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Manifold of polar smectic liquid crystals with spatial modulation of the order parameter

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We revisit a theoretical approach based on the discrete Landau model of polar smectic liquid crystals. Treating equilibrium structures on many length scales, we have analyzed different periodically modulated polar smectic phases. Besides already known smectic structures, we have obtained a number of other phases which are stable in a narrow range (that is why the phases can be termed as microphases) of model parameters and thermodynamic conditions. The sequence of microphases represents a so-called "harmless staircase" of structures with oscillating periods. We anticipate that the range of stabilities for various microphases can be extended (and therefore the microphases can be easier to detect experimentally) by applying external electric fields or/and investigating freestanding smectic films.

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I. INTRODUCTION

Liquid crystals discovered in 19th century are perhaps the oldest well-defined and ordered representatives of soft matter materials [1–3]. The vast majority of molecules that build up liquid crystals are polar, however, the simplest liquid-crystalline structures (nematics and smectic-A) constructed of these molecules are nonpolar. In order to have a bulk polar order, a liquid crystal must have a direction which cannot be reversed by any symmetry operation. For example, less symmetric tilted and chiral smectic-C liquid crystals can form polar structures. A rich variety of structures and strong response to external stimuli typical for liquid crystals enable many practical applications ranging from information displays (where liquid crystals are a cornerstone of the overall display industry), to sensors, to photonic devices. Having in mind these applications, the long story of investigations, and the fundamental challenges of understanding of partially ordered liquidlike systems, one might think that at least there are answers to all fundamental questions. But it is not the case. Liquid crystals (in particular, polar and chiral ones) turned out to be much more difficult and interesting than expected and we do not yet have a clear overall picture of the properties of these systems. Even after more than 100 years of research, it is not yet known whether all possible kinds of liquid crystals have been discovered already and identified. Especially the questions concern chiral polar smectic-C^* liquid crystals [1,4,5], for which unique and exotic types of ordering were discovered recently [6–8].

Polar smectic-C^* (SmC^*) type liquid crystals form layer structures in which molecules tilt with respect to the layer normal [1]. Their orientational structure may be described by two-component vectors $\boldsymbol{\xi}_i$ in each i layer (Fig. 1). Modulus $\boldsymbol{\xi}_i$ is the projection of the long molecular axis to the layer plane and determines the polar angle θ_i, whereas the direction of $\boldsymbol{\xi}_i$ describes the azimuthal orientation (angle φ_i). The manifolds of polar structures are formed by different orientations of $\boldsymbol{\xi}_i$ in the smectic layers (Fig. 1).

On the theoretical front, even simple structures and phase diagrams of polar, chiral, and smectic-C liquid crystals are sufficiently complex by the standards of classical condensed-matter physics. The most general form of the problem is exceptionally involved and tedious. However, despite the apparent intractability of the problem, all of these complications can be subsumed by a phenomenological Landau model. As is typical in any coarse-graining scheme, many microscopic details pertaining to the physical system on a given scale become condensed into a few effective parameters—Landau theory coefficients. The strength of the phenomenological (heuristic) arguments is their general validity. Aiming to clarify the issue about all possible polar smectic structures, we have elaborated the discrete Landau theory of phase transitions especially designed for these types of liquid crystals [9]. It is in fact the main message of our publications [9–11], that one needs not invent a new phenomenological model. All of the essential ingredients of the polar liquid crystals can be included into the Landau free-energy expansion over the two-component order parameter, introduced by de Gennes [1]. Once developed, it becomes a paradigm in the physics of liquid crystals as a kind of method to penetrate into the unknown domains where microscopic theories are not yet known. However, one should be careful to avoid oversimplifications. For the case of polar and chiral smectics, this dangerous oversimplification is to assume, e.g., in advance (prior to the minimization) that one component of the de Gennes smectic order parameter is constant and does not have space variation. The essence of our approach in this paper is to study systematically all possible structures with a spatially varying two-component order parameter. It requires to minimize an appropriate energy of polar smectic liquid crystals and to apply a multiscaling analysis, i.e., to treat equilibrium structures on many length scales. As a result, we have found, besides the already known (predicted theoretically and identified experimentally) smectic structures, a number of other phases which are stable in a narrow range (that is why the phases can be termed as microphases) of model parameters and thermodynamic conditions. The sequence of microphases represents the so-called "harmless staircase" (structures with oscillating periods known in the magnetic systems with competing interactions). We anticipate that the range of stabilities for various microphases can be extended (and therefore the microphases can be detected

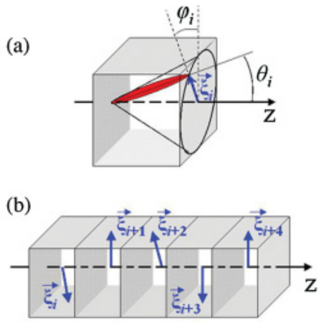

FIG. 1. (Color online) (a) Orientation of molecules in a layer of tilted smectic. **Z** is the layer normal. The vector $\boldsymbol{\xi}_i$ determines the molecular orientation (polar θ_i and azimuthal φ_i angles). (b) Different values and orientations of $\boldsymbol{\xi}_i$ in the layers form a manifold of polar structures.

experimentally) by applying external electric fields and/or investigating freestanding smectic films.

II. MODEL

In a discrete phenomenological Landau model of the phase transitions, the set of $\boldsymbol{\xi}_i$ is considered as a two-component order parameter characterized by the modulus and phase φ_i. The Landau expansion of the free energy $F_0 = F_1 + F_2$ consists of intralayer F_1 and interlayer F_2 interactions [9,12–14]. First we take a limited number of terms that are necessary to obtain all already experimentally observed structures. F_1 is the usual Landau expansion of the free energy:

$$F_1 = \sum_i \left[\frac{1}{2}\alpha(T - T^*)\xi_i^2 + \frac{1}{4}b_0\xi_i^4 \right], \tag{1}$$

where $a_0 = \alpha(T - T^*)$ and b_0 are Landau coefficients. Both α and b_0 are constant. In the absence of interlayer interactions, T^* is the temperature of the transition to the nonpolar (SmA) phase. Interlayer interaction is taken in the form

$$F_2 = \frac{1}{2}a_1 \sum_i \boldsymbol{\xi}_i \cdot \boldsymbol{\xi}_{i+1} + \frac{1}{8}a_2 \sum_i \boldsymbol{\xi}_i \cdot \boldsymbol{\xi}_{i+2} + b\sum_i [\boldsymbol{\xi}_i \times \boldsymbol{\xi}_{i+1}]^2. \tag{2}$$

The first term describes the interaction between nearest-neighbor (NN) layers. The essential feature of the energy F_2 is the positive sign of the coefficient a_2 in the interaction between next-nearest-neighbor (NNN) layers. Layer polarization favors an antiparallel orientation of $\boldsymbol{\xi}_i$ in NNN layers that is inconsistent with both synclinic ($\varphi_i = \varphi_{i+1}$) and anticlinic ($\varphi_i = \varphi_{i+1} + \pi$) structures. Just this frustration leads to formation of manifold of polar structures. If the interaction between the layers is restricted to only NNs, then there are no reasons for nontrivial spatial modulations. The third term in Eq. (2) is the free-energy barrier between the parallel and antiparallel orientation of $\boldsymbol{\xi}_i$ in polar phases. Its origin was discussed in a recent review [5]. Chirality is usually presented in the free energy by the Lifshitz term $F = f[\boldsymbol{\xi}_i \times \boldsymbol{\xi}_{i+1}]_z$. Free energy (1) and (2) was constructed from terms allowed by symmetry consideration for the two-component order parameter defined above. The Landau free-energy expansion is a very useful tool to determine structures and phase sequences. To find all the possible equilibrium structures and phase diagrams, one has to perform minimization of the Landau free energy over the set of two-component order parameters $\boldsymbol{\xi}_i$. Needless to say, the minimization in the general case is not feasible analytically. Even numerical minimization is not a trivial task. The method of numerical minimization of the free energy was described earlier [9,15]. The initial structure of the sample was taken as a random set of $\boldsymbol{\xi}_i$ in the layers. The structure with minimum energy was found by varying both the phase and the modulus of $\boldsymbol{\xi}_i$ in each layer of the sample using the quasi-Newton algorithm [9]. This procedure was repeated from 5×10^3 to 10^5 times, depending on the complexity of the structure. Each time a random starting structure was selected. This enabled to determine reliably the stable structures corresponding to the global energy minimum. The number of layers in the sample was several times larger than the periodicity of the phases. For such a thickness the boundaries do not affect the behavior inside the sample. Thus we were able to obtain in the calculations both commensurate and incommensurate ground-state structures. For commensurate structures simultaneous calculations were performed also in samples with periodic boundary conditions. Both approaches gave the same result. In the following, we provide the results for phases stable in the interval of parameters $\Delta(a_1/a_2) > 10^{-6}$ and $\Delta T > 0.03$ K. Calculation of phases with such a narrow stability range has been performed.

III. RESULTS AND DISCUSSION

At high temperatures, due to the biquadratic interaction term in (2), the barrier between synclinic and anticlinic orientation is small ($|\boldsymbol{\xi}_i| \ll 1$). Correspondingly, an equilibrium structure is formed due to competition between the two first terms in Eq. (2). Near the temperature T_0 of the transition to the SmA phase, a short pitch helical structure incommensurate with layer periodicity (SmC_α^* phase) exists at $|a_1/a_2| < 1$. At low temperatures the energy barrier prevents deviation $\boldsymbol{\xi}_i$ from synclinic or anticlinic molecular orientation by a large angle. As a result, the SmC_α^* phase is replaced by structures commensurate with layer periodicity. The structure of the unit cells depends crucially on the sign of ratio a_1/a_2. If one changes the sign of the ratio a_1/a_2 and simultaneously replaces synclinic configurations with anticlinic (and vice versa), the minima of the free energy F_0 remain the same. Thus, for each $|a_1/a_2|$, two structures of equal energy exist which correspond to different signs of a_1/a_2. The solid lines in Figs. 2(a) and 2(b) show the energy of the ground state for different values of the ratio $|a_1/a_2|$. Due to the symmetry of Eq. (2) with respect to sign of a_1/a_2, the energies are equal for the phases pointed in the upper part of Figs. 2(a) and 2(b) for $a_1/a_2 > 0$ and in the lower part of the figure for $a_1/a_2 < 0$ [e.g., SmC^* and SmC_A^*, SmC_{d3}^* and SmC_{d6}^*—Fig. 2(a)]. At $a_1/a_2 < 0$ the ferroelectric SmC^* and two antiferroelectric SmC_{d6}^* and SmC_{d4}^* phases are formed. At $a_1/a_2 > 0$, antiferroelectric SmC_A^*, ferrielectric SmC_{d3}^*, and antiferroelectric SmC_{d4}^* phases are equilibrium structures [16]. The structures of the different phases are shown in Fig. 3. The rectangles with dashed lines show the unit cells. For simplicity of representation, we show flat structures in this figure. Actually there is a deviation of $\boldsymbol{\xi}_i$ from the flat structures

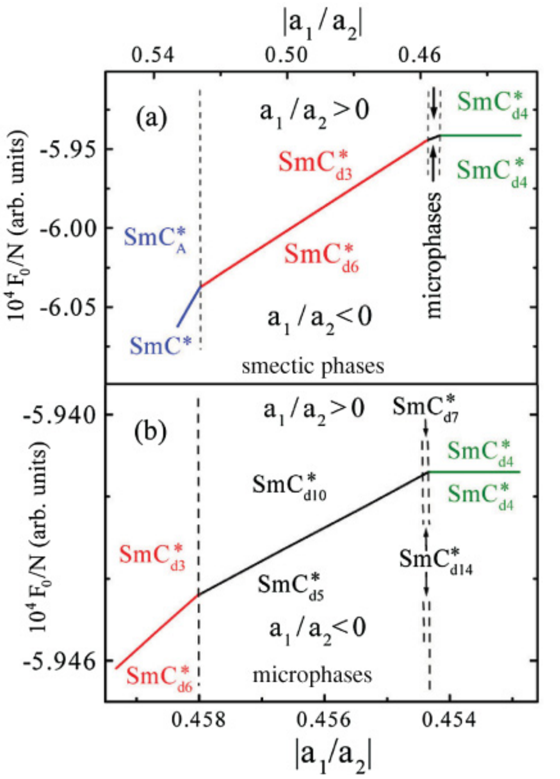

FIG. 2. (Color online) Energies of ground states (solid lines) of polar structures vs ratio a_1/a_2. F_0/N is the energy per layer. For positive and negative ratios a_1/a_2 different structures are formed. Between SmC^*_{d3} (SmC^*_{d6}) and SmC^*_{d4} phases the set of microphases is formed in a narrow range of ratio a_1/a_2. (b) is a magnification showing the interval with microphases. The set of model parameters is $\alpha = 0.01\ \mathrm{K}^{-1}$, $T^* - T = 4.5$ K, $b_0 = 1$, $a_2 = 0.015$, and $b = 0.04$.

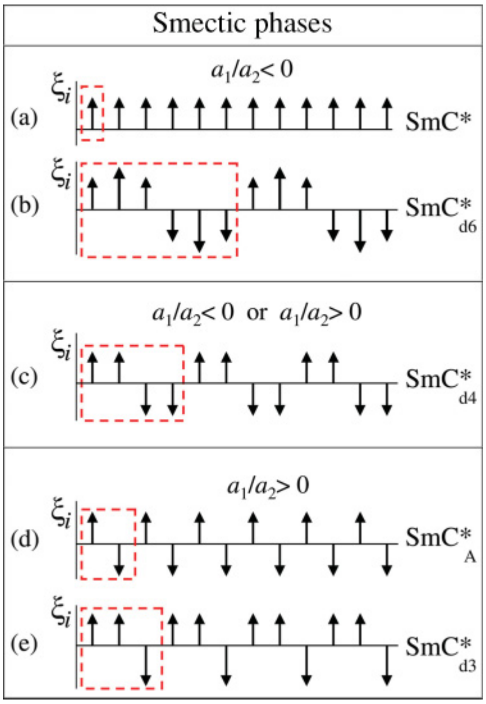

FIG. 3. (Color online) A schematic sketch of equilibrium polar phases formed at different signs of ratio a_1/a_2. Rectangles show the unit cells of the structures. In $\mathrm{Sm}C^*$, $\mathrm{Sm}C^*_{d4}$, and SmC^*_A phases the modulus of the order parameter $|\boldsymbol{\xi}_i|$ is equal along the structures. The $\mathrm{Sm}C^*_{d6}$ and $\mathrm{Sm}C^*_{d3}$ structures are formed by the change of both phase (φ_i) and modulus $|\boldsymbol{\xi}_i|$ of the order parameter. For simplicity of representation, planar "up-down" structures are drawn, and small distortion angles between nearly synclinic orientations are not shown.

which is related to the long helical pitch and distortion angles between the molecules inside the unit cells. The influence of chirality on structure and deviation from the flat structure will be discussed later in this section. The $\mathrm{Sm}C^*$ and SmC^*_A phases are the ground states in a wide range at a large ratio $|a_1/a_2|$. The $\mathrm{Sm}C^*_{d4}$ phase is stable for positive and negative a_1/a_2 up to $a_1/a_2 = 0$ as synclinic and anticlinic pairs are present in this phase in equal proportions. In other structures, one of the molecular orientations is dominant: synclinic (for $a_1/a_2 < 0$) or anticlinic (for $a_1/a_2 > 0$).

The structures of the $\mathrm{Sm}C^*$, $\mathrm{Sm}C^*_A$, $\mathrm{Sm}C^*_{d4}$ and $\mathrm{Sm}C^*_{d3}$, $\mathrm{Sm}C^*_{d6}$ phases are essentially different. The first three structures are formed by changing only the phase of the order parameter. In the $\mathrm{Sm}C^*_{d3}$ and $\mathrm{Sm}C^*_{d6}$ structures not only the phase but also the modulus of the order parameter $\boldsymbol{\xi}_i$ change along the structures [Figs. 3(b) and 3(e)]. The spatial modulation of $|\boldsymbol{\xi}_i|$ decreases the energy in these structures. So, the Landau theory of the phase transition with a two-component order parameter reproduces and rationalizes all experimentally observed structures [5,8,17–20], including the recently discovered $\mathrm{Sm}C^*_{d6}$ phase [Fig. 2(a)], and explains the mechanism of their formation. Between $\mathrm{Sm}C^*_{d3}$ ($\mathrm{Sm}C^*_{d6}$) and $\mathrm{Sm}C^*_{d4}$ phases a series of microphases are formed [Fig. 2(a)]. Investigations of their structures and phase sequence are important for a theoretical and experimental understanding of the underlying physics of the mechanisms responsible for polar phase formation and potential applications of these unusual liquid-crystalline phases.

Figure 2(b) shows the microphase region on an enlarged scale. Most of the phase diagram is occupied by the $\mathrm{Sm}C^*_{d5}$ ($\mathrm{Sm}C^*_{d10}$) phase. Then the $\mathrm{Sm}C^*_{d14}$ ($\mathrm{Sm}C^*_{d7}$) microphase follows. Structures and sequences of microphases are shown in Figs. 4 and 5. The width of the $\mathrm{Sm}C^*_{d9}$ ($\mathrm{Sm}C^*_{d18}$) microphase is an order of magnitude smaller than the width of the $\mathrm{Sm}C^*_{d14}$($\mathrm{Sm}C^*_{d7}$). Two microphases are formed for the same absolute value $|a_1/a_2|$. A distinct symmetry exists for these microphases. Their unit cells have periods differing in two times. The structures with a smaller period are ferrielectric, and structures with a double period are antiferroelectric (Fig. 4). In the ferrielectric microphases the periodicity of the structure with respect to the phase and modulus of the order parameter is the same. In the antiferroelectric microphases the periodicity in orientations of $\boldsymbol{\xi}_i$ is twice the periodicity of the modulus $|\boldsymbol{\xi}_i|$. Although the corresponding microphase stability regions are narrow, investigations of the structure and other properties of these phases do not only have a purely academic interest.

It is worth noting that the microphase sequence does not show the "devil's staircase" [1,4], which is very popular in elastic and spin-modulated commensurate systems. For the devil's staircase sequence, the resulting curve, describing the

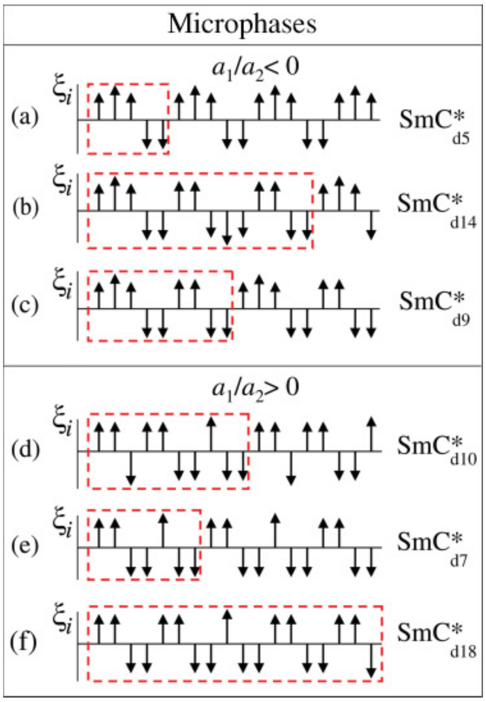

FIG. 4. (Color online) A schematic sketch of polar microphases formed at different signs of the ratio a_1/a_2. The sequence of microphases SmC^*_{d5}, SmC^*_{d14}, and SmC^*_{d9} forms between the SmC^*_{d6} and SmC^*_{d4} phases. Microphases SmC^*_{d10}, SmC^*_{d7}, and SmC^*_{d18} form between the SmC^*_{d3} and SmC^*_{d4} phases.

dependence of the modulation wave vector on the parameter controlling transitions (temperature in our case), is continuous but nonanalytical. On the contrary, the microphases are the special case of the so-called "harmless staircase" [21] with oscillating periods (Fig. 5). Phase transitions in "harmless" sequences are first-order phase transitions.

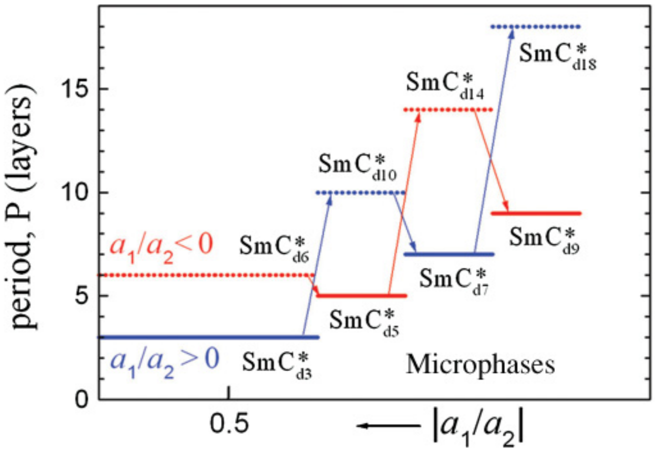

FIG. 5. (Color online) A schematic sketch of two staircases from polar microphases formed between SmC^*_{d3} (SmC^*_{d6}) and SmC^*_{d4} phases vs $|a_1/a_2|$. The value $|a_1/a_2| = 0.5$ corresponds to the SmC^*_{d3} (SmC^*_{d6}) phase. The arrow points to the direction of the increase of $|a_1/a_2|$. In every staircase the width of the microphases rapidly decreases with decreasing $|a_1/a_2|$ [see Fig. 2(b)]. For simplicity of representation of the staircases, the microphases are shown with equal width. The range of the existence of the microphases is indicated in Fig. 2 and in the text.

The formation of microphases follows a simple rule. If we go from a SmC^*_{d6} (SmC^*_{d3}) structure, every next microphase is obtained by inserting two additional synclinic layers between "three-up" or "three-down" clusters ($a_1/a_2 < 0$) and between two "two-up–one down" clusters ($a_1/a_2 > 0$). So, the quasicontinuous transition from SmC^*_{d6} (SmC^*_{d3}) to SmC^*_{d4} structure results by successively increasing the number of two-layer clusters in the structure. Of course, we should keep in mind that transitions between microphases are weak first-order transitions. In our staircases, ferrielectric and antiferroelectric microphases alternate (Figs. 4 and 5).

At first sight this staircase presents only a mathematical interest because of the narrow intervals of stability and no hope to observe the microphases in experiments. Fortunately it is not the case, and this is a motivation for studying modulated microphase structures. The width of the microphase stability regions can be increased in an external field. Especially, this refers to ferrielectric microphases with $a_1/a_2 < 0$ [Figs. 2(a) and 4] because in an electric field they become more favorable with respect to their neighboring antiferroelectric SmC^*_{d6} and SmC^*_{d4} phases. Another possible way to observe and identify the microphases is to study freestanding films. In the thin films with the thickness comparable to the periodicity of the microphases, the structure of the microphases can be dominant. Naturally one should expect that microphases dramatically affect the kinetic of the phase transition and the formation of perfect structures. In the x-ray experiments [8] in some region of the phase diagram between the SmC^*_{d6} and SmC^*_{d4} phases the authors were not able to determine periodicity. They have observed only multiple and noisy x-ray peaks [8]. We do believe that these x-ray scattering data are a manifestation of microphases with their structures not yet completely formed.

The above described Landau theory supplemented by some additional terms may well describe not only the possible structures of polar phases but also the phase diagrams, i.e., the phase transition sequences. It is sufficient to add a biquadratic NN interaction $b_1 \sum_i \boldsymbol{\xi}_i^2(\boldsymbol{\xi}_{i-1} \cdot \boldsymbol{\xi}_i + \boldsymbol{\xi}_i \cdot \boldsymbol{\xi}_{i+1})$ and long-range third-nearest-neighbor (TNN) interaction $a_3 \sum_i \boldsymbol{\xi}_i \cdot \boldsymbol{\xi}_{i+3}$ [11,14]. The flexoelectric origin of the long-range interactions was first explained by Čepič and Žekš [14]. For the formation of different microphases, it is essential that the sign of a_3 is negative [5]. One or a sequence of subphases can appear immediately below the SmA phase or between the ferroelectric SmC^* and antiferroelectic SmC^*_A phases. Both cases are described by the discrete Landau theory. Figure 6 shows the calculated temperature dependence of the modulus of the order parameter $|\boldsymbol{\xi}|$ when below the SmA phase different subphases appear. The experimentally observed unusual phase sequence SmA-SmC^*_α-SmC^*_{d6}-SmC^*_{d4}-SmC^* [8] is obtained in our calculations (Fig. 6) by choosing appropriate values of the model parameters. The recently discovered SmC^*_{d6} phase [8] forms a spatially modulated structure with two values of the modulus of the order parameter (Figs. 2 and 6). In microphases several values of $|\boldsymbol{\xi}|$ form the periodicity (e.g., three different values of $|\boldsymbol{\xi}|$ in the SmC^*_{d5} microphase—Figs. 4 and 6).

The question could arise why, in spite of the analogy of SmC^*_{d3} and SmC^*_{d6} phases (Fig. 2), the SmC^*_{d3} structure has been discovered long ago and is observed in numerous compounds [4], whereas the SmC^*_{d6} phase has been observed only recently. The reason may be due to the effect of the TNN

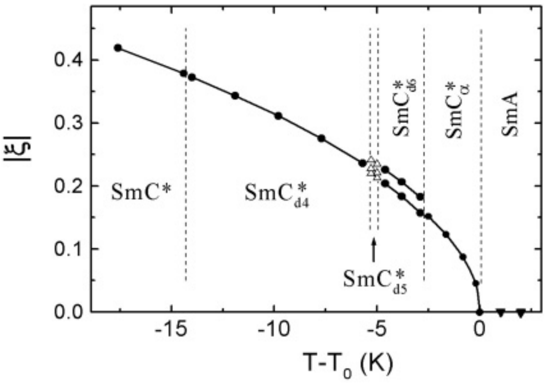

FIG. 6. Temperature dependence of the modulus of the order parameter $|\boldsymbol{\xi}|$ when polar subphases form below the SmA phase. The calculated sequence of phases SmA, SmC^*_α, SmC^*_{d6}, SmC^*_{d4}, and SmC^* corresponds to experimental observations [8]. The set of model parameter is as in Fig. 2 and $b_1 = -8 \times 10^{-4}$, $a_3 = -5 \times 10^{-5}$, and $a_1/a_2 = -0.463$. In the SmC^*_{d6} phase and in the microphases $|\boldsymbol{\xi}_i|$ has different values along the structures.

interlayer interaction. As pointed by Čepič and Žekš [14], the coefficient a_3 in this term is negative, that is, favoring parallel orientations of molecules in third nearest layers. This interaction decreases the range of the SmC^*_{d6} phase [11] and, reversely, increases the stability range of the SmC^*_{d3} phase. The SmC^*_{d3} phase can be more easiely observed. So, the results of our calculations correlate with the experimental findings and suggest that the TNN interaction in polar liquid crystals may be essential.

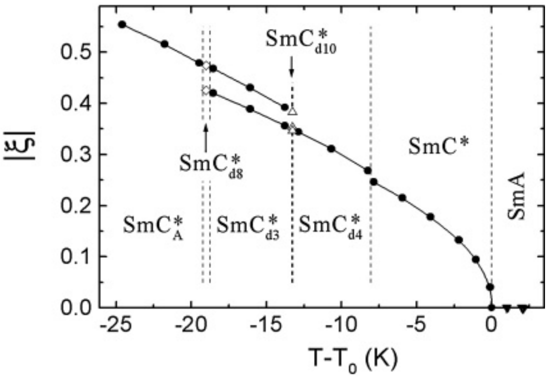

FIG. 7. Temperature dependence of the modulus of the order parameter $|\boldsymbol{\xi}|$ when polar subphases form between the SmC^* and SmC^*_A phases. In the SmC^*_{d3}, SmC^*_{d8}, and SmC^*_{d10} phases the modulus of the order parameter $|\boldsymbol{\xi}|$ varies from layer to layer. The SmC^*_{d10} microphase exists in a narrow temperature range of the order of 0.04 K. The set of model parameters is $\alpha = 0.01$, $b_0 = 1$, $a_1 = -0.018$, $a_2 = 0.018$, $a_3 = -8 \times 10^{-4}$, $b = 0.02$, $b_1 = 0.04$, and $f = 7.5 \times 10^{-4}$.

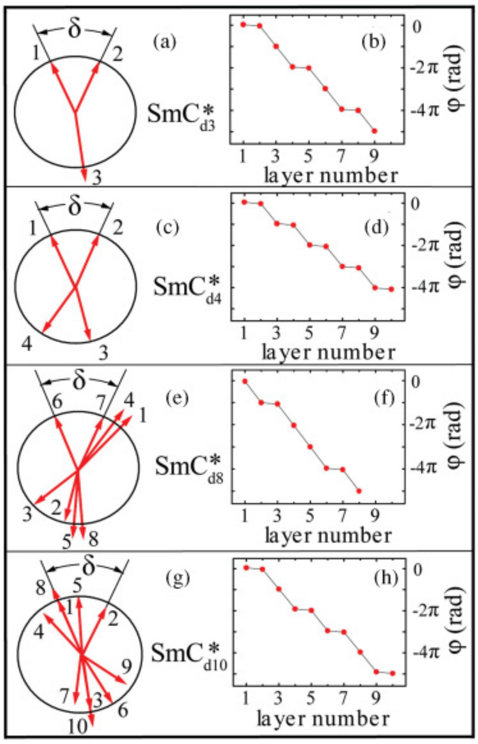

FIG. 8. (Color online) Schematic representation of the orientations of $\boldsymbol{\xi}$ in the unit cell of different phases (left-hand side) and the calculated values of the azimuthal angle (right-hand side). The distortion angle δ is related to chirality. Different lengths of the arrows in (a), (e), and (g) illustrate the variation of $|\boldsymbol{\xi}|$ from layer to layer. The helical pitch is ∼400 layers (SmC^*_{d3} phase), ∼300 layers (SmC^*_{d4} phase), ∼230 layers (SmC^*_{d8} microphase), and ∼500 layers (SmC^*_{d10} microphase). The set of model parameters is as in Fig. 7; $T - T_0 = -16.08$ K (SmC^*_{d3} phase), $T - T_0 = -10.68$ K (SmC^*_{d4} phase), $T - T_0 = -19$ K (SmC^*_{d8} microphase), and $T - T_0 = -13.28$ K (SmC^*_{d10} microphase).

At large $|b_1|$ and $|a_1|$ with b_1 positive and a_1 negative the SmC^* phase exists at high temperature and SmC^*_A at low temperature (Fig. 7). Frustration leads to the formation of intermediate structures between SmC^* and SmC^*_A phases. The relative temperature range of subphases depends on the value of the TNN interaction. The larger is $|a_3|$, the wider is the temperature range of the SmC^*_{d3} phase. TNN interaction not only changes the temperature range of the subphases, but also can lead to the formation of new structures. The SmC^*_{d8} microphase appears (Fig. 7) due to the long-range TNN interaction. Figure 8 shows the calculated orientations of $\boldsymbol{\xi}_i$ [Figs. 8(b), 8(d), 8(f), and 8(h)] and the schematic structure of the intermediate phases [Figs. 8(a), 8(c), 8(e), and 8(g)]. The different lengths of $\boldsymbol{\xi}_i$ in Figs. 8(a), 8(e), and 8(g) reflect different values of the modulus of the order parameter in the unit cells of the phases with periods of 3, 8, and 10 layers (Fig. 7). We remind that in the clock model [5] the modulus of the order parameter is constant in different layers. The distortion angle δ shown in Fig. 8 depends nearly linearly on chirality (Fig. 9).

Because many different theoretical models for the polar smectic structures have been proposed in the literature (see, e.g., a recent review in Ref. [5] and Refs. [9,12–14,22–27]), the ability to discriminate those experimentally is crucially important. However, the interpretation of the experimental observations for many exotic polar smectic phases with various molecular orientation is rather difficult. The fact is that the different azimuthal orientation does not produce Bragg reflections in conventional crystallography. The corresponding orientational ordering can be detected only using resonant

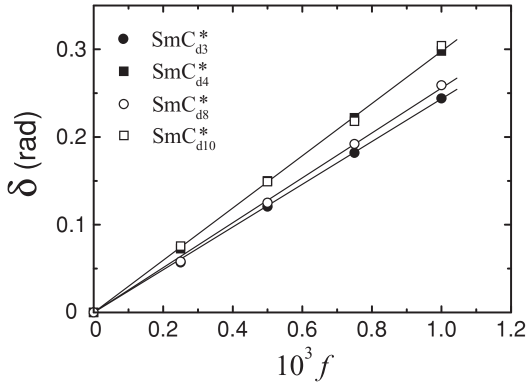

FIG. 9. Dependence of the distortion angle δ on chirality for different phases. The set of model parameters is as in Fig. 7; SmC^*_{d4} (closed squares, $T - T_0 = -10.68$ K), SmC^*_{d10} (open squares, $T - T_0 = -13.28$ K), SmC^*_{d3} (closed circles, $T - T_0 = -16.08$ K), and SmC^*_{d8} (open circles, $T - T_0 = -19$ K).

scattering techniques [16,18,28]. Unfortunately, from a strictly technical point of view, only a limited number of resonant elements can be used in resonant scattering, and these elements are not common in organic liquid-crystalline materials. Any opportunity to use nonresonant scattering methods is therefore merited to be studied. Spatial variation of the modulus of the order parameter [Figs. 3(b), 3(c), and 4] gives this opportunity. The modulation can be detected by nonresonant x-ray scattering [9,11,29]. A comparison of peak positions and intensities with calculations in the framework of the Landau theory allows us to describe completely the structure of different phases.

Spatially modulated systems are very common in nature (not only smectics but as well spin-density waves, charge-density waves, adsorbed atoms, and so on). Commensurate phases are structures where periodicity is a simple multiple of the basic microscopic scale (for smectics it is the interlayer spacing), and incommensurate phases where it is not the case. Polar smectics-*C* are characterized by both kinds (commensurate and incommensurate) of the modulated structures. The beauty and the power of the Landau theory is that the theory is a universal tool, independent of the physical nature of the order parameter. It depends only on the system dimension and number of components of the order parameter. Among many other systems where the ordering is described by a two-component order parameter. it is worth mentioning superconductors. The two-component order parameter for superconductors can be written in the following compact complex form, $\Psi = \Delta \exp(i\varphi)$, where Δ stands for the superconducting gap, and φ for the phase of the order parameter. This analogy is even more striking for layer (quasi-two-dimensional) materials (including high-temperature superconductors, which are stull puzzling to researchers). What do we learn from this analogy? First we learn that there are two characteristic lengths related to space variations of the two-component order parameter (as in superconductors where physics depends crucially on the relation between the so-called coherence length, characterizing variations of the module of the order parameter, and the penetration length, which describes phase variations). Of course one has to be careful not to extend this analogy too far. In superconductors the ordering produces spontaneous violation of gauge invariance, whereas in smectics we are dealing with rotational symmetry breaking. The severity of the results depending on this difference is not yet completely clear. This is one more motivation to study liquid crystals where the physical meaning of both components of the order parameter is very transparent: The module of the order parameter $|\boldsymbol{\xi}_i|$ is the projection of the nematic director (average rodlike molecule orientation), characterized by the polar angle θ_i, whereas the phase of the order parameter is the corresponding azimuthal angle φ_i. The analogy with superfluid helium is even more remarkable, because in this case the free energies are formally identical (no gauge field conjugated to the phase for noncharged systems, as helium-4). Furthermore, unlike superfluid or superconducting systems, for the smectic liquid crystals both components of the order parameter have a very clear physical meaning as well as the fields conjugated to these components (whereas there is no physical field conjugated to the superconducting gap, or superfluid density). It brings a possibility to use liquid-crystalline modeling of various nontrivial textures existing in superconductors or superfluids.

In conventional superconductors an arbitrarily small attraction between electrons (Fermi particles with half-integer spins) with identical but opposing spins and momenta can lead to the formation of pairs that have a bosonic nature. This is the remarkable Bardeen-Cooper-Schrieffer (BCS) phenomenon [30], yielding to the Bose condensed state where both components of the order parameter are constant (smectic-*C* phase in liquid-crystalline analogy). However, in the realm of superconductivity there is still an illusive state of matter that was proposed approximately 40 years ago by Fulde and Ferrell [31] and Larkin and Ovchinnikov [32] (the FFLO state). These scientists posed a question: What happens with the BCS state if the two fermionic spin states are not present in equal numbers in the system? In conventional superconductors such a spin imbalance can be created by applying an external magnetic field. At first glance it might become more difficult for fermions to form Bose pairs. However, it is not necessarily the case and the FFLO state proposes a clever compromise with certain modulation of the order parameter components. Although searches for such exotically paired superconductors have been carried out exhaustively in condensed-matter physics, in ultracold atomic gases, and even in the Universe, unambiguous experimental evidence remains elusive. However, polar smectic phases with modulated layer electronic density discovered experimentally [6] and described theoretically [9–11] can be considered as a realization of the FFLO state in polar smectics.

IV. CONCLUSION

Polar smectic liquid crystals are a rich state of matter, which is an active field of research, interesting in its own fundamental physics rights and in perspective applications which may still lie ahead. To date many experimental researches in this field have been done and a set of incommensurate and commensurate polar phases (SmC^*_α, SmC^*, SmC^*_A, SmC^*_{d3}, SmC^*_{d4}, and SmC^*_{d6}) was unambiguously identified. In principle (i.e., with an appropriate choice of model parameters) the discrete Landau theory described in this paper gives all possible equilibrium structures of polar smectics (in contrast to continuous models predicting naturally only two phases). The structures, together with their evolution on temperature, impressively agree with experimental observations. In this research, theory, experiment, and numerical simulations have to combine their efforts to get scientifically sounded results. That such a conceptually simple theory can predict such complex and subtle physical behaviors of polar smectics is remarkable. It demonstrates the power of the Landau model with two-component order parameters. We show that the discrete Landau theory predicts not only already known smectic structures, but as well a number of other phases (called as microphases) which are stable in a narrow range of model parameters and thermodynamic conditions. Polar and structural pecularities of these microphases have been described. The sequence of microphases represents a so-called "harmless staircase." We propose how to extend the range of stabilities for various microphases by applying external electric fields or by using freestanding polar smectic films. We also explain why the SmC_{d6}^* phase, which appears in the theory with a frustrating interaction, has been experimentally observed only recently. Besides, we have discussed striking similarities as well as distinctive differences of the phenomena in smectic liquid crystals and in other domains of condensed-matter physics. In this sense polar liquid crystals can be also useful model objects for studies of numerous systems with competing interactions.

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