Uniplanar smectic phases in free-standing films

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Structures of various phases that appear in antiferroelectric liquid crystals can be described within a simple discrete phenomenological model of antiferroelectric liquid crystals, which for the smectic-*C*-alpha (SmC_α) phase suggests a short-pitch helicoidal structure. In a paper presented here the same model is used to analyze theoretically free-standing films, formed by a finite number of smectic layers. In the bulk sample a transition from the smectic-*A* (Sm*A*) phase is either to the ferroelectric SmC^* phase, the SmC_A^* phase, or the antiferroelectric SmC_α phase, as observed from experiments as well as comprehended in the model. However in free-standing films uniplanar structures, which in a bulk sample were not observed experimentally nor predicted by the model, are shown to appear immediately below the transition from the high-temperature Sm*A* phase. In free-standing film uniplanar structure remains stable in a narrow temperature region between Sm*A* and SmC_α phase.

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Antiferroelectric liquid crystals appear in several smectic phases [1,2], characterized by one-dimensional quasi-long-range translational and long-range orientational order, that are established by molecules being arranged in layers and within each layer oriented along the common direction, denoted by a director $\boldsymbol{n}$. In the high-temperature smectic-*A* (Sm*A*) phase the molecules are perpendicular to the layers on the average. At some temperature interval below the Sm*A* phase, usually the ferroelectric SmC^* phase is stable [3]. In the SmC^* phase chiral interactions cause the director to rotate around the layers normal thus forming a helical superstructure, with pitch extending over approximately thousands of layers.

In a narrow temperature interval between the Sm*A* and the SmC^* phase, often a SmC_α phase appears. A discrete phenomenological model of antiferroelectric liquid crystals was introduced few years ago [4], which suggested that the SmC_α phase has a short-pitch helicoidal structure, caused by competing nearest-and next-nearest layer interactions. Ellipsometric measurements [5] and resonant x-ray scattering experiments [6] performed recently on free-standing films of different compounds confirmed the suggested structure of the SmC_α phase [7,8].

In the lowest-temperature antiferroelectric SmC_A^* phase, the director is tilted with respect to the layers normal for an angle θ and it alternates between almost opposite directions from one layer to the next [9]. Helical superstructure on the two sublatices, formed by next-nearest layers, is caused again by chiral interactions. The structures of the phases, that in some compounds exist at temperatures between the ferroelectric and antiferroelectric phases and have ferrielectric properties, were revealed through recent experiments [6] as periodical structures, with the period extending over three and four smectic layers.

In this paper we report about theoretical studies of antiferroelectric liquid crystals in films with finite number of smectic layers [10,11], derived within the discrete phenomenological model. The model is simplified by considering only those terms in the free-energy expansion, which give rise to appearance of the ferroelectric or antiferroelectric phase, or the short-pitch helicoidal SmC_α phase in a bulk sample. In the following we shall use a common name *uniplanar* structures for the structures, where molecules tilt within the same plane in all the film layers. We will not include explicitly the influence of chiral interactions, that impose additional long-pitch helicoidal modulation to any uniplanar structure or lift a degeneracy between left and right handedness of the short-pitch SmC_α structure.

In the following, the temperature where the stability limit of nontilted Sm*A* phase occurs, is determined in free-standing films with finite number of smectic layers. Description of the tilted phases, which in a continuous manner, evolve from the Sm*A* phase, is given. It is shown that the tilted phase immediately below the Sm*A* phase is in general uniplanar in free-standing films. In the last part the stability limit of the uniplanar phase is determined. It is shown that in films with *odd* number of layers any uniplanar structure except the ferroelectric or antiferroelectric is stable only in a narrow temperature region. Its width depends on the number of layers in the film and it might be few tenths of a degree in thin films. By further decreasing the temperature the uniplanar phase transforms into nonplanar SmC_α phase. However in films with *even* number of layers, a distinct four-layer uniplanar structure also remains stable down to arbitrarily low temperatures, beside the ferroelectric and antiferroelectric phases, and an explanation for this is given.

I. STABILITY OF THE SmA PHASE

Transition from the Sm*A* phase to a tilted phase, which may in bulk be Sm*C*, SmC_A, or SmC_α phase, as well as the structure of the tilted phase, is within the discrete phenomenological model conveniently described with the order parameter, which is a set of two-dimensional layer-tilt vectors $\boldsymbol{\xi}_i = (\xi_{i,x}, \xi_{i,y})$. These are the projections of the layer directors $\boldsymbol{n}_i$ onto the plane xy, that is parallel to the smectic layers. The index i stands for the ith layer. In a free-standing film there are altogether N layers.

Assuming the system is homogeneous inside each layer and therefore disregarding the (x,y) dependence of the tilt vectors $\boldsymbol{\xi}_i$, an expansion of the bulk free energy in the discrete order parameter $\boldsymbol{\xi}_i$ is [4]

$$G=\sum_i \left[\frac{1}{2}a_0\boldsymbol{\xi}_i^2+\frac{1}{4}b_0\boldsymbol{\xi}_i^4+\frac{1}{2}a_1\boldsymbol{\xi}_i\boldsymbol{\xi}_{i+1}+\frac{1}{8}a_2\boldsymbol{\xi}_i\boldsymbol{\xi}_{i+2}\right]. \tag{1}$$

In Eq. (1) the free energy is written in the most simple form that involves the least number of model parameters, but explains well the transition from the SmA phase to the tilted phase. The first and the second term describe the intralayer interactions. Parameter a_0 depends linearly on temperature $a_0=a(T-T_0)$, where a is positive and T_0 would be a temperature of transition from the SmA to the tilted phase, if there was no interaction between the neighboring layers. Assuming the existence of the second-order transition, parameter b_0 is the usual positive constant in the fourth-order term. The next two terms are the lowest-order terms describing interactions between neighboring layers. The term with parameter a_1 describes interactions between the nearest layers. The sign of a_1 determines the relative orientation of tilts in nearest neighboring layers. It may be positive or negative, thus favoring anticlinic or synclinic orientation of tilts in nearest-neighboring layers. The term with parameter a_2 represents the next-nearest layer interactions. If a_2 is negative synclinic tilts in next-nearest neighboring layers are favored and occur in a system with both synclinic or anticlinic tilts in nearest layers. Positive a_2 brings a certain frustration into the system, since favored anticlinic orientation of tilts in next-neighboring layers is not compatible neither with synclinic, nor anticlinic tilts in nearest layers. In the systems which exhibit SmC_α immediately below the SmA phase, a_2 should be positive and large enough, compared to a_1. Here we shall be concerned with such compounds, therefore a_2 will be assumed to be positive.

By including higher-order interlayer interaction terms into the free-energy expansion, the temperature dependence of interaction can be considered. It becomes more important at lower temperatures, where the magnitude of the tilt is larger. In the presented analysis the higher-order terms do not alter crucially the results, which refer mostly to a temperature region just below the stability limit of the SmA phase. Therefore we shall not consider them.

Depending on the values of the model parameters (which differ for different compounds and can be obtained from experiments), the transition from the SmA phase *in the bulk* is to the tilted SmC, SmC_A, or, SmC_α phase. Within our model the magnitude of the tilt in the bulk is the same in all the layers. For negative a_2, a stability of the SmA phase within the model is easily determined as well as the structure of the tilted phase. It is either uniplanar ferroelectric, totally synclinic, or uniplanar antiferroelectric, totally anticlinic. A choice between both is made solely by the sign of a_1, as we described. No interesting new result is obtained for negative a_2.

On the other hand, for positive a_2, one of three distinct tilted structures evolves from the SmA phase *in the bulk* [4]. They are characterized by the phase difference $\Delta\phi$, which is the difference in phase angles of tilt in nearest-neighboring layers. If $a_1<-a_2$, the tilted phase is ferroelectric, with $\Delta\phi=0$. If $a_1>a_2$, the tilted phase is antiferroelectric, with $\Delta\phi=\pi$. In between, for $-a_2<a_1<a_2$, the tilted phase is a short-pitch SmC_α phase, where the magnitude of the tilt is the same in all the layers, and the phase of the tilt changes regularly from one layer to the next for a certain angle $\Delta\phi$, defined by $\cos\Delta\phi=-a_1/a_2$. The temperature of transition from the SmA to a tilted lower temperature phase is $T_c^{bulk}=T_0-(a_1\cos\Delta\phi+\frac{1}{4}a_2\cos 2\Delta\phi)/a$. When the temperature decreases, the magnitude of the tilt increases, but the phase difference $\Delta\phi$ remains the same. If we have considered also higher-order interlayer interaction terms in free-energy expansion, temperature dependence of $\Delta\phi$ at lower temperatures could be obtained.

In the *free standing film* there are N smectic layers, therefore the sum in Eq. (1) is finite and formally correct, if we take $\boldsymbol{\xi}_i\equiv\boldsymbol{0}$ for $i<1$ or $i>N$. Trying to describe the free surfaces we do not introduce any special surface parameters; the same approach of the free boundary conditions as was discussed elsewhere [12] for other phases. Tilt vectors $\boldsymbol{\xi}_i$, which describe an equilibrium structure in a N-layers film therefore satisfy a set of N extremal equations, with i ranging from 1 to N,

$$\begin{aligned}\frac{\partial G}{\partial \xi_{i,x}}&=a_0\xi_{i,x}+b_0(\xi_{i,x}^3+\xi_{i,x}\xi_{i,y}^2)+\frac{1}{2}a_1(\xi_{i-1,x}+\xi_{i+1,x})\\&\quad+\frac{1}{8}\,a_2(\xi_{i-2,x}+\xi_{i+2,x})\\&=0,\\ \frac{\partial G}{\partial \xi_{i,y}}&=a_0\xi_{i,y}+b_0(\xi_{i,y}^3+\xi_{i,y}\xi_{i,x}^2)+\frac{1}{2}a_1(\xi_{i-1,y}+\xi_{i+1,y})\\&\quad+\frac{1}{8}{}_2(\xi_{i-2,y}+\xi_{i+2,y})\\&=0,\end{aligned} \tag{2}$$

where G is the free energy (1), and the stability condition, that a matrix $\boldsymbol{A}_0$ of the second derivatives is positive definite. The matrix $\boldsymbol{A}_0$ is a $2N\times 2N$ dimensional block matrix

$$\boldsymbol{A}_0=\begin{pmatrix}\boldsymbol{A}_x & 0\\ 0 & \boldsymbol{A}_y\end{pmatrix}, \tag{3}$$

where $\boldsymbol{A}_x$ and $\boldsymbol{A}_y$ are five-diagonal $N\times N$ dimensional matrices with nonzero elements

$$\begin{aligned}A_x(i,i)&=\frac{\partial^2 G}{\partial \xi_{i,x}^2}=a_0+b_0(3\xi_{i,x}^2+\xi_{i,y}^2),\\ A_y(i,i)&=\frac{\partial^2 G}{\partial \xi_{i,y}^2}=a_0+b_0(3\xi_{i,y}^2+\xi_{i,x}^2),\\ A_x(i,i\pm 1)&=\frac{\partial^2 G}{\partial \xi_{i,x}\partial \xi_{i\pm 1,x}}=A_y(i,i\pm 1)=\frac{1}{2}\,a_1,\\ A_x(i,i\pm 2)&=\frac{\partial^2 G}{\partial \xi_{i,x}\partial \xi_{i\pm 2,x}}=A_y(i,i\pm 2)=\frac{1}{8}\,a_2.\end{aligned} \tag{4}$$

Eigenvectors of $\boldsymbol{A}_0$ describe the fluctuations of the tilt and the corresponding eigenvalues are related to the relaxational frequencies of the fluctuations. A certain structure, satisfying Eq. (2), is stable as long as eigenvalues of the matrix of the second derivatives are all positive. An analysis presented in the following, basically consists of two parts. In the first one the structure, satisfying Eq. (2), is found, and in the second the stability of the structure is explored through an analysis of the matrix of the second derivatives (3) and its eigenvalues.

An equilibrium structure of the Sm*A* phase is given by a trivial solution of Eq. (2), $\boldsymbol{\xi}_i \equiv 0$ for all i. This solution exists at all temperatures, but is stable only where corresponding matrix of the second derivatives $\boldsymbol{A}_0^{(SmA)}$ (diagonal elements without b_0 terms!) is positive definite.

In the Sm*A* phase a double degeneracy of $\boldsymbol{A}_0^{(SmA)}$ is obvious. Due to the invariance of the Sm*A* phase structure to the rotations about the smectic layers normal, the choice of x and y axes within the plane of the smectic layers is arbitrary and all the eigenvalues of the matrix $\boldsymbol{A}_0^{(SmA)}$ in the Sm*A* phase are doubly degenerate. Therefore the analysis of $\boldsymbol{A}_0^{(SmA)}$ in one of the nondegenerate $N\times N$ dimensional subspaces is performed only, the chosen plane is $y=0$, and corresponding matrix of the second derivatives is $\boldsymbol{A}_x^{(SmA)}$.

If temperature is high enough all the eigenvalues of $\boldsymbol{A}_x^{(SmA)}$ are positive and corresponding structural deformations, described by eigenvectors of $\boldsymbol{A}_x^{(SmA)}$, are all energetically undesirable. The trivial solution describing the orthogonal structure of Sm*A* phase is stable and the only solution of Eq. (2). By lowering the temperature the eigenvalues become smaller. The critical temperature T_c is reached when the first eigenvalue becomes zero. At T_c the structure of the Sm*A* phase destabilizes and at temperatures below does not correspond to the minimum free energy any more. The critical order parameter fluctuation that freezes in at the temperature T_c of transition from the Sm*A* to a tilted phase is given by the corresponding eigenvector of $\boldsymbol{A}_x^{(SmA)}$. With regard to the chosen subspace (plane $y=0$), it describes a uniplanar fluctuation, where tilt vectors in all the layers lay on the same straight line, parallel to the x axis.

For any number of layers the Sm*A*↔*tilted phase* transition line in a $(a_0/a_2, a_1/a_2)$ phase diagram can be found numerically. It is shown for films with different number of layers in Fig. 1. Additionally the stability line of the Sm*A* phase in 4- and 5-layer films together with schematic representation of the critical uniplanar fluctuations, that correspond to the tilted structures below the transition, is shown in Figs. 2(a) and 2(b).

As can be seen from Fig. 1 at given ratio of model parameters a_1/a_2, the temperature of the transition from the Sm*A* phase to the tilted phase depends on the number of smectic layers in the film. It is lower in thin films, grows with increasing the number of layers and assimptotically approaches the bulk transition temperature from below. This can be understood if we recall, that the interactions between the neighboring layers increase the transition temperature $T_c^{bulk} > T_0$. In films with limited number of layers there are surface layers, which do not have neighboring layers (nearest and next nearest, within the model) outside the film to interact with, therefore also interlayer interactions at the surfaces contribute less to a rise of the transition temperature. So the transition temperature in a free-standing film is higher than

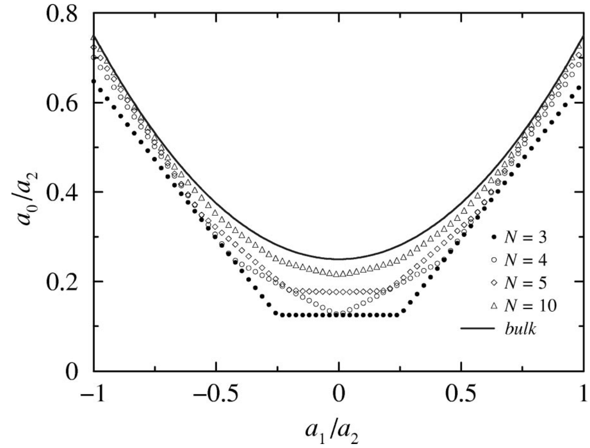

FIG. 1. Renormalized temperature a_0/a_2, where the nontilted Sm*A* phase becomes unstable, in dependence of the ratio of model parameters a_1/a_2 for free-standing films with various numbers of smectic layers.

T_0, but lower than T_c^{bulk}. With similar reasoning we also understand why the minimum transition temperature in the film, with given thickness, occurs at $a_1=0$. With smaller $|a_1|$, the interlayer interactions are weaker and the increase of the transition temperature is smaller. In the bulk and free-standing films the transition temperature depends only on the strength of interactions $|a_1|/a_2$ and not on the sign of a_1, therefore the stability lines are symmetric about $a_1=0$.

At this point it is worth while to mention, that we have not taken into account the effects of possibly large surface tension, which is always present in free-standing films and which makes them stable. Surface tension suppresses the

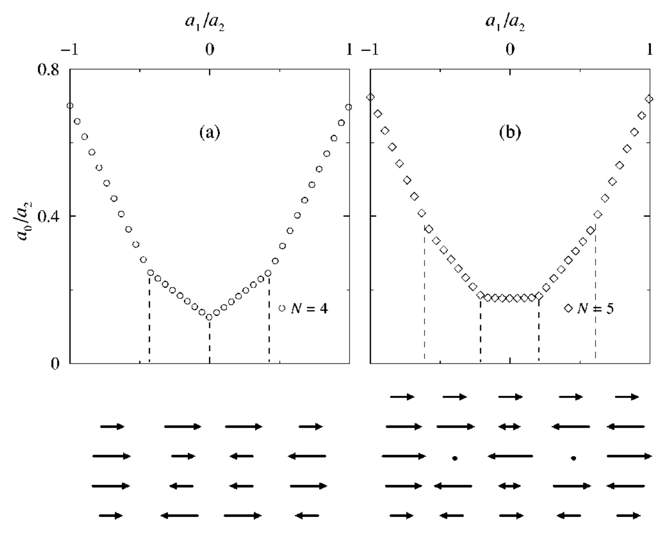

FIG. 2. Stability lines of the Sm*A* phase in (a) four-and (b) five-layers-thick films. A schematic representation of the corresponding uniplanar fluctuations of the tilt, that destabilize the non-tilted phase, is shown below. The arrows denote the relative amplitudes and phases of the tilt fluctuations in separate film layers. In films with odd number of layers any antisymmetric fluctuation has zero magnitude of the tilt in the middle layer, that is represented with a dot in (b). Arrows pointing in both directions for a five-layers-thick film at $a_1/a_2 \approx 0$ are used to demonstrate that the relative phases of the tilt fluctuation in the second and the fourth layers depend on the sign of a_1.

smectic-layer displacement fluctuations at the free surfaces [13] and is most likely the reason for commonly observed enhanced smectic order at free surfaces and consequently increased temperature of the phase transition in surface layers [14]. Being restricted to the layers near surfaces, the transition at higher temperature is called the surface transition. The influence of enhanced surface order on the transition temperature is opposed to the influence of the missing interlayer interactions at the surface, described above. We have explored the enhanced surface order effects within our model to a certain extent in our previous paper [15].

In a free-standing film with N smectic layers, there exist N different uniplanar fluctuations. Due to a symmetry of the free energy under the reflection about the middle of the film, all of the uniplanar fluctuations have particular symmetry—they are either symmetric or antisymmetric with respect to the middle of the film. Among them ferro- and antiferroelectric are the two extrema, as we shall see.

Which of N uniplanar fluctuations is actually critical depends on the ratio of the model parameters a_1/a_2, as can be observed from Figs. 2(a) and 2(b). If $a_1<0$, a synclinic tilt in neighboring layers is preferred by which it is meant, that for the two neighboring layers the tilt in the same direction is favored. The larger the ratio $|a_1|/a_2$, the more pronounced is the synclinic ordering in the uniplanar structure in the sense that the major part of the layers have the neighboring layers with molecules tilted to the same direction. And for $a_1>0$ the same holds for the anticlinic tilt ordering. Anticlinic in the sense that, for the two neighboring layers, tilt in the opposite direction is favored. When the ratio a_1/a_2 is changing continuously, the symmetric and antisymmetric uniplanar structures alternate. When the number of pairs of synclinic tilts in nearest layers is changed by one, the symmetry of the tilted structure converts from symmetric to antisymmetric or vice versa.

Another observation can be made by looking at Figs. 1 and 2. If the ratio of the model parameters a_1/a_2 is smaller than some limiting ratio, $a_1/a_2<-r_N$, the critical uniplanar fluctuation on the whole is synclinic, that is, ferroelectric, with molecules in all the layers tilted to the same side. On the other hand, if $a_1/a_2>r_N$, the critical uniplanar fluctuation on the whole is anticlinic, that is antiferroelectric, from one layer to the next the tilt alternates from one side to the opposite. The limiting ratio r_N depends on the film thickness, as can be seen from Fig. 3. With increasing N it approaches its bulk value $r_N\to r_{bulk}=1$ from below. On the other side, for two layers, a decision between the only two uniplanar structures is made solely by the sign of interaction between the nearest layers. A plain solution is $r_2=0$.

Until here we have discussed nothing else but uniplanar fluctuations, that destabilize the orthogonal structure of the Sm*A* phase in the plane $y=0$. However the complete matrix, which is relevant to a stability of the Sm*A* phase in free-standing film with N layers, is doubly degenerate $2N\times 2N$ dimensional $\boldsymbol{A}_0$. Therefore at critical temperature T_c two eigenvalues simultaneously become zero. They correspond to the *same* uniplanar fluctuations in two perpendicular planes, $y=0$ and $x=0$. Arbitrary linear combination of the two critical fluctuations results in another critical fluctuation. In free-standing film an arbitrary linear combination of the same two

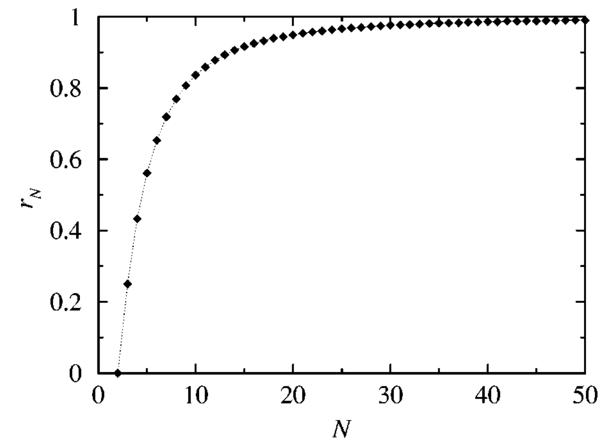

FIG. 3. The limiting ratio r_N of model parameters a_1/a_2, that determines the transition from the Sm*A* phase to either ferroelectric of antiferroelectric phase, as it depends on the number of layers *N*.

uniplanar fluctuations in perpendicular planes results in the same critical fluctuation within an arbitrary plane, perpendicular to smectic layers.

In the bulk the situation is different, due to a discrete translational symmetry present in the bulk, but not in the free-standing film. Uniplanar fluctuations in bulk are described by sinusoidal plane waves and defined by a wave vector q. In the bulk q is continuous, while in free-standing films with N layers it is a discrete parameter, that can have only N different values. The same uniplanar fluctuations (the same parameter q) in perpendicular planes may in a free-standing film sum only with zero spatial phase shift, due to the symmetry under the reflection about the middle of the film. If in the $x=0$ plane the fluctuation ''amplitude'' is a maximum in ith layer, the same must be true in the perpendicular $y=0$ plane. The sum of both is the same uniplanar fluctuation within the arbitrary plane, with the maximum amplitude again in ith layer. But in the bulk sample, due to a discrete translational symmetry, additional degeneracy is present. The same sinusoidal uniplanar fluctuations in perpendicular planes may therefore combine also with arbitrary spatial phase shift. Resulting sum is anything from the same pure uniplanar sinusoidal fluctuation for the zero phase shift, to a perfect circular fluctuation for a phase shift $\pm\pi/2$, or ellipsoidal fluctuation for a phase shift being anything else. All of them are described by the same q.

Below T_c, a degeneracy among different combinations is lifted by higher-order terms, in our case b_0 term. A decision about the combination, leading to an equilibrium lower temperature structure, is thus made by the higher-order terms. We have already described possible stable structures in the bulk systems and seen, that the tilted phase below the Sm*A* phase may be pure uniplanar ferroelectric or antiferroelectric phase, or nonplanar, helicoidal SmC_α phase, evolved from a circular fluctuation. But in free-standing film the critical fluctuation in the Sm*A* phase is uniplanar and therefore also the tilted phase just below the second-order transition from the Sm*A* phase is undoubtedly uniplanar. Except for few special ratios of model parameters a_1/a_2, where two different uniplanar fluctuations, corresponding to different parameters q, become unstable at the same critical temperature. In Fig. 1 we can observe such situations in breaking points of the

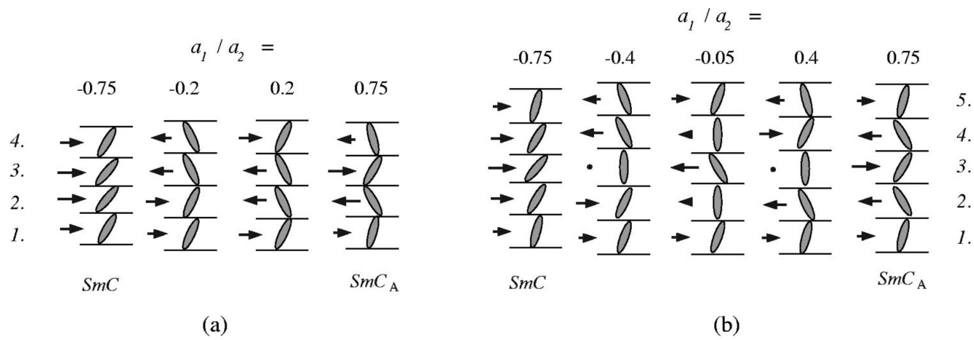

FIG. 4. A schematic representation of the tilted uniplanar phases in films with (a) four and (b) five layers, for different values of a_1/a_2. Molecules in all the layers tilt within the same plane. Relative magnitudes and directions of the tilt are shown in all the layers. In two antisymmetric five-layers uniplanar structures, for $a_1/a_2 = \pm 0.4$, tilt is zero in the middle layer.

Sm*A* phase stability lines, most clearly for thin films. Two different uniplanar fluctuations in perpendicular planes may in free-standing film combine in a nonplanar, helicoidally modulated fluctuation, and the tilted structure below T_c corresponds to the SmC_α phase, as we shall see in the following section.

II. UNIPLANAR PHASES

Structure of the uniplanar phase at temperature lower than T_c can be found by solving a set of extremal nonlinear equations (2) with $\xi_{i,y}=0$ for any *i*. An iterative numerical procedure of finding the structure of the uniplanar phase is based on an assumption, that the structure changes continuously with temperature. The equilibrium tilt vector in the *i*th layer at temperature $T-\Delta T$ can then be written as a sum of the equilibrium tilt vector at higher temperature T and a small correction. We linearize Eqs. (2) in corrections and then solve obtained linear equations repeatedly; at each step we improve the initial approximation for the structure at $T-\Delta T$ with the solution for the correction and then search for the next improvement, until the resulting set of tilt vectors satisfies the complete, nonlinear extremal equations (2) within a desired numerical precision. The first approximation for the tilted structure just below the transition from the Sm*A* phase is the eigenvector of $\boldsymbol{A}_x^{(SmA)}$, corresponding to the critical fluctuation.

A schematic representation of various uniplanar tilted structures is shown in Fig. 4 for free-standing films with four and five layers. The structures preserve the symmetry of the fluctuation they evolve from. Antisymmetric uniplanar structures in odd films have zero tilt in the middle layer. If we recall that the corresponding temperatures, where the uniplanar phases exist, are above T_0, this is not surprising. The magnitude of tilt in surface layers is smaller than in interior layers. The reason for this is the same as for the decrease of the transition temperature compared to T_c^{bulk}, as explained above.

The uniplanar structure at temperature T does not necessarily remain such at lower temperature $T-\Delta T$. For that reason at each temperature lowering step we check the eigenvalues of corresponding matrix of the second derivatives $\boldsymbol{A}_0$ given by Eq. (3).

At all temperatures below the transition from the Sm*A* phase, one of the eigenvalues of $\boldsymbol{A}_y$ equals zero. The corresponding eigenvector describes a rotation of the tilt plane and corresponds to the zero-frequency Goldstone mode originating in rotational symmetry of the Sm*A* phase, that vanishes at the transition to the uniplanar phase. If all other eigenvalues are positive, the uniplanar phase is stable. By lowering the temperature we may reach a certain point, where another eigenvalue becomes zero and which is a stability limit of the uniplanar phase. The corresponding eigenvector describes a critical out-of-plane fluctuation, that destabilizes the tilted uniplanar structure. Below the stability limit of the uniplanar phase the structure becomes helicoidally modulated.

Resulting phase diagrams are for some film thicknesses presented in Fig. 5. At some special values of the ratio a_1/a_2, the stability limits of the uniplanar phases coincide with the stability limits of the Sm*A* phase [that can be seen clearly from Figs. 5(a) and 5(b)]. As we have mentioned already, in these points of the phase diagram, the Sm*A* phase is destabilized by two different uniplanar fluctuations in perpendicular planes, which may combine in nonplanar, non-Goldstone fluctuation. Formally that corresponds to a case, where by lowering the temperature from the Sm*A* phase, we reach a certain critical temperature, where the first two eigenvalues of the matrix $\boldsymbol{A}_x^{(SmA)}$ (the first four eigenvalues of $\boldsymbol{A}_0^{(SmA)}$) become zero. At these particular values of a_1/a_2, a tilted phase below the Sm*A* phase is nonplanar, spatially modulated SmC_α phase.

A distinct *odd-even* effect can be also recognized immediately. Among various uniplanar structures, that appear below the Sm*A* phase in free-standing films for different ratios of model parameters a_1/a_2, in films with *odd* number of layers only two, completely synclinic Sm*C* and completely anticlinic SmC_A remain stable at any lower temperature. They both exist in the outermost parts of the phase diagram with extreme values of the ratio a_1/a_2. All the other uniplanar phases, with synclinic and anticlinic tilts in neighboring layers, are stable merely in narrow temperature regions. Their width strongly depends on the film thickness and on the ratio a_1/a_2. If the number of layers increases, the temperature regions where uniplanar phases are stable, get narrower. An estimation of their width can be made on the basis of an assumption, that a shift of the Sm*A*↔*tilted phase*-transition temperature, caused only by next-nearest layer interactions, from T_0 for the no interlayer interactions case $(a_1=a_2=0)$ to T_c^{bulk} $(a_1=0,\ a_2>0)$, is of the order of a

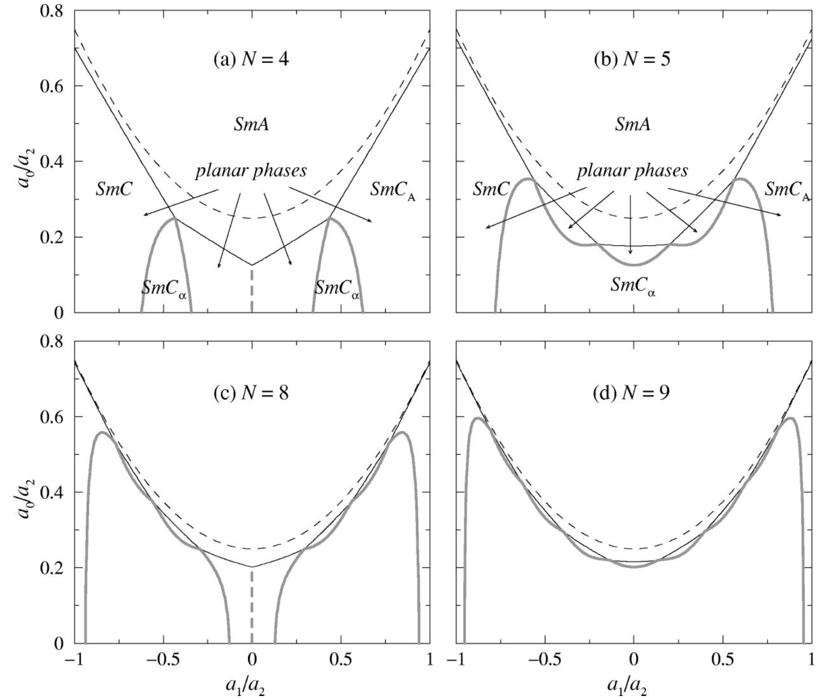

FIG. 5. Stability limits of the Sm*A* phase and uniplanar phases are shown with solid and thick gray lines, respectively, for films with (a) four, (b) five, (d) eight and (d) nine layers. A dashed line represents the stability limit of the Sm*A* phase in the bulk. A qualitative difference between phase diagrams for films with even [(a) and (b)] and odd [(b) and (d)] number of layers is evident. In addition to ferroelectric and antiferroelectric uniplanar phases in the outermost parts of the phase diagram, in films with an even number of layers also the two uniplanar phases in the vicinity of $a_1/a_2=0$ remain stable down to arbitrary low temperatures within this model. An estimation for a width of the temperature regions, where uniplanar phases are stable, is a few tenths of a degree for thin films.

degree to several degrees in real substances. In Fig. 5 a temperature parameter $a_0/a_2=0$ corresponds to the temperature T_0 and $a_0/a_2=0.25$ corresponds to T_c^{bulk} for only the next-nearest-layer interactions that are present. Observing Fig. 5 we can realize, that the uniplanar phases are stable in the regions of a few tenths of a degree in thin films.

In films with *even* number of layers, there is in addition a region of values of a_1/a_2 near $a_1/a_2\approx 0$ where two (for $a_1/a_2<0$ or $a_1/a_2>0$) tilted uniplanar structures also remain stable down to arbitrary low temperatures. In both structures tilts in next-nearest neighboring layers are anticlinic and the unit cell extends over four layers. The structures would be the same in the bulk, but they differ in finite films. The difference is in the number of synclinic and anticlinic tilts in nearest layers. However for small a_1 is, if it is negative, synclinic tilts in nearest layers are preferred and the four-layer structure in film with an even number of layers would have one pair of synclinic tilts in nearest layers more than anticlinic; Vice versa for positive a_1, as can be observed from schematic representation of the uniplanar structures for the four-layers film in Fig. 4(a).

For all the other uniplanar structures the same is true as for uniplanar structures in films with an odd number of layers. In the following we shall try to explain, why the *even* and the *odd* films differ for $a_1/a_2\approx 0$.

Let us look at a somewhat special example, when the parameter a_1 equals zero. In this case the system of smectic layers in the film decomposes into two decoupled sublattices, formed by the next-nearest layers (in five-layers film the first independent sublatice consists of three layers, the first, the third, and the fifth layer, and the second sublattice consists of the two layers, the second and the fourth). In each sublattice, interlayer interactions extend only up to the nearest-neighboring layers (in the sublattice the third layer is the nearest-neighboring layer of the first and of the fifth layer), the strength of interactions being defined by the parameter a_2. The structure on the sublattice is defined according to the model, where only nearest layers interactions are taken into account. In the sublatice the transition is from the Sm*A* phase either to a completely synclinic phase, if $a_2<0$ (tilt vectors in all the layers in the sublatice point in the same direction), or to completely anticlinic, if $a_2>0$ (tilt vectors alternate from one to the opposite direction from layer to layer in the sublatice).

In films with an *even* number of layers, the two decoupled sublattices have the same number of layers. In the case with $a_2>0$, nontilted structures of both sublatices are destabilized at the same temperature by the same anticlinic uniplanar fluctuation. Since with $a_1=0$ the sublattices are perfectly decoupled, and an angle between the two tilt planes corresponding to the two sublattices can be anything from 0 to π. All the structures with various angles between the two tilt planes have the same energy and remain degenerate down to arbitrary low temperatures.

For *odd* number of layers one of the sublattices has one layer more than the other. For $a_1=0$ they are decoupled. By lowering the temperature in the Sm*A* phase the nontilted structure in the larger sublattice is destabilized first by anticlinic $(a_2>0)$ uniplanar fluctuation. Below the critical temperature the structure in the film is such, that the molecules are tilted anticlinic in every second layer and nontilted in the layers in between. When the second critical temperature is reached, also the nontilted structure in the smaller sublattice becomes unstable to anticlinic fluctuation. Since the sublatices are decoupled, the angle between the tilt planes is arbitrary and all possible structures remain degenerate by lowering the temperature.

But as soon as a_1 just slightly deviates from 0, the overall symmetry requirements come into operation that distinguish the *even* and the *odd* cases. For a_1 near, but not exactly 0, the a_2 term (that is positive) is of major importance to a tilted structure. The structure tends to minimize as much as possible the a_2 part of the free energy. Therefore we may reasonably assume, that the tilted structures on the sublattices are still uniplanar and anticlinic. Yet they are coupled, since $a_1 \neq 0$. And although the coupling is weak, in films with an *odd* number of layers, it eliminates immediately all the structures but the two nonplanar ones, where the angle between the two tilt planes is either $\pi/2$ or $-\pi/2$. Such combinations of the sublattice structures result in left- and right-handed helicoidally modulated structures with the pitch extending over four layers. Among all the structures built from two uniplanar anticlinic sublattices, these are the only two structures, that in *odd* films fulfill the overall symmetry conditions, for the structure being symmetric or antisymmetric with respect to the middle of the film. In films with an *even* number of layers all the structures with various angles between the tilt planes satisfy the symmetry conditions, and the coupling between the sublattices just lifts the degeneracy among them. Obviously, one of the two four-layer uniplanar structures remains stable by lowering the temperature in a narrow region around $a_1/a_2 = 0$ in films with an even number of layers and a decision about them is made by the sign of a_1, as we have already described.

Below the stability limit of the uniplanar phases an equilibrium structure is a spatially modulated short-pitch helicoidal structure. Although in free-standing films the magnitude of the tilt is not the same in all the layers and the helix is not ideal, the structure is called the SmC_α phase. It was determined exactly in Ref. [16] and shown to match excellently the experimental data from optical [5,7] and x-ray scattering experiments [6,8].

III. CONCLUSIONS

Within the discrete model for antiferroelectric liquid crystals we have studied free-standing films made of polar smectic liquid crystals, that in the bulk appear in higher-temperature Sm*A* phase and in lower-temperature Sm*C*, SmC_A, or SmC_α phases. We have determined the temperature of the second-order transition from the Sm*A* to the tilted phases. It is lower than the bulk transition temperature due to the missing interlayer interactions of the surface layers.

The tilted phase below the transition was found to be uniplanar in free-standing films. The phenomenon is due to two distinctive properties of the free-standing films. The first one is the broken translational symmetry and consequently lifted degeneracy among various spatial phase shifts between the same critical uniplanar fluctuations in perpendicular planes. The second is a discreteness of the parameter q, that plays a role of the wave vector of the fluctuation, connected to the finite number of layers in the film. When the critical fluctuation with definite q_j becomes unstable in free-standing films, it is always uniplanar (except at few particular values of a_1/a_2). The tilted structure below the critical temperature is uniplanar too until the second critical temperature is reached, where the second fluctuation, with q_{j+1} or q_{j-1}, becomes unstable.

At some particular values of the ratio a_1/a_2, two different uniplanar fluctuations (with different parameters q_j and q_{j+1}) become unstable at the same temperature T_c, and combined into nonplanar fluctuation, leads to an evolution of the nonplanar structure immediately below T_c. This also explains why the temperature region, where the uniplanar structure is stable, strongly depends on the number of layers in the film. It may well be a few tenths of a degree wide in thin films with less then five or six layers, but gets narrower in thicker films and is practically unnoticeable in films thicker than 15 layers. The narrowing of the stability region is due to increasing density of parameters q in the first Brillouin zone, when the number of layers is increased. In the bulk q is continuous.

In films with odd number of layers only two extreme uniplanar structures, totally synclinic and totally anticlinic ferroelectric and antiferroelectric structures, respectively, can remain stable at low temperatures. However in films with an even number of layers, for the ratio of model parameters a_1/a_2 around zero, two four-layers structures may also remain stable at low temperatures. The difference in odd and even cases is again due to the conditions, imposed by the symmetry of the free-standing film.

The uniplanar phases shown to appear below the Sm*A* phase in free-standing films are not to be mistaken for the uniplanar structures that appear as a sequence of phases within the axial next-nearest-neighbor Ising (ANNNI) model [2] in the bulk. The ANNNI model assumes from the beginning that the molecules are tilted within one plane, while within our model this comes out as a result, that is conditioned by the symmetry and finite thickness of the free-standing films.

In the analysis presented here we have not included explicitly the chirality of the system, that would affect any uniplanar structure by imposing additional modulation along the plane normal, so the structure below T_c would not be uniplanar but slightly twisted. However free-standing films are usually much thiner than a period of a helicoidal structure, induced by chiral interactions, and deviations of the tilt vectors from the plane would be small.

At the end we stress that the symmetry arguments and conclusions we have come to, apply in general to transitions between the orthogonal Sm*A* and tilted phases in free-standing films. They are independent of the model we have used. In free-standing films the tilted structure immediately below the Sm*A* phase should be uniplanar with negligible twisting, conditioned by chiral interactions. Short-pitch SmC_α phase develops only below the uniplanar phase. Our results could be tested experimentally, with resonant x-ray scattering [6], depolarized reflected light microscopy [17], ellipsometry [5], or by some other means.

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