Structure and dynamics of freely suspended film of the smectic-C^*_α phase in an external transverse electric field

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We present a theoretical analysis of static and dynamic properties of freely suspended films of the smectic-C^*_α phase in an external electric field, applied along the smectic layers. The analysis is performed within the ''clock'' model, where the interactions up to next-nearest neighbors are considered. The calculated critical electric field for the unwinding of the smectic-C^*_α phase is of the order of several 100 V/mm and strongly depends on the interlayer interactions. The calculated relaxation rates of the eigenfluctuations of a system of N layers are in the kilohertz range for phase fluctuations and several megahertz for amplitude fluctuations.

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I. INTRODUCTION

In recent years, there has been a considerable interest in understanding the structure of the novel phases of antiferroelectric liquid crystals. Different experimental techniques, such as the resonant x-ray scattering [1], dielectric spectroscopy [2,3], optical rotation [4], and ellipsometry on freely suspended films [5,6] have been used to characterize the structure of these phases, such as the smectic-C^*_α and the two ferrielectric phases. It is now quite clear that the smectic-C^*_α phase is a tilted smectic, incommensurate helical phase, with the helical period that extends over typically ten smectic layers [1,5]. This phase is therefore similar to the conventional ferroelectric smectic-C^* phase, the only difference being in the length of the helical period and the mechanism, responsible for the helical arrangement of the molecules.

There has also been a considerable debate on the structure of the ferrielectric smectic phases, which appear to be periodic phases, with a unit cell equal to three and four smectic layers, respectively [1]. The ferrielectric smectic-C_{FI1} phase, also known as the smectic-C^*_γ phase, is the phase with three smectic-layers unit cell. The arrangement of the molecules within this unit cell is asymmetrically deformed [4] and forms a polar unit cell. This unit cell repeats along the normal to the smectic layers, so that a helicoidal and polar ferrielectric phase is formed, with a helical period in the region of several microns. On the other hand, the second, the smectic-C_{FI2} phase, is a four smectic layers unit cell structure [1]. The molecular arrangement of the unit cell is strongly deformed and approaches nearly Ising-like planar structure [4,7]. The deformation is symmetric, so that a nonpolar structure is formed, showing small antiferroelectriclike response to an external electric field.

The structure of these phases, as well as the ferroelectric and antiferroelectric phase, is successfully described within the ''clock model,'' first developed by Čepič and Žekš [8]. This is a 3D-XY phenomenological model, based on the interlayer interactions, first introduced by Sun and Orihara [9]. Within this model, each smectic layer is treated as an independent system, coupled via interactions to the nearest and next-nearest neighbors. Whereas the first version of this model [8,10] could not explain the deformed ferrielectric phases, a refined version solved this problem and is capable of reproducing the deformation of the unit cell and the phase sequence as well [11].

Whereas the clock model explains these different structures of antiferroelectric liquid crystals, little is known about the interactions between the smectic layers, that presumably drive the phase sequence and determine the structures. These interactions are effectively included into the free-energy expansion [8] and are difficult to extract from the present experiments. Obviously, new experiments are needed that would give a deeper insight into the nature of interlayer interactions. In this situation, free-standing films of smectic-C_α and ferrielectric phases represent a unique system, where there might be a possibility of systematical tracing the interlayer interactions by systematically varying the number of smectic layers and observing the changes in the overall structure and dynamics of freely suspended films.

Following this idea, we analyze in this paper the equilibrium structure and the dynamics of a free standing film of the smectic-C^*_α phase, consisting of N smectic layers in an external transverse electric field. The equilibrium structures are

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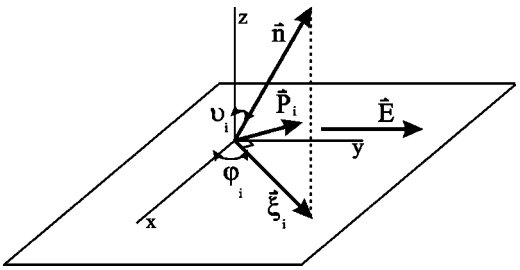

FIG. 1. The coordinate system with z axis perpendicular to the smectic layers. The director $\vec{n}_i$ determines the average tilt of the molecules in the ith layer; its projection onto the smectic layer is the order parameter $\vec{\xi}_i$. Spontaneous polarization is perpendicular to the tilt vector $\vec{\xi}_i$.

obtained after minimizing the total free energy of the system of N coupled smectic layers, using a method, first proposed by Rovšek *et al.* [12]. The fluctuation spectrum of a system of N coupled smectic layers is also analyzed by applying Landau-Khalatnikov dynamical analysis. We calculate the relaxational eigenvalues and eigenvectors of fluctuations and we follow the changes in the spectrum, induced by the application of an external electric field. We observe that there is a certain critical field, where the helical structure becomes unstable and a transition to an uniformly polarized ferroelectric phase occurs. The chirality of the system has a significant influence on this instability and also strongly hinders the complete unwinding. In some cases, depending on the relative strength of the first and second neighbor interactions, an intermediate, field-induced phase is stable in between the deformed smectic-C_α^* phase and the uniform, field-unwound phase. This phase is absent for large values of chiral interaction.

II. EQUILIBRIUM STRUCTURE OF A FREELY SUSPENDED FILM OF A SMECTIC-C_α^* PHASE IN AN EXTERNAL dc ELECTRIC FIELD

We consider a freely suspended film of the smectic-C_α^* phase, formed of N smectic layers. The molecular orientation within the ith layer is described by the two-dimensional order parameter, shown schematically in Fig. 1,

$$\xi_i = \vartheta_i(\cos\varphi_i, \sin\varphi_i). \tag{1}$$

Here, ϑ_i is the magnitude of the tilt angle and φ_i is the phase of the director in the ith layer.

We analyze the stability of the structure of the smectic-C_α^* phase by expanding the free energy of a system of N coupled smectic layers (2). It includes the nonchiral interaction between a given layer and its nearest and next-nearest neighbors, the chiral interaction with nearest neighbors and the term that describes the interaction between the electric polarization of each smectic layer and the external electric field, which is applied in the $y$direction.

The free energy of a system of N coupled smectic layers is

$$G = \sum_{i=1}^{N} \frac{a_0}{2}\vartheta_i^2 + \frac{b_0}{4}\vartheta_i^4 + \frac{a_1}{2}\ \vartheta_i\vartheta_{i+1}\cos(\varphi_i - \varphi_{i+1}) + \frac{a_2}{8}\ \vartheta_i\vartheta_{i+2}\cos(\varphi_i - \varphi_{i+2}) + \frac{f}{2}\ \vartheta_i\vartheta_{i+1}\sin(\varphi_i - \varphi_{i+1}) - CE\vartheta_i\cos\varphi_i . \tag{2}$$

The coefficients $a_0 = \alpha(T - T_0)$ and b_0 describe the intralayer interactions and to the largest extent determine the value of the tilt angle. The next two terms are the lowest order terms describing the interactions between the neighboring layers. The coefficient f is of chiral origin and describes the nearest neighbor chiral interactions. The last term describes the coupling of spontaneous polarization of each layer with the external electric field. The surface interactions of the outer layers are implicitly taken into account, if we define the order parameter $\xi_i = 0$ for $i < 1$ and $i > N$. Physically, this means that the first and the last smectic layer (i.e., the two outer layers), as well as their first interior neighbors, do interact only with the layers in the interior of the film, whereas there is no molecular interaction with empty space outside the film. This leads to equilibrium tilt angles, which are slightly different for the surface layers, in agreement with experiments [13].

The equilibrium structure of the smectic-C_α^* phase in an external electric field is calculated by minimizing the free energy of a system with respect to a set of $2N$ order parameter components. Following the procedure of Rovšek *et al.* [12], we expand the free energy (2) by writing each component of the order parameters as a sum of its equilibrium value ξ_i^0 and a small correction $\delta\xi_i$,

$$\vartheta_i = \vartheta_i^0 + \delta\vartheta_i, \quad \varphi_i = \varphi_i^0 + \delta\varphi_i . \tag{3}$$

The expansion is performed up to the second order in corrections. In the second step, we obtain stationary values of the free energy by the minimization with respect to small corrections of the tilt and phase in each layer,

$$\frac{\partial G}{\partial \vartheta_i} = 0, \quad \frac{\partial G}{\partial \varphi_i} = 0, \quad i = 1, \ldots, N. \tag{4}$$

We obtain a system of coupled linear equations for the set of corrections $\delta\vartheta_i$ and $\delta\varphi_i$. The two sets of equations are solved separately. First, we solve the system of nonhomogenous linear equations for the corrections of the tilt $\delta\vartheta_i$, keeping φ_i constant. This system is

$$A_\vartheta \delta\vartheta + B_\vartheta = 0. \tag{5}$$

Here $\delta\vartheta = (\delta\vartheta_1, \delta\vartheta_2, \ldots, \delta\vartheta_N)$ is a N-dimensional vector of corrections of the tilt. B_ϑ is a N-dimensional vector with components

$$B_\vartheta(i) = -a_0\vartheta_i^0 - b_0(\vartheta_i^0)^3 - \frac{a_1}{2}[\vartheta_{i+1}^0 \cos(\varphi_i^0 - \varphi_{i+1}^0) + \vartheta_{i-1}^0 \cos(\varphi_i^0 - \varphi_{i-1}^0)] - \frac{a_2}{8}[\vartheta_{i+2}^0 \cos(\varphi_i^0 - \varphi_{i+2}^0) + \vartheta_{i-2}^0 \cos(\varphi_i^0 - \varphi_{i-2}^0)] - \frac{f}{2}[\vartheta_{i+1}^0 \sin(\varphi_i^0 - \varphi_{i+1}^0) + \vartheta_{i-1}^0 \cos(\varphi_{i-1}^0 - \varphi_i^0)] + CE\cos\varphi_i^0 \quad (6)$$

and A_ϑ is a symmetric $N\times N$ five-diagonal matrix,

$$A_\vartheta(i,i) = a_0 + 3b_0(\vartheta_i^0)^2, \quad i=1,\ldots,N,$$

$$A_\vartheta(i,i+1) = \frac{a_1}{2}\cos(\varphi_i^0 - \varphi_{i+1}^0) + \frac{f}{2}\sin(\varphi_i^0 - \varphi_{i+1}^0), \quad i=1,\ldots,N-1,$$

$$A_\vartheta(i,i+2) = \frac{a_2}{8}\cos(\varphi_i^0 - \varphi_{i+2}^0), \quad i=1,\ldots,N-2. \quad (7)$$

We use an iterative numerical procedure, which starts with some preselected values of the tilt and phase angles. Usually, the initial approximation for the structure of the smectic-C_α^* phase at zero electric field was taken to have some constant value of the tilt and the symmetric orientation of the phase through the set of layers. Then, we repeatedly improve the initial approximation for the structure until the resulting set of tilt vectors satisfies a desired numerical precision.

The same procedure is then applied to the system of nonhomogenous linear equations for $\delta\varphi_i$, keeping the calculated equilibrium value of ϑ_i constant. This system of equations for the unknown phase angles is again written in the matrix form,

$$A_\varphi\delta\varphi + B_\varphi = 0. \quad (8)$$

Here, $\delta\varphi = (\delta\varphi_1, \delta\varphi_2, \ldots, \delta\varphi_N)$ is a N-dimensional vector of corrections of the phase and B_φ,

$$B_\varphi(i) = \frac{a_1}{2}[\vartheta_i^0\vartheta_{i+1}^0 \sin(\varphi_i^0 - \varphi_{i+1}^0) + \vartheta_i^0\vartheta_{i-1}^0 \sin(\varphi_i^0 - \varphi_{i-1}^0)] + \frac{a_2}{8}[\vartheta_i^0\vartheta_{i+2}^0 \sin(\varphi_i^0 - \varphi_{i+2}^0) + \vartheta_i^0\vartheta_{i-2}^0 \times \sin(\varphi_i^0 - \varphi_{i-2}^0)] - \frac{f}{2}[\vartheta_i^0\vartheta_{i+1}^0 \cos(\varphi_i^0 - \varphi_{i+1}^0) - \vartheta_i^0\vartheta_{i-1}^0 \cos(\varphi_{i-1}^0 - \varphi_i^0)] - CE\vartheta_i \sin\varphi_i^0. \quad (9)$$

The components of a matrix A_φ are

$$A_\varphi(i,i) = -\frac{a_1}{2}[\vartheta_i^0\vartheta_{i+1}^0 \cos(\varphi_i^0 - \varphi_{i+1}^0) + \vartheta_i^0\vartheta_{i-1}^0 \cos(\varphi_i^0 - \varphi_{i-1}^0)] - \frac{a_2}{8}[\vartheta_i^0\vartheta_{i+2}^0 \cos(\varphi_i^0 - \varphi_{i+2}^0) + \vartheta_i^0\vartheta_{i-2}^0 \cos(\varphi_i^0 - \varphi_{i-2}^0)] - \frac{f}{2}[\vartheta_i^0\vartheta_{i+1}^0 \sin(\varphi_i^0 - \varphi_{i+1}^0) - \vartheta_i^0\vartheta_{i-1}^0 \sin(\varphi_{i-1}^0 - \varphi_i^0)] + CE\vartheta_i \cos\varphi_i^0, \quad i=1,\ldots,N,$$

$$A_\varphi(i,i+1) = \frac{a_1}{2}\vartheta_i^0\vartheta_{i+1}^0 \cos(\varphi_i^0 - \varphi_{i+1}^0) + \frac{f}{2}\vartheta_i^0\vartheta_{i+1}^0 \times \sin(\varphi_i^0 - \varphi_{i+1}^0), \quad i=1,\ldots,N-1,$$

$$A_\varphi(i,i+2) = \frac{a_2}{8}\vartheta_i^0\vartheta_{i+2}^0 \cos(\varphi_i^0 - \varphi_{i+2}^0), \quad i=1,\ldots,N-2. \quad (10)$$

This two-stage iteration process is then repeated at some higher value of the applied electric field and the new equilibrium structure is calculated in the same way as described above.

As an example, we show in Fig. 2 the behavior of a system of five-layer film of a smectic-C_α^* phase ($N=5$) in an external electric field, applied perpendicularly to the layer normal. The structure was calculated for different values of the chiral parameter $f=0$, $f=0.01*a_1$, and $f=0.1*a_1$. The typical value observed in bulk polar systems is $f=0.01*a_1$. The values of the other material parameters are: $a_0/\alpha = -4$ K, $b_0/\alpha = 40$ K, $a_1/\alpha = -1.1$ K, $a_2/\alpha = 2.5$ K, $\alpha = 4\times10^3$ J/m^3 K, and $C = 1.5\times10^8$ V/m [14]. The coefficients a_0 and b_0 are chosen in such a way that they represent a smectic-C_α^* phase at a temperature of 4 K below the smectic-A phase. The ratio of a_1 and a_2 is chosen so that it represents a smectic-C_α^* phase with a period of approximately five layers. At zero field, the molecular arrangement is already asymetric, as the phase angles of the surface layers (see layers 1 and 5 in Fig. 2) are different from those in the interior. The tilt magnitudes are close to 12° and are also slightly different for the outer layers. This reflects the absence of intermolecular interactions between the surface layers and the empty space outside the film. We should stress that the helical molecular arrangement of the smectic-C_α^* phase is obtained already in the achiral case, when $f=0$. Of course, the sense of the helix is in this case degenerate, which means that right- and left-handed smectic-C_α^* phases are equally probable. By introducing a finite chiral f term, this degeneracy is removed, and one sense of the helical structure becomes energetically favorable.

As one can expect, by increasing the field strength, the molecules tend to align in the plane, perpendicular to the field, as the electric dipoles are preferentially aligned into the field direction. In a nonchiral system, $f=0$ [Fig. 2(a)], the short-helix smectic-C_α^* structure is unwound at some value of the critical field E_c and we have a uniformly aligned and

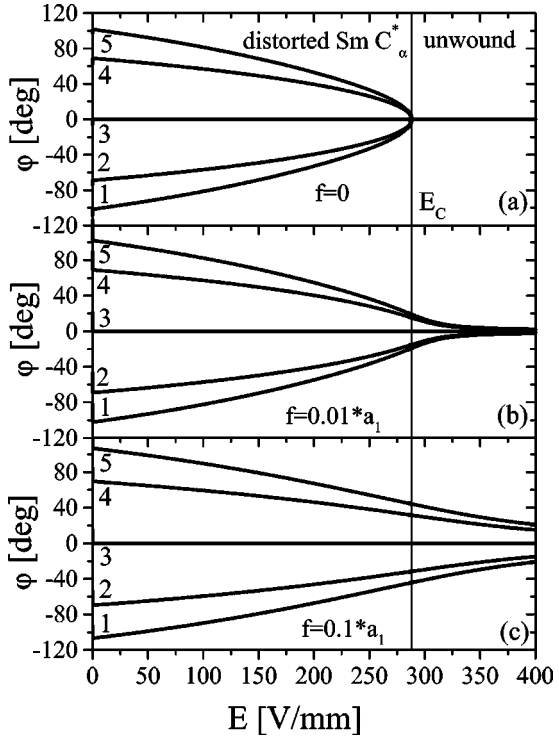

FIG. 2. The behavior of a five-layer film in an external applied electric field for different values of the chiral term f. (a) $f=0$: by increasing the field strength, the molecules tend to align in the plane perpendicular to the field, as the electric dipoles are preferentially aligned into the field direction. The result is the unwound structure above some value of the critical field E_c. (b) and (c) At somewhat higher values of f, the phase transition disappears and the structure remains twisted for any value of the field. The values of the material parameters are $a_0/\alpha=-4$ K, $b_0/\alpha=40$ K, $a_1/\alpha=-1.1$ K, $a_2/\alpha=2.5$ K, $\alpha=4\times10^3$J/m^3 K, $C=1.5\times10^8$ V/m, $f=0$, $f=0.01{*}a_1$, and $f=0.1{*}a_1$, respectively [14].

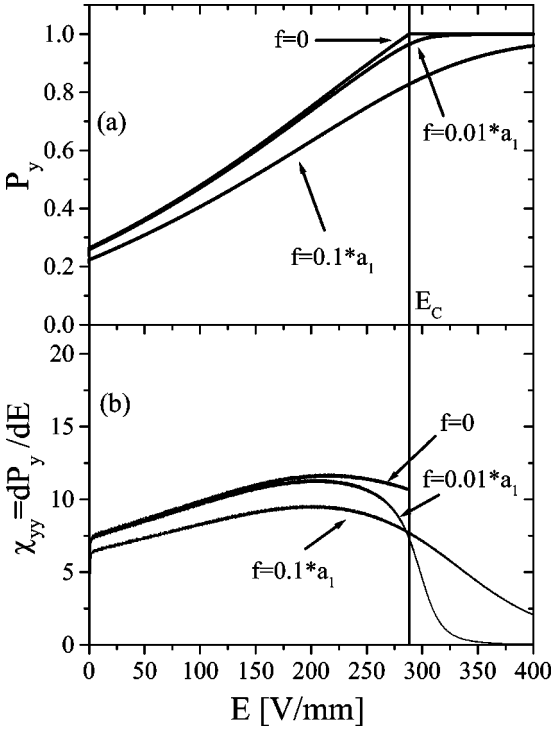

FIG. 3. (a) The field dependence of the P_y component of the static induced electric polarization for the five-layer film. P_y increases with electric field and reaches a saturation level at the critical field E_c only in the nonchiral system with $f=0$. For finite f, the transition is smeared out. (b) The static electric susceptibility. The values of the material parameters are $a_0/\alpha=-4$ K, $b_0/\alpha=40$ K, $a_1/\alpha=-1.1$ K, $a_2/\alpha=2.5$ K, $\alpha=4\times10^3$ J/m^3 K, $C=1.5\times10^8$ V/m, $f=0$, $f=0.01{*}a_1$, and $f=0.1{*}a_1$, respectively [14].

unwound smectic-$\tilde{C}^*_\alpha$ phase. The unwinding transition is similar to the very well-known unwinding of the helicoidal ferroelectric smectic-C^* phase in a transverse electric field [15]. The critical electric field E_c strongly depends on the value of the piezoelectric constant C, describing the bilinear coupling between the polarization and the tilt. This constant is of the order of 10^6 V/m in the ferroelectric liquid crystal DOBAMBC [15], which has a spontaneous polarization $P_s=3\times10^{-5}$ A s/m^2. As the spontaneous polarization of most materials that form smectic-C^*_α phase is of the order of 100 times larger, we choose somewhat larger value of $C\sim10^8$ V/m. This results in critical electric fields of the order of $E_c\sim300$ V/mm, which is definitely within experimental reach.

However, the situation is quite different for nonzero values of the chiral term f. In this case, shown in Figs. 2(b) and 2(c), the phase transition disappears and the short-helix smectic-C^*_α structure is never really unwound. The structure gets a tail of nonzero values of phase angles in each layer. As a result, we obtain a long-pitch twisted structure that is very persistent to external electric field and only gradually approaches unwound state in the limit of very large electric fields. This unusual persistence of the twisted structure can be understood using a simple argument, based on the competition between chiral, elastic, and dipole-field interactions. A simple calculation of the free-energy contributions of chiral, elastic, and dipole-field coupling terms shows that the chiral and elastic free energies are linear in the total twist angle but opposite in sign, whereas the dipole-field free energy is quadratic in a total twist angle. Because of competing free-energy contributions the minimum of the free energy is therefore always located at a finite value of the total twist and the structure is never unwound, contrary to bulk materials [16].

Figure 3(a) shows the field dependence of the static induced electric polarization for the nonchiral ($f=0$) and chiral ($f=0.01{*}a_1$ and $f=0.1{*}a_1$) five-layer film. As expected, the y component of the polarization increases with increasing field, as dipoles are more and more aligned into the field direction. However, above the critical field, the polarization is fully saturated only in the nonchiral system, $f=0$. The static electric susceptibility of the five-layer film is shown in Fig. 3(b). The susceptibility increases in the vicinity of the critical field, but there is no divergence, characteristic for bulk systems [16].

The field-induced transition is for this number of smectic layers and this range of free-energy parameters continuous

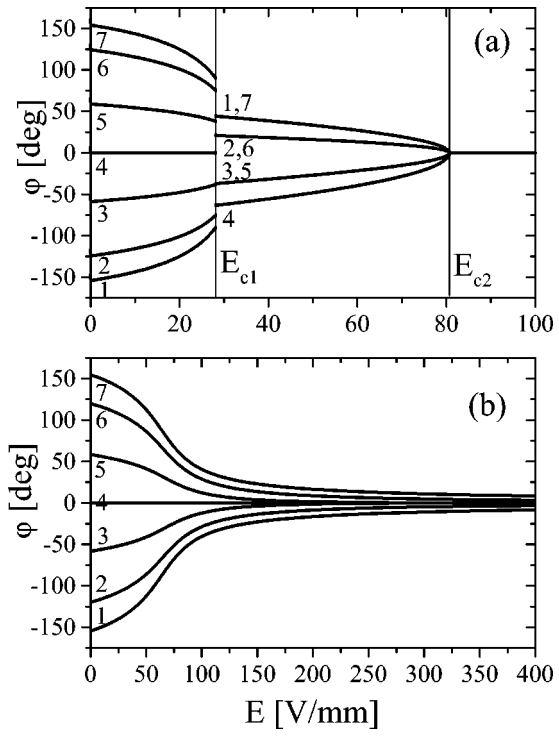

FIG. 4. (a) The behavior of a seven-layer film in an applied electric field. The structure is characterized by two critical fields E_{c1} and E_{c2}. At E_{c1} the smectic-C_α^* phase is deformed into an antihelical structure. This structure persists up to the field E_{c2}, where it transforms into the unwound structure. The values of the material parameters are $a_0/\alpha=-4$ K, $b_0/\alpha=100$ K, $a_1/\alpha=-0.5$ K, $a_2/\alpha=1.0$ K, $\alpha=4\times10^3$ J/m^3 K, $C=1.5\times10^8$ V/m, $f=0$ [14]. (b) The antihelical structure is absent for large values of the chiral parameter $f=0.1^*a_1$. The rest of the parameters are the same.

and the phase of each smectic layer continuously merges zero. By increasing chirality, the transition is only smeared out. However, we obtain in some cases an unexpected result by increasing the field strength: a discontinuous transition into a novel phase that is in between the distorted smectic-C_α^* phase and the unwound phase. This novel phase can be obtained either by choosing a different set of free-energy parameters at a given number of layers, or by taking a different number of layers at the same parameters. Figure 4(a) shows such an example of a structure of a $N=7$ layer film, which is obtained for the parameters: $a_0/\alpha=-4$ K, $b_0/\alpha=100$ K, $a_1/\alpha=-0.5$ K, $a_2/\alpha=1.0$ K, $\alpha=4\times10^3$ J/m^3 K, $C=1.5\times10^8$ V/m, and $f=0$ [14]. In this case, the electric-field dependence of the structure is characterized by two critical electric fields E_{c1} and E_{c2}. When the first critical field E_{c1} is exceeded, the distorted smectic-C_α^* phase is transformed into a new structure that is substantially different from the ordinary smectic-C_α^* phase. Whereas, the ordinary smectic-C_α^* phase is characterized by a uniform increase of the phase angle, as we move along its short-period helix, this new phase is quite different, as one can see from Fig. 4(a). First, by following Fig. 4(a), one can see that the phase angle decreases, as we are moving from the first to the fourth layer. This means that the molecules in neighboring layers are arranged in a clockwise manner, as we move along the layer normal. But, then, at the fifth layer, the sense of this short-period helix is inverted. The phase angle increases as we move to the next layers and the sense of the helix is now anticlockwise. This peculiar arrangement turns out to be very resistive against the applied electric field and persists up to 80 V/mm. In view of its peculiar structure, we call this field-induced phase an antihelical structure.

We should, however, mention that the stability of this structure strongly depends on the strength of the chiral term *f*. As an illustration, we show in Fig. 4(b) the behavior of the same film for an increased value of the chiral term $f=0.1^*a_1$. It is evident that the strange antihelical structure disappears for large values of *f*.

Let us now discuss the influence of the chirality of the system on the structure of the smectic-C_α^* phase in an electric field, as obtained within the clock model. We could see from the calculations that the chiral term significantly influences both the stability of different field-induced structures, as well as the unwinding process. Chirality is therefore of crucial importance and the question arises, what are realistic values of the chiral term *f*?

It is generally accepted that the chiral term is small compared to other terms in the free-energy expansion of bulk ferroelectric liquid crystals [15]. Its magnitude in ferroelectric liquid crystals is $\approx0.01^*a_1$ and determines the length of the helical period, which is typically around 1 μm. Such a small value of the chiral term was also successfully used in a clock model to fit the experimental results of the high resolution study of the birefringence and optical rotation in various antiferroelectric liquid crystals [14]. Interestingly, these materials exhibit relatively short helical periods, which leads to the conjecture that the magnitude of the chiral term may be large in these systems. However, it was shown a long time ago [17] that the chiral (Lifshitz) term is not the only term in the Landau free-energy expansion of chiral smectics that determines the length of the helical period. Other terms of achiral origin are also important and strongly influence the length of the helical modulation. For example, the biquadratic coupling between the tilt and polarization, which is of achiral origin, is an essential term in the generalized Landau model [15,17] that can explain strong temperature dependence of the helical period in typical ferroelectric materials like DOBAMBC and CE-8, as well as reentrant phenomena in these materials. This achiral interaction is also intrinsically present in the clock model and leads to a strong helical winding of the smectic-C_α^* phase even in the absence of chirality. In this achiral case, left- and right-handed smectic-C_α^* phases are equally probable. By introducing chiral interaction, the twist degeneration is removed and only a given sense of the helical structure is energetically preferred.

To summarize this discussion on the role and realistic values of the chiral term in the free-energy expansion of antiferroelectric liquid crystal, we can foresee two different limiting situations: (i) the chiral term *f* is for some intrinsic reason large and has a dominating role for the magnitude of helical modulation. This situation is quite realistic, as can be evidenced from the miscibility studies of the chiral-racemic smectic-C_α^* phase [18]. In this case, there is no sharp un-

winding transition in free standing films of smectic-C_α^* phase in a transverse dc electric field. The phase can never be truly unwound and the strange antihelical phase is absent. (ii) The chiral term f is small, similar to ordinary ferroelectric materials. In this case, there is a sharp unwinding transition and the antihelical phase is present. The system is nearly achiral and the free energies of the right- and left-handed smectic-C_α^* phases are nearly degenerate. The energy splitting is only due to a small chiral contribution that prefers a given sense of the helical period and removes the degeneracy. In this nearly achiral case, it is likely that domains of left- and right-handed smectic-C_α^* phase could exist in a given sample. Due to negligible optical rotation, they cannot be discriminated optically but may be distinguished due to disclination walls between regions of opposite twist.

III. DYNAMICAL PROPERTIES OF A FREELY SUSPENDED FILM OF A SMECTIC-C_α^* PHASE IN AN EXTERNAL dc ELECTRIC FIELD

For the analysis of the dynamical properties of the smectic-C_α^* phase, we use the well-known Landau-Khalatnik formalism, which describes the regression of a given fluctuation of the order parameter ξ towards equilibrium

$$-\gamma \frac{d\xi}{dt} = \frac{\partial G}{\partial \xi}. \tag{11}$$

Here, γ is the rotational viscosity coefficient and $\partial G/\partial \xi$ is a thermodynamic restoring force that drives the system back to equilibrium. Here we consider only the fluctuations with the wave vector along the normal layer, whereas there is no component of the fluctuations along the smectic layers. Similar to Eq. (3), we express each component of the order parameter in the ith layer as a sum of its equilibrium value and a small excitation. The solution of Eq. (10) is of the form

$$\delta\xi_i = \xi_i^0 \exp[-t/\tau_i] \tag{12}$$

and the system of Landau-Khalatnikov differential equations is then transformed into a set of coupled nonlinear equations.

For our system of N coupled smectic layers, the linearized set of equations can be represented in a matrix form and represents an eigenvalue problem for the fluctuations of a N-layer film,

$$\left| \frac{\partial G}{\partial \delta\Psi_i} - \frac{\gamma}{\tau_i} I \right| = 0. \tag{13}$$

The magnitudes of each component of a given collective fluctuation are now arranged as a $2N$-dimensional vector $\vec{\delta}\Psi$. The first N components represent the fluctuations of the magnitude (i.e., amplitudons) and the rest of N components represent the fluctuations of the phase of the tilt (i.e., phasons),

$$\delta\Psi_i = (\delta\vartheta_i, \delta\varphi_i).$$

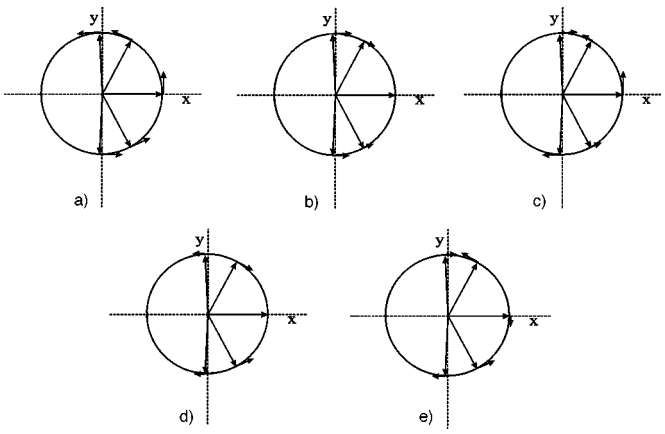

FIG. 5. The eigenvectors of phase modes in a five-layer film at zero electric field. The small arrows indicate the direction of the fluctuation of molecules in each of five layers.

The partial derivatives $\partial G/\partial \delta\Psi_i$ are thus conveniently arranged in a $2N\times 2N$-dimensional matrix following the same procedure as in Eqs. (3), (5), and (8),

$$\frac{\partial G}{\partial \delta\vec{\Psi}} = \begin{pmatrix} A_\vartheta & 0 \\ 0 & A_\varphi \end{pmatrix}. \tag{14}$$

Here, A_ϑ and A_φ are $N\times N$ matrixes defined before in Eqs. (7) and (10). The off-diagonal terms in the matrix $\partial G/\partial \delta\vec{\Psi}$ can, however, in most cases be neglected.

For a N-layer film we have, therefore, $2N$ degrees of freedom and we should thus find $2N$ eigenvalues and $2N$ corresponding eigenvectors. Each eigenvalue represents a distinct relaxation rate of a distinct fluctuation of a coupled system of N smectic layers. The corresponding fluctuations of the magnitude and the phase of the tilt in the ith layer can be determined from the components of the calculated eigenvector.

Figures 5 and 6 show an example of the calculated relaxation rates for a five-layer film of the smectic-C_α^* phase at zero electric field and $f=0$. As expected, we obtain a set of ten fluctuation modes, which in general represent coupled

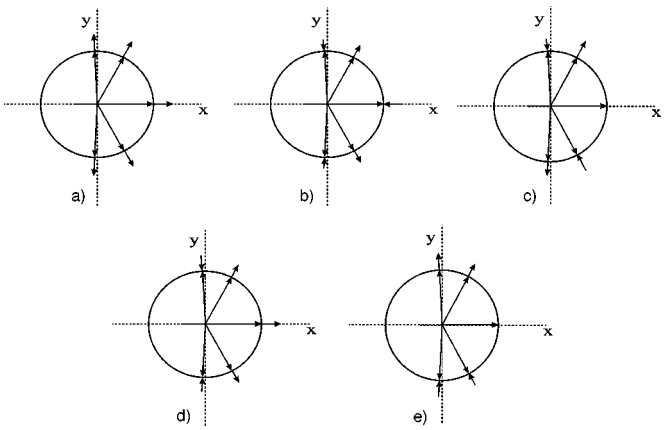

FIG. 6. The eigenvectors of tilt modes in a five-layer film at zero electric field. The small arrows indicate the direction of the fluctuation of molecules in each of five layers.

tilt-phase modes, where the fluctuations of the tilt magnitude and phase are mixed. However, in most cases (such as sufficiently low temperature), the coupling between the magnitude and the phase can be considered small and we obtain two independent sets of modes. Five of them represent pure phase-magnitude-fluctuation modes, shown in Fig. 5, and the other five represent pure tilt-fluctuation modes, shown in Fig. 6. The relaxation rates of the tilt modes are typically three orders of magnitude faster than the corresponding phase modes. We therefore expect that similar to the other polar smectics, the phase modes will give dominant contribution to the linear response and quasielastic light scattering.

It is interesting to look at the symmetry of these modes, presented in Figs. 5 and 6. In zero electric field, the mode with the lowest frequency is of particular interest. It is shown in Fig. 5(a) and one can see that it represents pure phase fluctuation. It is recognized as the Goldstone mode of the system, which represents the rotation of the sample as a whole and has therefore zero relaxation rate or infinite lifetime. The mode that has a slightly larger relaxation rate is shown in Fig. 5(b). It is similar to the Goldstone mode, with a difference that the molecules rotate in pairs in the opposite directions. The third mode that has slightly larger relaxation rate is shown in Fig. 5(c). It represents a mixed situation, where the most significant is the movement of the molecules within two pairs of the outer-layer molecules. In one pair, molecules move out of phase compared to the movement in the other pair. The rest of the two modes have nearly the same relaxation rates. As shown in Figs. 5(d) and 5(e), these modes represent an in-phase movement of the molecules in the outer layers.

The modes representing the fluctuations of the magnitude of the tilt are shown in Figs. 6(a) to 6(e). The relaxation rates of these modes are much higher, which is a general characteristic of the amplitude modes.

As one can see from Fig. 7, the fluctuation spectrum is considerably changed by the application of external electric field. As the field breaks the continuous rotational symmetry of a free space, the system of N smectic layers can no longer freely rotate around the normal to the smectic layers. As a result, we expect that the Goldstone, zero frequency mode, would no longer exist. This is indeed reflected in the spectrum of fluctuations for finite fields, which clearly shows that even lowest-frequency mode gains a finite relaxation rate in a field and a finite frequency gap appears in the spectrum. The frequency gap is of the order of several kilohertz close to the critical field. The modes therefore become ''massive'' in an external applied electric field.

Particular attention has to be paid also to the mode representing the critical fluctuation that condenses and is responsible for the phase transition into the unwound smectic-C^*_α phase. This is the second phase mode in Fig. 7 and is represented as the second mode in Fig. 5. One can see that it indeed represents a coherent molecular movement that tries to constrain the molecules in the x direction and the dipoles in the y direction. Its relaxation rate indeed goes to zero at the critical field, as expected from simple symmetry arguments.

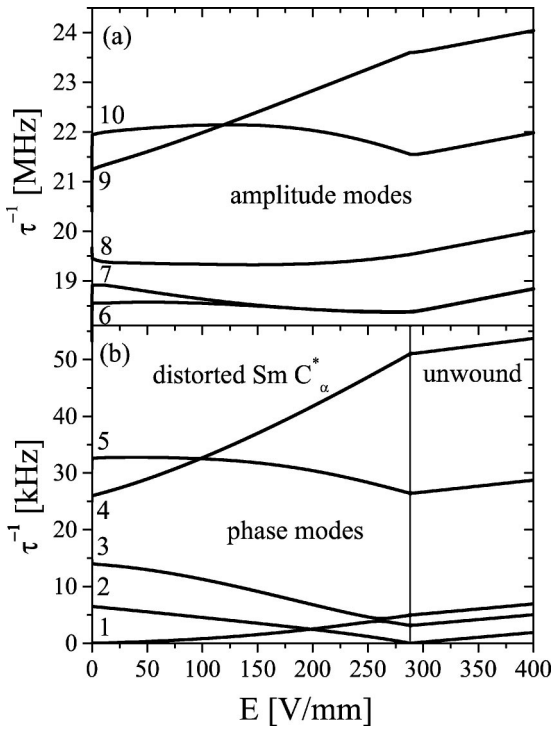

FIG. 7. The fluctuation spectrum in the external electric field for a five-layer film: (a) five phase fluctuation mode frequencies; (b) five amplitude fluctuation mode frequencies. The values of the material parameters are $a_0/\alpha=-4$ K, $b_0/\alpha=40$ K, $a_1/\alpha=-1.1$ K, $a_2/\alpha=2.5$ K, $\alpha=4\times10^3$ J/m^3 K, $C=1.5\times10^8$ V/m, $f=0$ [14].

After the critical field has been reached, the relaxation rates of all modes grow linearly with the magnitude of the applied field. This is consistent with perfect alignment of electric dipoles of molecules of the liquid crystal into the direction of the applied field.

By introducing a chiral term in a system, the fluctuation spectrum is only marginally influenced by the finiteness of f. As this term induces smearing out of the critical electric field and the smectic-C^*_α phase is never really unwound, the relaxation rate of the previously defined critical mode retains a finite value of the order of several kilohertz. The chiral term therefore induces a frequency gap at the value, where the critical electric field is observed for an achiral system. The rest of the modes are not influenced by increased chirality of the system.

IV. CONCLUSIONS

In conclusion, we have presented theoretical analysis of the static and dynamic properties of freely suspended film of the smectic-C^*_α phase in an external static electric field, applied in the plane of the smectic layers. Using realistic values of the free-energy parameters, we have shown that the critical electric field for the unwinding of the nonchiral smectic-C^*_α phase in freely suspended films is of the order of 300 V/mm, which is definitely feasible. We have also shown that by increasing the strength of the chiral term, the unwinding transition is smeared out and the smectic-C^*_α phase in free

standing film is never unwound. The second important result is the range of the relaxation rates of phase fluctuations. For a five-layers film, the relaxation rates of the phase modes are of the order of several kilohertz and are therefore easily observable in linear response and quasielastic light scattering experiments. The third important result is rather strong influence of the chirality on the unwinding of the smectic-C_α^* phase in external electric field. For strong chirality, the unwinding transition is smeared out, the phase is never really unwound and the antihelical phase is absent. These results, therefore, open new possibilities in the study of interlayer interactions in the smectic-C_α^* phase of antiferroelectric liquid crystals. The analysis of the electro-optic linear response and quasielastic light scattering cross sections will be presented in another publication and we expect it would stimulate new experiments on freely suspended films.

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