surface and also because the surface layers are in the hexatic phase. This polarization Pj
is longitudinal (i.e., parallel to the tilt plane) and points in opposite directions in the upper and lower parts
of the film [12, 13, 14]. These interactions (electrostatic and elastic) contribute differently into the energy of
alternative configurations associated with existence of the domain walls, and may lead to stabilization of the
equilibrium stripe period (as in solid crystal ferroelectric domains).

In liquid crystal films with the broken polar symmetry there is also another cause of the stripe formation
[15, 16, 17, 18, 19, 20, 21]. Indeed, the broken polar symmetry allows linear over space gradients terms into the
Landau type free energy expansion. These terms affect the elastic constants, which even may tend to zero. In
this situation the free energy of the defect structure may become more favorable than the uniform structure.
Thus the uniformly ordered state becomes unstable with respect to the striped phase with periodic domain
walls. The equilibrium modulated structure arises to optimize the gain in the elastic energy of the orientational
deformation inside the stripes and the energy cost to have the defect.

In literature devoted to theoretical descriptions of the modulated phases in smectic films mostly models
for polar smectic liquid crystal films with transverse polarization are discussed [16, 17, 18, 19, 20]. Apparently
it is not the case for our system. There are several distinctions between the stripes shown in Fig. 3a (see also
their schematic representation in Fig. 4b,c) and periodic stripes discussed in [16, 17, 18, 19, 20, 21]. First, in
our case the structure of the surface layers is hexatic and it dictates the value of director jump at the domain
boundary. Second, the neighboring stripes found in the works [16, 17, 18, 19, 20, 21] have identical structures, whereas in our case the azimuthal molecular orientation in the adjacent stripes differs: c-director is rotated clockwise with respect to the symmetric orientation in the left stripe (Fig. 4b,c) and counterclockwise in the right stripe (Fig. 4b,c). Next, inside the stripes investigated in [16, 17, 18, 19, 20] elastic deformation is of the bend type with the same sign of the bend in all stripes and with defect walls in which the c-director jumps back. In our case the reorientation of the c-director between stripes is of the splay type. Moreover, there is no visible orientational deformation of the c-director inside stripes (Fig. 3a). Thus care must be taken when comparing published theoretical results to our experimental data. Below we examine one important aspect of the liquid crystal modulated phase formation which does not appear to have been investigated in any generality.

In our opinion, unusual structure of the stripes we have observed is related to the nature of the geometrical frustration in the films formed by non-chiral material. It was recognized quite some time ago that because of the up-down asymmetry, the achiral smectic film exhibits polar properties, in particular the c-director may be considered as a true vector (i.e., c and c states are not equivalent). In ferroelectric SmC* phases the chiral asymmetry favors a bend (↗→↘) in the c-director \( \lambda_b \nabla \times \mathbf{c} \). The preferred bend direction (the sign of the coefficient \( \lambda_b \) at the linear over space derivatives term) is determined by handedness of the material (or by the direction of the ferroelectric polarization) which is the same in the whole film.

We argue below, that in achiral systems the instability arises from a competition between two elastic energies, the usual quadratic Frank elastic energy, which favors a uniform orientation of the c-director, and an additional surface elastic term linear in c gradient which promotes spontaneous splay distortions. The linear over gradients terms like \( \nabla \times \mathbf{c} \) are not allowed by the symmetry. However, in such a film the broken chiral symmetry occurs as a result of asymmetry between the surfaces (possessing hexatic ordering) and the interior of the film (which is in the SmC state). Our measurements show that not only the tilt angle but even the orientational order parameter \( P_2 \) differs essentially in SmC and hexatic structures. The surface-induced term linear over the gradients of \( c \times (\nabla \lambda_b \nabla \cdot \mathbf{c}) \) favors a splay deformation (↗→↘) in the c field and has the opposite signs (direction of splay curvature) in the top and bottom parts of the film [3, 15]. The c-director is also the order parameter of the film. It allows one to describe its macroscopic physics, in particular, to write its free energy in the spirit of the Landau theory

\[
F = \frac{1}{2} K_s (\nabla \cdot \mathbf{c})^2 + \frac{1}{2} K_b (\nabla \times \mathbf{c})^2 + \lambda_b \nabla \cdot \mathbf{c} + \frac{1}{2} A \mathbf{c}^2 + \frac{1}{4} B \mathbf{c}^4. \tag{3.1}
\]

The first two terms are the splay and bend elastic energies, and Frank elastic moduli \( K_s \) and \( K_b \) are proportional to the film thickness. The last two terms are conventional Landau expansion. The third term \( \nabla \cdot \mathbf{c} \) is a total derivative that can be transformed to boundary terms. Therefore it is relevant only for the thin films. For the thick films another term with the same symmetry can be constructed

\[
\lambda_c^s c^2 \nabla \cdot \mathbf{c}, \tag{3.2}
\]

and to avoid its reduction to the pure surface contribution, variations in the \( \mathbf{c} \) amplitude are needed. These kinds of the contributions into the free energy (terms linear over the splay distortion \( \nabla \cdot \mathbf{c} \)) lead to formation of the unusual modulated structure we have observed in this work.

If the molecules forming the system carried permanent dipole moments \( \mu \) with a non-vanishing component along the direction \( \mathbf{c} \), then the phase would exhibit spontaneous electric polarization \( \mathbf{P} \). This spontaneous polarization is proportional to the polar order parameter. For simplicity and for the lack of different compelling indications from the experimental part of our work, the dipolar forces will be neglected in the stripe period estimation below. It might be the case if the molecules involved have relatively large shape anisotropy (and not a large electric dipole moment), and ionic impurities screen the Coulomb interaction. However, it is not the whole story. In order to get the correct structure of the splay phase, one has to take into account the complete order parameter, including the modulus \( |\mathbf{c}| \). Besides, there is a price to be paid, because \( |\mathbf{c}| \) can not be constant, where the splay is constant. Indeed, in 2D the splay distortion of the orientation can not occur in a defect-free fashion. Instead, to relieve this frustration, the system will form a modulated phase consisting of a regular network of defect walls and points.

It is interesting and tempting to hypothesize the following stripe structure satisfying such kind of the symmetry breaking. The uniform SmC structure of the top part of the film breaks up into finite regions with splay deformation of the c-director (Fig. 4d). Regions with the same favorable sign of the splay (counterclockwise in Fig. 4d) are separated by defect lines in which the c-director abruptly rotates back. In the bottom part of the film (Fig. 4e) the c-director rotation is the opposite (clockwise). The lines in which the c-director jumps back are shifted in the x-direction on the stripe period \( d_{st} \) with respect to the top part of the film (Fig. 4d,e). In this structure the direction of the splay modulation in \( \mathbf{c} \) is favorable on the both sides of the film. Remarkably the net magnitude of the c-director orientation \( \varphi \) across the film is constant in each stripe in the agreement
with our experimental data. Their values $\varphi = \pm 15^\circ$ are dictated by structure of the surface SmL phase. To be stable a splay modulated structure has to overcome the unfavorable core defect energy ($\varepsilon$) and the ordinary nematic order parameter contribution. In the zero approximation the periodic stripe phase exists when the gain in the surface-elasticity energy exceeds the energy $\varepsilon$ of the domain wall. Competition between these energies determines the stripe width [15]:

$$d_{st} \approx \frac{K}{\lambda_s - \varepsilon},$$

(3.3)

where $K = (1/2)(K_s + K_b)$ is the mean Frank constant. In the temperature window $T > T_C$ ($T_C$ is the bulk SmC–HSmB transition temperature) we are interested in, the main temperature dependent factor in (3.3) is $\lambda_s$. The very existence of this linear splay distortion is due to the asymmetry of the order parameter profile over the film. Induced by the surface ordering $\Psi_s$, hexatic (bond) order parameter $\Psi$ decays toward the interior of the film

$$\Psi(z) \propto \Psi_s \cosh[(z - L)/\xi] \cosh(L/\xi),$$

(3.4)

where $L$ is the film thickness, and $\xi$ is the bulk phase transition correlation length

$$\xi \approx \frac{\xi_0}{\sqrt{(T - T_C)/T_C}}$$

(3.5)

with $\xi_0$ designating the bare microscopic correlation length. The asymmetry of the profile $\Psi$ determines the value of the parameter $\lambda_s$

$$\lambda_s \propto \tanh(L/\xi),$$

(3.6)

and the transition from the homogeneous to the modulated phase occurs if the asymmetry is strong enough (see, (3.3)). Thus we end up with the conclusion that the stripe phase (soliton regime) appears spontaneously on cooling and then the period of the distortion increases with decreasing temperature. The second conclusion from (3.3) is that upon cooling when $\lambda_s$ exceeds $\varepsilon$, the periodic stripe structure becomes unstable. The both conclusions conform to our experimental observations.

We observe complex phase behavior with various equilibrium structures. A separate question how to calculate all equilibrium structures of a specific system, requires full minimization of the global free energy, and it depends on unknown phenomenological Landau expansion coefficients. We will not even attempt the calculation of such a complex phase diagram in this paper but will content ourselves with one remark. Modulated phases we found have nonuniform density or orientation distributions, that is to say their symmetry is that of a solid or a liquid crystal. The difference between the phases which appear under the name of modulated structures, and solids or liquid crystals, is that generally the period of modulation is larger.

IV. CONCLUSION

It is not a major goal of this work to achieve quantitative agreement between the results obtained with our phenomenological model and experimental measurements. However, since the present understanding of the mechanism leading to modulated structures in achiral tilted hexatic films is incomplete, the model may be an appropriate tool for working out typical trends that may be testable in experiments. In this paper we have presented results of studies of structural transformations in thin liquid crystal films with the smectic-C (SmC) to hexatic (HSmB) phase transition, and their interpretation within a simple phenomenological model. The free energy was written in the most simple form that involves the least number of model parameters, and we have shown that this simple model can capture many of the features seen in experiment. Our interpretation of the results is based on the simple consideration that because of the up-down asymmetry, the achiral smectic film exhibits polar properties. One note of caution is in order here. In fact the structure of any SmC phase is inherently polar since the tilt singles out a unique direction about the layer normal $\nu$ (although, the directors $n$ and $-n$ are physically indistinguishable). Therefore in the SmC structure one may have a pseudo-vector

$$l = (\nu \times n)(\nu n).$$

(4.1)

Obviously $l$ is perpendicular to the tilt plane, and this kind of the polarity (along the pseudo-vector $l$) is of fundamentally different nature from the polarity along $c$ we investigated in our paper. Indeed, $l$ polarity is
compatible with mirror symmetry in the tilt plane, whereas the polar splay distortion responsible for the stripe structure, changes its sign under such a mirror reflection.

A question of primary importance is the understanding of the origin of the thermodynamic behavior we found in our work. It is well known [22] that for a film with the uniform ordering (like nematic or ferromagnetic), when the interaction at the boundaries is such that it enhances local order, it may happen that a surface transition takes place at temperatures above the critical temperature of the bulk. In such a transition, the layers close to the surface become ordered although the bulk remains disordered. Depending on the nature of the interactions between the bulk and the surface, the system may exhibit various surface phase transitions, for instance, wetting transitions. In the latter case at temperatures just below the bulk transition, the thickness of the surface ordered layer is infinite. Unlike this scenario, non-uniformly ordered (modulated) systems not necessarily exhibit wetting phenomena, in which the thickness of surface ordered layer diverges. Instead of it, the system might exhibit a transition from one surface state to another, where both surface states have a finite thickness [10]. Since we have to deal in this work with modulated (non-uniform) structures, aforesaid arguments provide the physically appealing thermodynamic interpretation of our results.

First of all since we have deal with films, the basic thermodynamics of phase transitions should be formulated for this kind of the restricted geometry. Such a problem has been discussed for various systems long ago, and the results borrowed from the textbooks [22, 23] read as follows. In a film of thickness $L$, the thermodynamic potential $G$ per unit area is

$$ G = -pL + 2\gamma, \quad (4.2) $$

where $\gamma$ is the surface free energy, $p$ is the bulk pressure, and $A$ is the area. We denote the surface free energies of the smectic $C$ and hexatic phases by $\gamma_C$, and $\gamma_H$ respectively, and the Laplace condition yields

$$ \gamma_C = \gamma_H + \gamma_{C-H} \cos \theta, \quad (4.3) $$

where $\theta$ is the contact angle between Sm$C$ and hexatic, and $\gamma_{C-H}$ is the surface energy at the interface. In the bulk the coexistence temperature $T_C$ is defined by the equilibrium condition

$$ p_C(T_C) = p_H(T_C). \quad (4.4) $$

In the finite thickness $L$ film

$$ T_m = T_C + \Delta T(L), \quad (4.5) $$

and from $G_C = G_H$ one finds

$$ -p_H(T_m) + \frac{2\gamma_H}{L} = -p_C(T_m) + \frac{2\gamma_C}{L}. \quad (4.6) $$

Since

$$ p = p(T_C) + S(T_C)\Delta T \quad (4.7) $$

($S$ is the entropy) we get

$$ \Delta T(L) = \frac{2(\gamma_C - \gamma_H)T_C}{LQ}, \quad (4.8) $$

and $Q = T_C(S_C - S_H)$ is the latent heat at the bulk transition. The same can be expressed (see (4.3)) as

$$ \Delta T(L) = \frac{2T_C\gamma_{C-H} \cos \theta}{LQ}. \quad (4.9) $$

However, in (4.8) we did not consider the interaction $\Pi(L)$ [24] between the film surfaces (or between the walls). Repeating the same thermodynamics as above, one ends up with the same kind of the equation but where the disjoining pressure $p_d$ [24] renormalizes the surface energy $\gamma$

$$ 2\gamma(L) = 2\gamma + Lp_d + \Pi. \quad (4.10) $$

According to (4.9) when the contact angle $\theta = 0$, the HSm$B$ phase is favored near the boundary, when $\theta = \pi$, the Sm$C$ phase is favored, and the intermediate values of $\theta$ apply to intermediate structures. In any case for the
finite film thickness there are two possible scenarios depending on the film thickness. In one scenario the phase transition will occur before the surface HS\textit{mB} layer has had a chance to grow thick. In the another scenario, one can have a phase transition at a temperature at which HS\textit{mB} thickness at the surface is already larger than the sample thickness $L$.

There are clearly several open questions and future challenges. One of them is related to dipolar forces. Indeed, since the molecules are tilted, and the interface and the interior symmetry of the film are different from each other, the film has only one symmetry element, the vertical mirror plane, which is perpendicular to the film and parallel to the molecules. The film is therefore equivalent to a two-dimensional polar nematic, and it bears an electric polarization. If this polarization is small compared to the elastic energies involved, our arguments given above apply. On the other hand, if electric energies dominate, another kind of the texture can be stable, since all splay centers act as charge centers, and in this case a lattice of several small charges is more stable than one big charge. Another interesting question is how to tune parameters of the various modulated structures to optimize properties of technological interest. For instance, a wide area of research is clearly the problem to what extent the investigated systems can be useful to achieve interesting electro-optical properties. The treatment above can be generalized to more realistic systems (e.g. dipolar forces including), with the same conceptual ingredients, albeit at the expense of a rapidly increasing complexity.

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**Figure Captions**

Fig. 1
Temperatures of transitions observed in 5O.6 films of different thickness. The high-temperature state corresponds to the SmC phase. Closed symbols denote structural transitions, open symbols transitions associated with change of director orientation in the film. In thick films \((N = 17)\) an additional transition to Sm\(T_4\) state takes place (filled diamond) with texture typical for the Sm\(F\) phase.

Fig. 2
High temperature textures in a 7-layer film: Sm\(C\), \(T = 60.1^\circ\)C (a), Sm\(T_1\), \(T = 59.2^\circ\)C (b). In frame (a) a point topological defect with characteristic brushes is observed. DRLM. The horizontal size of the frames is about 420\(\mu\)m.

Fig. 3
State with narrow periodic stripes, \(T = 55^\circ\)C, \(N = 7\) (a). Inset: stripes in the same film after cooling to \(T = 52.3^\circ\)C. Structure with linear aperiodic domains, \(T = 51.3^\circ\)C, \(N = 17\) (b). Honeycomb texture may form on cooling in a narrow temperature range (c), \(T = 50.8^\circ\)C , \(N = 7\). The horizontal size of the frames (a) and (b) is about 720\(\mu\)m, frame (c) 480\(\mu\)m, and inset 160\(\mu\)m, DRLM.

Fig. 4
Schematic representation of stripe structure. Stripes are oriented along the y-axis. (a) Monodomain state (Sm\(F\)). (b) In the Sm\(L\) phase the c-director may have two orientations with respect to bond orientational order \((\varphi = \pm 15^\circ)\). (c) Net orientation of the c-director in the stripes with jump in director orientation on the stripe boundary (Sm\(T_2\) state, Fig. 3a). Structure of the Sm\(C\) top (d) and bottom (e) layers of the film in the stripe state.

Fig. 5
Temperature dependence of the stripe period in a four-layer film. The period monotonically increases with decreasing temperature. The solid line is a fit to the eye.

Fig. 6
Structures formed in films at low temperatures. Aperiodic domains, \(N = 7\), \(T = 50.8^\circ\)C (a). Two sets of crossing domains in a thick film, \(N = 200\), \(T = 49.1^\circ\)C (b). On further cooling a transition to the Sm\(F\) structure occurs (c) \(N = 17\), \(T = 48.1^\circ\)C, DRLM. The horizontal size of the images is 374\(\mu\)m.