Equilibrium structures and pretransitional fluctuations in a very thin hybrid nematic film

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The stability of different structures of a nematic liquid crystal in a planar hybrid film is examined within the framework of a Gaussian description of order fluctuations. In a very thin film the director field is not bent smoothly but exhibits a steplike change if the anchorings at the confining substrates are strong ($G \gtrsim 10^{-3}$ J/m^2) and comparable in magnitude. A (dis)continuous structural transition to the bent-director state which occurs with increasing film thickness or decreasing temperature is governed by the lowest bending director fluctuation mode. Its relaxation rate exhibits a critical slowdown when the film thickness approaches the ''supercooling'' limit or transition point, respectively. The (dis)continuity of the structural transition depends on the temperature and film thickness. The upper limit for the corresponding tricritical point is determined. The lowest order parameter mode, which corresponds to fluctuations of the position of the central exchange region, is characterized by a nearly critical behavior of the relaxation rate. The spectra of the two noncritical biaxial fluctuation modes are degenerate, whereas the fluctuation profiles are just mirror images with respect to the middle plane of the film. [S1063-651X(99)05508-7]

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I. INTRODUCTION

Recently, the equilibrium ordering as well as dynamic properties of confined liquid crystals have attracted a lot of attention of experimentalists and theorists. Studies devoted to the determination of the equilibrium order in different confining geometries with various constraining properties [1] have lately been followed by investigations of the pretransitional dynamics. The understanding of collective order fluctuations gives a better insight into equilibrium ordering in the vicinity of phase and structural transitions as well as in the mechanism of the transition itself [2–9].

Possible technological applications have stimulated an increase of interest in hybrid nematic geometries [10]. Using a quasielastic light scattering method Wittebrood *et al.* (see Ref. [11] and the references therein) experimentally studied thickness dependence of the nematic-isotropic phase transition temperature and stability of ordered structures in a hybrid nematic film obtained after a spread of a liquid crystal droplet on a solid substrate. In their experimental setup with unequal anchoring strengths of the confining substrates (solid substrate and a free liquid crystal surface) they were able to determine the critical cell thickness for the hybridly aligned order which was in good agreement with the theoretical expression obtained long ago by Barbero and Barberi [12]. In their study an approximate director picture omitting positional dependence of the scalar order parameter and biaxiality was used. In the framework of Frank elastic theory an extensive study of pretransitional director dynamics in a hybrid cell was done by Stallinga *et al.* [5]. Using the director description of the nematic liquid-crystalline ordering they calculated relaxation times for tilt and twist fluctuations in hybridly aligned structure and director fluctuations in uniform director field structure. However, in their study they neglected spatial dependence of the uniaxial and biaxial degrees of nematic order, which are quite important in the case of strong anchoring and thin cells. A couple of years ago, Palffy-Muhoray *et al.* [13] showed that in highly constrained hybrid cells the nematic order can be either biaxial with the steplike profile of the director's tilt angle or the director field can be bent continuously. They predicted a structural transition between the two possible ordered configurations but did not probe the stability of both configurations. However, a more detailed description of the nematic order in planar hybrid geometry in relation to film thickness and anchoring strength has been provided by Galabova *et al.* [14]. Another aspect of a nematic liquid crystal in a planar hybrid geometry are stripe domains studied by Pergamenshchik [15]. In his study, using Frank elastic theory with surface terms, it was shown that equilibrium modulated structures can appear. However, in that study only spatial dependence of the nematic director was taken into account whereas other degrees of freedom of the nematic order have been neglected. In a cylindrical geometry Ziherl and Žumer [6] studied director fluctuations in the vicinity of a disclination line of strength 1 whose structure is similar to structures in hybrid cells. They extended the approach based on Frank elastic theory by introducing spatially dependent rotational viscosity and elastic constants.

This brief review shows that there is a lack of information on the dynamics related to the structural transition between different nematic configurations in highly constrained systems when nondirector degrees of freedom are crucial. This motivated us to start our analysis. In order to provide a simple but detailed description of a highly frustrated system we have examined a thin planar film with hybrid surface conditions. In contrast to previous studies [5,6,12] we have focused our attention on highly constrained films where biaxiality and non-homogeneous degree of nematic order play an important role. Although the origins of a highly frustrated system can be different, i.e., specific confining substrates in planar geometry or geometry induced hybrid properties (e.g., in cylindrical geometry), its effects on the liquid-crystalline order and pretransitional dynamics are similar [16–18]. Therefore one can study the basic effects of high frustration within the analysis of a planar system.

In the following section the model and theoretical ap-

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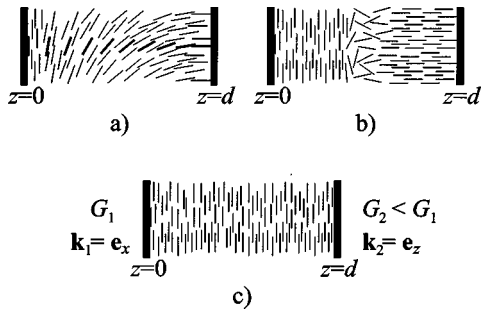

FIG. 1. Schematic representation of three possible ordered configurations in a hybrid film: (a) the bent-director structure, (b) biaxial structure with director exchange, and (c) uniform director structure.

proach are described briefly, whereas for the detailed description our previous papers should be referenced [7,8]. In Sec. III different equilibrium structures are discussed and the structural transition thicknesses are determined. Section IV deals with the pretransitional dynamics of the biaxial structure in the vicinity of the structural transition to the distorted configuration. Conclusions are given in Sec. V.

II. THEORETICAL DESCRIPTION OF THE MODEL

Our model system is a very thin hybrid film consisting of a nematic liquid crystal confined by two parallel substrates inducing uniaxial nematic order in mutually perpendicular directions. In order to simplify the description it is assumed that there is no surface induced smectic order although at least partial formation of smectic layers is often observed [19]. Suppose that the first substrate ($z=0$) induces uniaxial nematic order in a particular direction in the plane of the confining substrate (say parallel to the x axis); the other substrate (in the plane $z=d$) is then characterized by a homeotropic anchoring. The geometry of the model hybrid film is shown schematically in Fig. 1. Usually, the elastic distortions in such films are studied within the Frank elastic theory [20], where the nematic order is assumed to be uniaxial with the director field continuously bent from one substrate to the other; the scalar order parameter and the elastic constants are assumed to be temperature dependent only. However, long ago Barbero and Barberi [12] showed that in a hybrid film with different surface anchoring strengths the bent-director configuration can only exist if the film is thicker than the critical thickness, $d_c \equiv K(1/W_2 - 1/W_1)$, where K is the elastic constant in the one-elastic-constant approximation ($K_{ii} = K$), and $W_2 < W_1$ are the out-of-plane strengths of the surface interaction at the two confining substrates, respectively. In thinner films the director field is uniform with the nematic director in the direction of the easy axis of the substrate with stronger anchoring. For a typical liquid-crystalline material (such as 8CB; $K \approx 4.4\times10^{-12}$ N) in a contact with an in-plane aligning substrate yet homeotropically ordered at free surfaces ($W_1 \gg W_2 \approx 1.1\times10^{-5}$ J/m^2) the critical film thickness is found to be approximately 0.4 μm [11]. However, in the case of two confining substrates (without free surface) with very different surface anchorings (such as substrates modified with different aliphatic acids with $W_1 \approx 10^{-3}$ J/m^2 and $W_2 \approx 10^{-4}$ J/m^2 [21]) the critical value would be as small as $d_c \approx 40$ nm. As implied by the above expression for the critical film thickness this value should be even smaller if the anchoring strengths of the confining substrates would be comparable, therefore, in such hybrid films the order should always be distorted. However, in the case of hybrid yet equally strong anchoring conditions the director field is uniform below a finite critical film thickness, whereas the boundary conditions are fulfilled with the eigenvalue or director exchange [see Fig. 1(b)] [13,22]. Here the term ''uniform director field'' refers to the corresponding uniform orthonormal triad, whereas the director's tilt angle exhibits a steplike change. The other interesting consequence of equivalent confining substrates is a geometry induced biaxial ordering of a uniaxial nematic liquid crystal. The effect is interesting because in thermotropic nematic liquid crystals biaxiality cannot be observed very often.

In the following, the described properties will be studied within the model system which consists of a nematic liquid crystal sandwiched between two parallel substrates inducing uniaxial nematic order in mutually perpendicular directions. The nematic order and pretransitional dynamics in a system will be described in the framework of the phenomenological Landau–de Gennes theory of phase transitions [23]. Using this approach, in the vicinity of phase transition the free energy density can be expanded in terms of scalar invariants of the order parameter Q, which is a symmetric, traceless, second-rank tensor:

$$f = \frac{1}{2}A(T-T^*)\,\mathrm{tr}\,\mathsf{Q}^2 - \frac{1}{3}B\,\mathrm{tr}\,\mathsf{Q}^3 + \frac{1}{4}C(\,\mathrm{tr}\,\mathsf{Q}^2)^2 + \frac{1}{2}L\nabla\mathsf{Q}\vdots\nabla\mathsf{Q}, \tag{1}$$

where A, T^*, B, and C are temperature-independent material constants, T is the temperature and L is the elastic constant in the one-elastic-constant approximation. Since the one-elastic-constant approximation is used the equilibrium spontaneous periodic modulation is not possible [15]. The surface contribution to the free energy is modeled by [24]

$$\mathcal{F}_{S_i} = \frac{1}{2}G_i\,\mathrm{tr}\,(\mathsf{Q}-\mathsf{Q}_{S_i})^2\mathcal{A}, \tag{2}$$

where G_i is the strength of the interaction, Q_{S_i} is the preferred value of the tensor order parameter at the substrate, $\mathcal{A}$ is the substrate area, and the indices $i=1,2$ correspond to the substrates at $z=0$ and $z=d$, respectively. In the case of uniaxial nematic order the elastic constants K and L and anchoring strengths W and G introduced in Frank and Landau–de Gennes formalism, respectively, are simply related; $K = 9LS^2/2$ and $W = 3GS^2$, where S is a scalar order parameter.

As already discussed in detail in our previous papers [7,8] the mean-field ordering of the liquid crystal is determined by the minimum of the total free energy, whereas its dissipative dynamics can be described by an effective relaxation equation, i.e., a time-dependent Ginzburg-Landau equation,

$$-\Gamma\frac{\partial\mathsf{Q}}{\partial t} = \frac{\delta f}{\delta\mathsf{Q}}, \tag{3}$$

where Γ is the effective rotational viscosity and $\delta/\delta\mathsf{Q}$ refers to the functional derivative with respect to the Q [25,26]. In general, the effective rotational viscosity is a tensor and couples different director distortions, however, to simplify calculations it is usually assumed to be a scalar. Furthermore, in order to study the Gaussian excitations around the mean-field equilibrium the tensor order parameter $\mathsf{Q}(\mathbf{r},t)=\mathsf{A}(\mathbf{r})+\mathsf{B}(\mathbf{r},t)$ is split into (A) the mean-field equilibrium part which corresponds to the minimum of the total free energy and (B) a small fluctuating part which is governed by a linearized form of the equation of motion [Eq. (3)].

The two tensorial equations, one for the mean-field part of the tensor order parameter $[\mathsf{A}(\mathbf{r})]$, and the other one for the temporal evolution of its fluctuating part $[\mathsf{B}(\mathbf{r},t)]$, can each be split into five coupled scalar differential equations (partial differential equations) for the five independent degrees of freedom. If the liquid-crystalline ordering is uniaxial, a suitable tensorial base is given by $\mathsf{T}_0=(3\mathbf{n}\otimes\mathbf{n}-\mathsf{I})/\sqrt{6}$, $\mathsf{T}_1=(\mathbf{e}_1\otimes\mathbf{e}_1-\mathbf{e}_2\otimes\mathbf{e}_2)/\sqrt{2}$, $\mathsf{T}_{-1}=(\mathbf{e}_1\otimes\mathbf{e}_2+\mathbf{e}_2\otimes\mathbf{e}_1)/\sqrt{2}$, $\mathsf{T}_2=(\mathbf{e}_1\otimes\mathbf{n}+\mathbf{n}\otimes\mathbf{e}_1)/\sqrt{2}$, and $\mathsf{T}_{-2}=(\mathbf{e}_2\otimes\mathbf{n}+\mathbf{n}\otimes\mathbf{e}_2)/\sqrt{2}$, where $\mathbf{n}$ is the nematic director, $\mathbf{e}_1$ and $\mathbf{e}_2$ are mutually perpendicular unit vectors, and I is the unit second rank tensor [27]. The base tensors can be interpreted as follows: the component of Q along T_0 is the sum of the equilibrium mean-field scalar order parameter and order parameter fluctuations, the components along $\mathsf{T}_{\pm1}$ are biaxial fluctuations, and the parts along $\mathsf{T}_{\pm2}$ are director fluctuations.

It is useful to rewrite the quantities into a dimensionless form [7]. Thus in the following, all coordinates will be measured in terms of the film thickness and the nematic correlation length at the bulk nematic-isotropic phase transition, $\zeta d=\xi(T_{NI})=\sqrt{27CL/B^2}\approx 8$ nm. The order parameter will be rescaled in units of the scalar order parameter of the nematic phase at the phase transition temperature, $S_C=2B/3\sqrt{6}C\approx 0.27$, and the temperature will be controlled by $\theta=(T-T^*)/(T_{NI}-T^*)$, where $T_{NI}=T^*+B^2/27AC$ is the bulk nematic-isotropic phase transition temperature. These values as well as the results presented in the following sections correspond to hybrid films of different thicknesses and a typical liquid-crystalline material such as 5CB ($A=0.13\times10^6$ J/m^3 K, $B=3.89\times10^6$ J/m^3, $C=3.92\times10^6$ J/m^3, $L=9\times10^{-12}$ N, and $T^*=307.1$ K) [21,28].

III. MEAN-FIELD STRUCTURES

In this section we discuss needed details about the equilibrium ordering of a hybrid nematic film which can exhibit distorted (hybridly bent) or undistorted director structure. The undistorted structure is characterized by either biaxial director exchange configuration in the case of equally strong but hybrid surface anchorings or uniform director field in the case of hybrid confining substrates characterized one by a strong anchoring and other by a weak anchoring. Which of the two possible configurations—distorted or undistorted—will actually occur depends on the temperature and film thickness. However, the existence of either of the two undistorted structures depends on the strength of the surface coupling. We study both distorted and undistorted structures using the same free energy density expansion. By comparing the total free energy dependences on temperature and film thickness the structural transition is determined.

A. Uniform director field

Although the aim of this paper is to describe the hybrid film with equivalent strong surface interactions (in which the biaxial configuration occurs) in the few following lines the uniform director field structure will be outlined in order to introduce some general expressions and to get the idea of the subject in question.

The equilibrium structure corresponds to a minimum of the free energy. In order to minimize the surface contribution to the free energy the nematic director will lie in the direction of the easy axis of the substrate with stronger anchoring, say the substrate at $z=0$ ($G_1>G_2$). Thus the nematic order can be described with a scalar order parameter S and, in general, with the additional parameter P measuring biaxiality of the order ($\mathsf{Q}=S\mathsf{T}_0+P\mathsf{T}_1$, with the orthonormal triad $\mathbf{n}=\mathbf{e}_x$, $\mathbf{e}_1=\mathbf{e}_y$, and $\mathbf{e}_2=\mathbf{e}_z$). Usually, the biaxiality of the nematic order is neglected but in highly frustrated systems such an approximation is not justified. The positional dependence of the two chosen parameters can be obtained by solving Euler-Lagrange equations

$$\begin{aligned}\zeta^2S''-\theta S+3S^2-2S^3-3P^2-2SP^2=0,\\ \zeta^2P''-\theta P-2P^3-6SP-2S^2P=0,\end{aligned}\tag{4}$$

where the prime denotes d/dz. The corresponding boundary conditions are determined by

$$\begin{aligned}S'(z=0)&=g_1[S(z=0)-a_S]/\zeta^2,\\ P'(z=0)&=g_1P(z=0)/\zeta^2,\\ S'(z=1)&=-g_2[S(z=1)+a_S/2]/\zeta^2,\\ P'(z=1)&=-g_2[P(z=1)+a_S\sqrt{3}/2]/\zeta^2,\end{aligned}\tag{5}$$

where a_S is the preferred value of the scalar order parameter which is taken to be equal at both substrates and $g_i=(27C/B^2d)G_i$ is the dimensionless strength of the surface interaction.

Since the confining substrates induce uniaxial order the biaxiality is small, especially at the substrate whose easy axis is parallel to the nematic director (Fig. 2). If the anchoring of the other substrate is strong as well the equilibrium uniform director structure is the one that will be discussed in Sec. III C (biaxial structure). However, in the case where one of the confining substrates is characterized by very weak anchoring the parameter of biaxial order can be omitted and the equations reduce to $\zeta^2S''-\theta S+3S^2-2S^3=0$, i.e., describing Sheng's surface aligned nematic ordered structures [29].

B. Bent-director structure

Our discussion of the bent-director configuration is only slightly simplified by the assumption that the order is uniaxial but it allows both positionally dependent scalar order parameter and director field, whereas in most previous studies only the variation of the director field has been taken into account. The effect of biaxiality can be neglected since it is very small comparing to the scalar order parameter ($P<\zeta^2\ll S\sim 1$). Using the dimensionless form of the free energy density expansion [Eq. (1)] and the ansatz $\mathsf{Q}(z)$

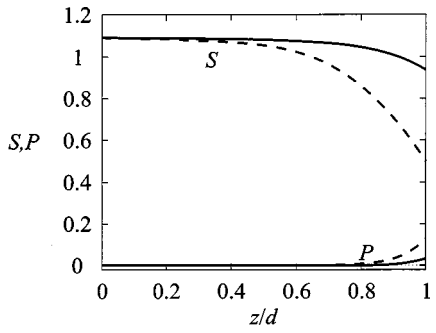

FIG. 2. Uniform director structure in a hybrid film with unequal anchoring strengths. The mean-field profile is characterized by a spatially dependent degree of nematic order and increasing biaxiality profile when approaching the substrate with weaker anchoring [$\theta=0.9$, $\zeta^2=0.03$, $a_S=1.1$, $G_1=1.2\times10^{-3}$ J/m^2, and $G_2=1.2\times10^{-4}$ J/m^2 (solid line), $G_2=4\times10^{-4}$ J/m^2 (dashed line)].

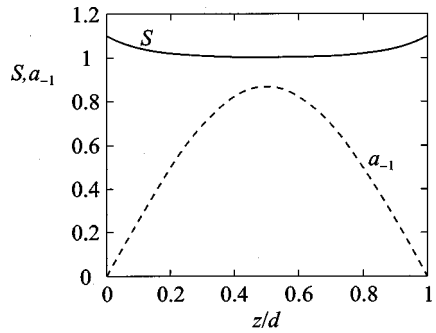

FIG. 3. Mean-field bent-director structure in a hybrid film. The solid line corresponds to the scalar order parameter and the dashed line represents the $a_{-1}=(\sqrt{3}/2)S\sin 2\phi$ amplitude of the tensor order parameter, which describes the bending of the director field in the plane (x,z) ($\theta=0.9$, $\zeta^2=0.01258$, $g\to\infty$, and $a_S=1.1$).

$=S(z)(3\mathbf{n}\otimes\mathbf{n}-\mathsf{I})/\sqrt{6}$, where the nematic director has the form $\mathbf{n}=(\sin\phi,0,\cos\phi)$ and $\phi=\phi(z)$, the two independent parameters S—the scalar order parameter—and ϕ—the angle between the nematic director and the substrate normal—are determined by the equations

$$\zeta^2 S''-\theta S+3S^2-2S^3-3\zeta^2 S(\phi')^2=0,$$
$$(S^2\phi')'=0. \tag{6}$$

In the case of a very strong surface anchoring the boundary values of S and ϕ are set to the values preferred by the confining substrates [scalar order parameter a_S and $\phi(z=0,d)=\phi_{S_{1,2}}$, where $\phi_{S_1}=\pi/2$ and $\phi_{S_2}=0$] otherwise they are determined with boundary conditions

$$S'=\pm g_{1,2}[2S+a_S-3a_S\cos^2(\phi-\phi_{S_{1,2}})]/2\zeta^2\ \big|_{z=0,1},$$
$$S\phi'=-g_{1,2}\ a_S\sin 2\phi/2\zeta^2\ \big|_{z=0,1}, \tag{7}$$

where the signs $+$ and $-$ and the subscripts 1 and 2 correspond to $z=0$ and $z=1$, respectively.

As suggested, above the critical film thickness or below the critical temperature (with constant temperature or film thickness, respectively) the order in a hybrid nematic film can be described by a bent-director field. Since we allow the scalar order parameter to vary with the distance from one of the substrates the director tilt angle is not changing linearly as it would in the case of the uniform scalar order parameter (see Figs. 3 and 4). However, the difference is very small and, as expected, decreases further with the increasing film thickness and when the boundary value of the scalar order parameter is getting closer to the value $S_b(\theta_{\rm eff})$. Here $S_b(\theta)=0.75(1+\sqrt{1-8\theta/9})$ is the bulk degree of the nematic order and the renormalized dimensionless temperature

$$\theta_{\rm eff}=\theta+(3\pi^2/4)\zeta^2 \tag{8}$$

corresponds to a hybrid film with homogeneous scalar order parameter ($S'=0$) and linearly varying nematic director [see Eq. (6)]. In the case of strong surface anchoring the discrepancies from the uniform case are $\Delta S=S(0)-S(1/2)\approx a_S-S_b$ and $\Delta\phi'=\phi'(0)-\phi'(1/2)\approx\pi(a_S^2-S_b^2)/(a_S^2+S_b^2)$ (see also Ref. [30]).

C. Biaxial configuration

As already mentioned in the Introduction, the biaxial configuration was introduced by Palffy-Muhoray *et al.* [13] and recently discussed by Galabova *et al.* [14]. However, their studies were made for a special case where the temperature corresponds to the bulk supercooling limit ($T=T^*$), whereas some other choices of temperature give rise to different physical phenomena. In order to better understand the pretransitional dynamics in such a biaxially ordered structure, a detailed description of the biaxial configuration is presented in this section.

In general, in the case of a hybrid film the director field is not uniform. However, the easy axes of the confining substrates are one in the direction of the x axis and the other parallel to the z axis; therefore it can be assumed that the director will lie in the plane (x,z), i.e., perpendicular to the y axis. Thus $\mathbf{n}=\mathbf{e}_y$, $\mathbf{e}_1=\mathbf{e}_z$ and $\mathbf{e}_2=\mathbf{e}_x$ can form a suitable uniform orthonormal triad.

The biaxial configuration has been determined using the expansion of the tensor order parameter in terms of the base tensors, $\mathsf{A}(\mathbf{r})=\sum_{i=-2}^{2}a_i(z)\mathsf{T}_i$. Due to the symmetry reasons

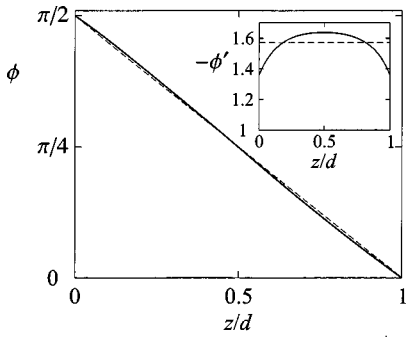

FIG. 4. Spatial dependence of the tilt angle and its derivative (inset) for the bent-director structure in a hybrid film. Dashed lines correspond to the appropriate parameters in the case of the uniform scalar order parameter ($\theta=0.9$, $\zeta^2=0.0126$, $a_S=1.1$, $g\to\infty$).

and boundary conditions, the configuration can be described by two amplitudes, a_0 and a_1. The former refers to the scalar order parameter with respect to the y axis, whereas the latter denotes biaxiality of the order in perpendicular directions. In our case, the negative/positive sign of the amplitude a_1 tells whether the actual director is in the direction of the x or z axis, respectively. Both nonzero amplitudes are the solutions of two coupled equations arising from minimization of the free energy [Eq. (1)] and the expansion of the tensor order parameter in terms of the base tensors,

$$\zeta^2 a_0'' - \theta a_0 + 3(a_0^2 - a_1^2) - 2a_0(a_0^2 + a_1^2) = 0,$$
$$\zeta^2 a_1'' - \theta a_1 - 6a_0 a_1 - 2a_1(a_0^2 + a_1^2) = 0, \tag{9}$$

where the prime denotes d/dz. The boundary conditions are determined by the surface interaction. In our case, the induced order is assumed to be uniaxial at both substrates but in mutually perpendicular directions, therefore $\mathsf{Q}_S(0) = a_S(3\mathbf{e}_x \otimes \mathbf{e}_x - \mathsf{I})/\sqrt{6}$ and $\mathsf{Q}_S(1) = a_S(3\mathbf{e}_z \otimes \mathbf{e}_z - \mathsf{I})/\sqrt{6}$, where $a_S \geqslant S_b(\theta)$ is the preferred degree of order at the substrates (and is assumed to be equal at both substrates). Thus the boundary conditions read

$$a_0'(z=0,1) = \pm g[a_0(z=0,1) + a_S/2]/\zeta^2,$$
$$a_1'(z=0,1) = \pm g[a_1(z=0,1) \pm a_S\sqrt{3}/2]/\zeta^2, \tag{10}$$

where the signs + and − correspond to $z=0$ and $z=1$, respectively. If the anchoring is very strong ($g \to \infty$), the order at the surface is the same as the one preferred by the confining substrate, otherwise, the parameters can differ from the preferred ones.

The actual significance of the two nonzero amplitudes is obvious when they are rewritten into $a_0^x = -(a_0 + \sqrt{3}a_1)/2$ and $a_0^z = (-a_0 + \sqrt{3}a_1)/2$, where the former sum refers to the scalar order parameter with respect to the director $\mathbf{n} = \mathbf{e}_x$ and the latter sum denotes the scalar order parameter with respect to the director $\mathbf{n} = \mathbf{e}_z$. As shown in Fig. 5, on the average, near the first surface ($z=0$) the liquid-crystal molecules are oriented parallel to the x axis while they are parallel to the z axis close to the other substrate ($z=1$). In the vicinity of the surfaces the order is uniaxial, however, with increasing distance from the substrates it becomes slightly biaxial. Both biaxiality and order parameter profiles are symmetric with respect to the middle of the film (plane $z=1/2$). The biaxiality profile has two maxima near the symmetry plane. In between them the molecular ordering can be described with a director perpendicular to the plane of the molecules ($\mathbf{n} = \mathbf{e}_y$), yet the scalar order parameter is negative. In the region of negative scalar order parameter the director or eigenvalue exchange occurs.

The maximum biaxiality and the thickness of the exchange region depend on the film thickness, the temperature, and the anchoring strength. The biaxiality is more pronounced in thinner films and when the temperature is closer to the phase transition temperature. From the point where the surface wetting layers are in contact the exchange region thickness is—within the numerical accuracy—independent of temperature. On the other hand, the relative exchange region increases with decreasing film thickness, however, the absolute exchange region thickness decreases.

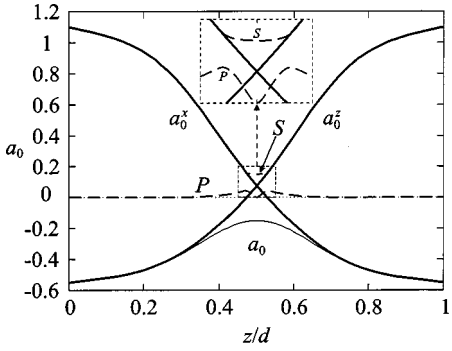

FIG. 5. Mean-field profiles of the nonzero degrees of freedom. The thin solid line refers to the scalar order parameter with respect to the uniform director $\mathbf{e}_y$, whereas thicker lines represent scalar order parameters with respect to the easy axes x and z, $a_0^x = -(a_0 + \sqrt{3}a_1)/2$ and $a_0^z = (-a_0 + \sqrt{3}a_1)/2$. Dashed lines correspond to scalar order parameter [$S = (\sqrt{6}/2)|\mathsf{Q}_{ii}|$, where Q_{ii} has a sign opposite to that of the two other eigenvalues of Q] and biaxiality of the order ($P = |\mathsf{Q}_{jj} - \mathsf{Q}_{kk}|/\sqrt{2}$, where $j,k \neq i$), respectively. Inset: the magnified detail of the profiles in the exchange region ($\theta = 0.9$, $\zeta^2 = 0.01258$, $a_S = 1.1$, $g \to \infty$).

The biaxially ordered configuration is typical for highly constrained nematic liquid crystals, i.e., systems with high surface-to-volume ratio and strong surface anchoring ($G \gtrsim 10^{-3}$ J/m^2). In such systems the surface wetting layers may be in contact with each other, thus the structure they form becomes progressively ordered on approaching the phase transition temperature. Because of the continuous growth of the ordered biaxial structure there is no nematic-isotropic phase transition. However, there is the transition to the low-temperature bent-director field configuration. Because the initial structure is ordered too, the transition between the two phases is structural rather than the phase one. In the case of unequal but strong surface anchorings the high-temperature phase is biaxial as well, but the exchange region is located closer to the surface with weaker anchoring (Fig. 6). As already discussed in Sec. III A, biaxial structure reduces to the uniform director field state with spatially de-

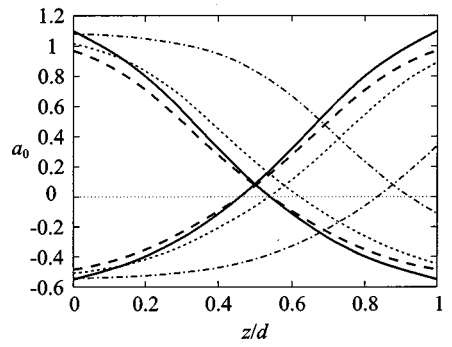

FIG. 6. The degree of nematic order with respect to mutually perpendicular directors $\mathbf{n} = \mathbf{e}_x$ and $\mathbf{n} = \mathbf{e}_z$ in intervals $z \in [0,0.5]$ and $z \in [0.5,1]$, respectively. Different lines correspond to different anchoring strengths: $G_1, G_2 \to \infty$ (solid line), $G_1 = G_2 = 1.2 \times 10^{-3}$ J/m^2 (dashed line), $G_1 = 1.2 \times 10^{-3}$ J/m^2 and $G_2 = 1.1 \times 10^{-3}$ J/m^2 (dotted line), and $G_1 = 1.2 \times 10^{-3}$ J/m^2 and $G_2 = 0.6 \times 10^{-3}$ J/m^2 (dash-dotted line) ($\theta = 0.9$, $\zeta^2 = 0.03$, $a_S = 1.1$).

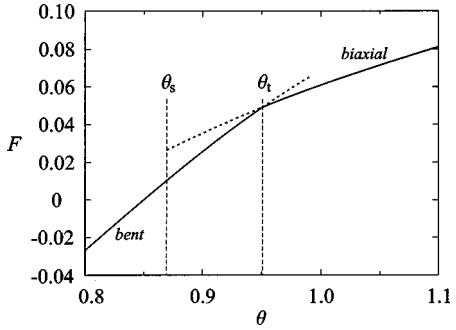

FIG. 7. Temperature dependence of the total free energy of biaxial and bent-director structure. The structural transition occurs at the point where the free energies of the two configurations are equal ($\theta_t=0.951$), whereas $\theta_s=0.869$ represents the ''supercooling'' limit of the biaxial structure. However, for a typical liquid-crystalline material the difference between the two temperatures is very small, $\Delta T=T_s-T_t\sim 0.09$ K, and the corresponding latent heat is by an order of magnitude smaller than the latent heat of the nematic-isotropic phase transition. The dotted continuation of the total free energy represents the regions where the two structures are metastable ($\zeta^2=0.02$, $a_S=1.1$, $g\rightarrow\infty$).

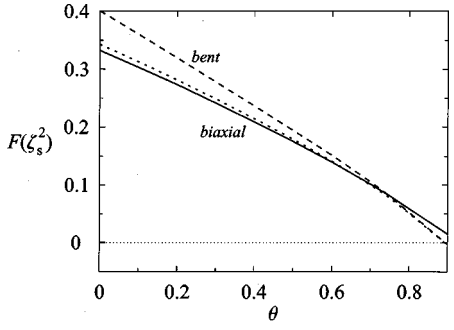

FIG. 8. Temperature dependence of the total free energy of biaxial and bent-director structure at the ''supercooling'' film thickness [$\zeta_s=\zeta_s(\theta)$]. Because of the approximate determination of bent-director structure the corresponding free energy is too high but even rough calculations show that the correction (dotted line) would cause the transition to become continuous below some critical temperature and film thickness (tricritical point). Above the tricritical point (the upper limit $\theta_{\mathrm{TP}}=0.746$ and $\zeta^2_{\mathrm{TP}}=0.054$) the transition becomes progressively discontinuous.

pendent degree of nematic order and negligible biaxiality (except at the substrate where the nematic director is perpendicular to the easy axis) if one of the confining substrates is characterized by weaker anchoring ($G\lesssim 10^{-4}$ J/m^2), i.e., it reduces to the case studied in Ref. [11].

D. Structural transition between bent-director structure and biaxial structure

By comparing the total free energies of the two ordered configurations we determine the structural transition film thickness. However, the bent-director structure was determined approximately, therefore the total free energy of the actual configuration is lower than the one obtained in our calculations. Since the neglected biaxiality is of order of $P\sim c\zeta^2$, where $0<c<1$, the difference between the actual and approximated free energy should be very small, i.e., $F-F_{\mathrm{approx}}\sim-\zeta^4[c(\pi^2\sqrt{3}/4)S-c^2(\theta/2+3S+S^2)]$, where $S=S(\theta)$ is the bulk degree of nematic order parallel to the director. As expected, the correction is getting smaller as the film thickness is increased.

Near the nematic-isotropic phase transition temperature ($T_{NI}-T=0.1$ K) and in a hybrid film of a typical liquid-crystalline material (such as 5CB) the nematic order is distorted if the film is thicker than $d_t\approx 47$ nm, whereas the metastable biaxial structure ceases to exist if the film thickness is larger than $d_s\approx 71$ nm (determined by pretransitional dynamics—see Sec. IV). As the temperature is decreased both values are decreased too and so is the difference between them. The same structural transition can be realized if the film thickness is held constant and the temperature is varied. A typical temperature dependence of the free energies of both ordered phases at constant film thickness ($\zeta^2=0.02$) is shown in Fig. 7. It is obvious that the slopes of the functions are not equal at the transition point, so that the structural transition is discontinuous. However, the corresponding latent heat, $q_l=\Delta(\partial F/\partial T)T_t=\Delta(\partial F/\partial\theta)[\theta_t+T^*/(T_{NI}-T^*)]\approx 8\times 10^4$ J/m^3, is even smaller than the nematic-isotropic phase transition latent heat ($\approx 1.5\times 10^6$ J/m^3) [31], therefore the structural transition is only weakly discontinuous.

The (dis)continuity of the structural transition can be changed if the temperature and film thickness are low enough. Within our approximation, in such a case the free energies of bent and biaxial structures do not intersect and the free energy of the bent structure exceeds the biaxial one at the ''supercooling'' limit. This can be understood if one considers the approximate determination of the bent-director structure in which the biaxiality is omitted. However, even a rough calculation such as the one introduced at the beginning of this section shows that included biaxiality lowers the free energy of the bent structure so that the transition becomes continuous. Such a nature of the structural transition was found also in previous papers [13,14]. The two different regimes are separated with a tricritical point (tricritical temperature and film thickness) below which the transition is continuous. Because of the approximate description of the bent-director structure only its upper limit has been determined: $\theta_{\mathrm{TP}}=0.746$ and $\zeta^2_{\mathrm{TP}}=0.054$, which corresponds to $T_{NI}-T_{\mathrm{TP}}=0.28$ K and $d_{\mathrm{TP}}=34$ nm for a typical nematic liquid crystal, such as 5CB. In Fig. 8 the temperature dependence of total free energies of both ordered structures at the ''supercooling'' film thickness is shown. One should notice that the dimensionless total free energies are decreasing functions of temperature. That indicates that in the range of film thicknesses where biaxial structure can be realized the elastic part of the free energy is dominant over the ordering terms. The elastic term whose magnitude is determined by $\zeta^2\propto 1/d^2$ is decreasing with temperature because the ''supercooling'' film thickness is an increasing function of temperature.

IV. PRETRANSITIONAL DYNAMICS

Once we have calculated the mean-field profiles we can begin with the analysis of fluctuations. In this paper the analysis is restricted to fluctuations in the biaxial (director exchange) structure and their temperature/film thickness de-

pendence when approaching the structural transition to the bent-director configuration and the ''supercooling'' limit. The same approach can be used also with the uniform director structure but the analysis is not performed here because this structure does not appear in highly frustrated systems. However, the detailed analysis of the pretransitional dynamics of all five degrees of freedom around the bent-director configuration is somewhat more complicated because of the nonuniformity of the base tensors.

The Gaussian dynamics of five scalar components of collective excitations—introduced by the expansion $\mathsf{B}(\mathbf{r},t)=\Sigma_{i=-2}^{2} b_i(\mathbf{r},t)\mathsf{T}_i$—is derived by projecting the linearized form of the relaxation equation [Eq. (3)] onto the base tensors. Since the mean-field profiles depend on the z coordinate only, the normal modes can be factorized as follows:

$$b_i(\mathbf{r},t)=\exp[i(k_x x+k_y y)]\beta_i(z)\exp(-\mu_i t), \qquad (11)$$

where k_x and k_y are the in-plane components of dimensionless wave vector of fluctuations which are assumed to be subjected to periodic boundary conditions, μ_i's are the dimensionless relaxation rates of the eigenmodes, and time is measured in units of $\tau_a=(27C/B^2)\Gamma\sim 10^{-8}$ s [26]. Considering the introduced ansatz [Eq. (11)] and the mean-field profiles of the system the amplitudes $\beta_i(z)$ are determined by the equations

$$\begin{aligned}
&\zeta^2\beta_0''-(\theta-\lambda_{0,1}-6a_0+6a_0^2+2a_1^2)\beta_0-2a_1(3+2a_0)\beta_1=0,\\
&\zeta^2\beta_1''-(\theta-\lambda_{0,1}+6a_0+2a_0^2+6a_1^2)\beta_1-2a_1(3+2a_0)\beta_0=0,\\
&\zeta^2\beta_{-1}''-(\theta-\lambda_{-1}+6a_0+2a_0^2+2a_1^2)\beta_{-1}=0,\\
&\zeta^2\beta_{\pm 2}''-(\theta-\lambda_{\pm 2}-3a_0\mp 3\sqrt{3}a_1+2a_0^2+2a_1^2)\beta_{\pm 2}=0,
\end{aligned} \qquad (12)$$

where $\beta_i'=d\beta_i/dz$ and $\lambda_i=\mu_i-\zeta^2(k_x^2+k_y^2)$ are the reduced relaxation rates of the modes. When deriving these equations, one must consider that the modes which are coupled relax with the same relaxation rate, therefore $\lambda_0=\lambda_1=\lambda_{0,1}$. In the case of a very strong surface anchoring ($g\to\infty$) no fluctuations are allowed at the substrate, thus $\beta_i(z=0,1)=0$, otherwise the boundary conditions read

$$\beta_i'(z=0,1)=\pm g\beta_i(z=0,1)/\zeta^2, \qquad (13)$$

where the signs $+$ and $-$ refer to $z=0$ and $z=1$, respectively.

In the case of a purely uniaxial nematic ordering and uniform director field ($a_i=0$, $i\neq 0$) the five fluctuating modes are independent, therefore the two equations for the amplitudes $\beta_0(z)$ and $\beta_1(z)$ are uncoupled. Furthermore, due to the symmetry reasons the two biaxial modes (b_i with indices $i=\pm 1$) are degenerate and so are the two director modes (indices $i=\pm 2$) [7,8].

As implied by Eqs. (12) this is not the case when dealing with fluctuations in a biaxially ordered hybrid film. Since the mean-field profiles are described by two nonzero amplitudes, a_0 and a_1, the corresponding fluctuation modes, β_0 and β_1, are coupled. The significance of these modes is transparent when considering their linear combinations $\beta_{0,1}^x=-(\beta_0+\sqrt{3}\beta_1)/2$ and $\beta_{0,1}^z=-(\beta_0-\sqrt{3}\beta_1)/2$, which denote the order parameter fluctuations with respect to the nematic director parallel to the x and z axis, respectively. The other three fluctuation modes are uncoupled and represent either director fluctuations (β_{-1} and low $\beta_{\pm 2}$ modes) or biaxial fluctuations, high β_2 and β_{-2} modes.

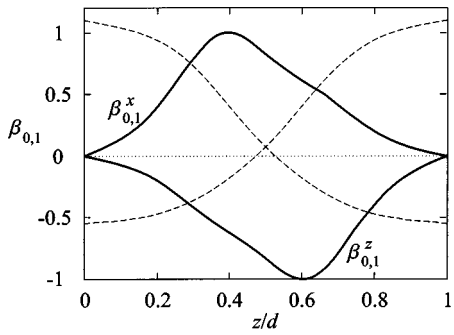

FIG. 9. Spatial dependence of the lowest order parameter mode. Thick curves correspond to coupled fluctuations of the degree of order with respect to the two mutually perpendicular easy axes. Dashed lines correspond to the mean-field profiles (Fig. 5) ($\theta=0.9$, $\zeta^2=0.012\,58$, $a_S=1.1$, $g\to\infty$).

Due to the inhomogeneous mean-field profiles the eigenmodes of fluctuations can only be determined numerically. In the following sections the spectra of collective excitations and the eigenamplitudes for different fluctuating modes will be interpreted.

A. Order parameter fluctuations

The term order parameter fluctuations denotes coupled fluctuations of the two nonzero mean-field amplitudes. As is well known the eigenfunctions of an operator invariant to the space reflection are either symmetric or antisymmetric with respect to the same transformation [32]. Since the operator which governs the order parameter fluctuations [see Eq. (12) and the results for the mean-field profiles a_0 and a_1] is symmetric with respect to the plane $z=1/2$ the eigenfunctions of the system can be divided into two classes, i.e., the symmetric and antisymmetric functions with respect to the symmetry plane. The lowest symmetric mode is associated with fluctuations of the thickness of the central director exchange region and therefore also with the fluctuations of the magnitude of biaxiality of the nematic order. However, the lowest antisymmetric mode corresponds to fluctuations of the position of the boundary between the two parts of the film which are determined by mutually perpendicular nematic directors. The portrait of the lowest antisymmetric order parameter mode is plotted in Fig. 9. One should notice that the two corresponding profiles, $\beta_{0,1}^x$ and $\beta_{0,1}^z$, are ''localized'' at the part of the film with director $\mathbf{e}_x$ and $\mathbf{e}_z$, respectively. The positions of their maxima coincide with the position of maximum slope of the scalar order parameter. Thus, the lowest antisymmetric order parameter mode is responsible for the growth of the surface wetting layers (see Refs. [7,8]). Higher symmetric and antisymmetric modes change the shape of the exchange region in a symmetric or an antisymmetric manner, respectively.

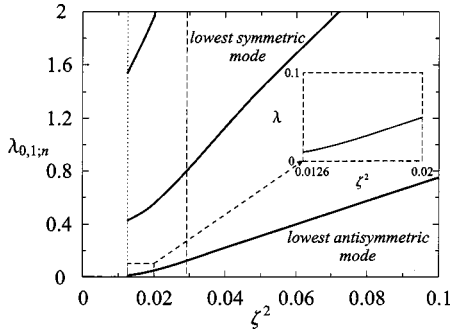

FIG. 10. Lower part of the spectrum of collective order parameter excitations with respect to the film thickness. Dotted and dashed verticals denote the ''supercooling'' and the structural transition film thickness, respectively. Inset: magnified detail of the lowest order parameter relaxation rate. Notice that the relaxation rate remains finite even at the ''supercooling'' limit and approaches the limit with the zero slope ($\theta=0.9$, $a_S=1.1$, $g\to\infty$).

The lowest relaxation rate corresponds to the lowest antisymmetric mode. When increasing the film thickness toward the structural transition thickness (decreasing the parameter ζ^2) all the relaxation rates are decreased, especially the lowest one (see Fig. 10). However, it stays finite ($\lambda_{0,1;n=0}>0$) even at the ''supercooling'' limit (transition) point above (below) the tricritical point.

B. Director fluctuations

Director fluctuations β_{-1} represent changes of the orientation of the nematic director in the plane of the two easy axes. They bend the nematic director in the $\mathbf{n}=\mathbf{e}_x$ half of the film toward the direction $\mathbf{e}_z$ and the $\mathbf{n}=\mathbf{e}_z$ director in the other half toward the perpendicular x direction. The corresponding eigenmodes are spread over the whole sample and are similar to the sine functions. The lowest director mode represents the change in the tensor order parameter that is similar to the one characteristic for the bent-director configuration (see Figs. 3 and 11). Its relaxation rate exhibits a critical slowdown when the film thickness approaches the ''supercooling'' limit/transition point above/below the tricritical point, respectively. In the case of discontinuous structural transition the lowest director mode is almost critical even at the structural transition, which is in agreement with our previous conclusion that the transition is only weakly discontinuous. Therefore, in both regimes the soft director mode can be assumed to govern the structural transition between the two ordered configurations. As shown in Fig. 12, higher modes relax faster and do not contribute essentially to the pretransitional change in the director field.

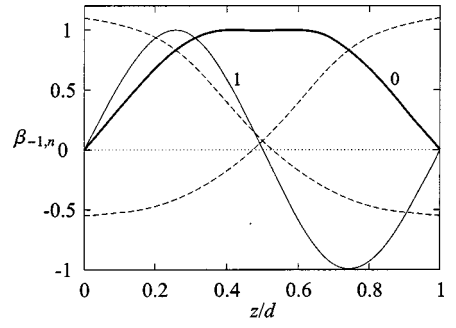

FIG. 11. Spatial dependence of the lowest two director modes labeled by the number of nodes. Dashed lines correspond to the mean-field profiles plotted in Fig. 5 ($\theta=0.9$, $\zeta^2=0.012\,58$, $a_S=1.1$, $g\to\infty$).

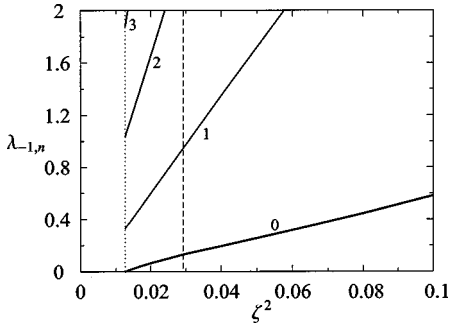

FIG. 12. A few lowest relaxation rates of director modes versus film thickness. The rates are decreasing with increasing film thickness, especially the lowest mode's rate which drops to zero as the film thickness approaches the ''supercooling'' limit. Dotted and dashed verticals denote the ''supercooling'' and the structural transition film thickness, respectively ($\theta=0.9$, $a_S=1.1$, $g\to\infty$).

C. Biaxial fluctuations

Biaxial fluctuations $\beta_{\pm2}$ are described by the last two equations in Eq. (12). If these equations are rewritten in the more appropriate form

$$\zeta^2\beta''_{\pm2}-[\theta-\lambda_{\pm2}+6a_0^{x,z}+2(a_0^2+a_1^2)]\beta_{\pm2}=0, \quad (14)$$

and the symmetry relations between the equilibrium amplitudes a_0^x and a_0^z are considered (see Fig. 5) it can be easily seen that the spectra for the two biaxial modes are degenerated, whereas the eigenfunctions are just mirror images with respect to the plane $z=1/2$.

As shown in Fig. 13 the few lowest modes of fluctuations $\beta_2(z)$ and $\beta_{-2}(z)$ are expelled from the part of the film

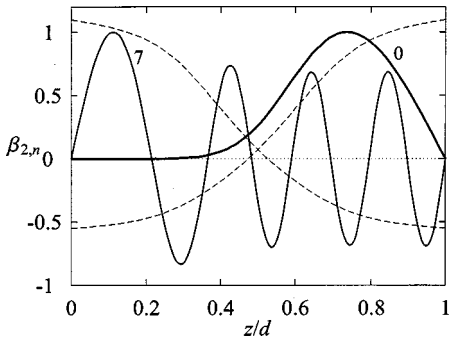

FIG. 13. Portrait of two typical biaxial fluctuation modes β_2 (the β_{-2} modes are just their mirror images with respect to the symmetry plane $z=1/2$). The lowest modes are expelled from the part of the film where these fluctuations represent biaxial fluctuations. Higher modes are spread over the whole sample. Labels denote the number of nodes of the mode and the dashed lines correspond to the mean-field profiles of biaxial structure ($\theta=0.9$, $\zeta^2=0.012\,58$, $a_S=1.1$, $g\to\infty$).

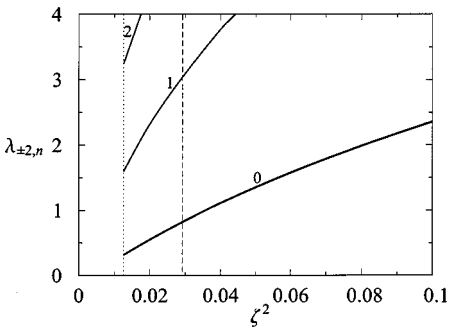

FIG. 14. The lowest part of the spectrum of relaxation rates of biaxial fluctuations. Note that the relaxation rates are higher than the relaxation rates of other modes (cf. Figs. 10 and 12). Since the biaxial fluctuations represent deformations of the order parameter in the *y* direction they do not play any important role at the structural transition. Dotted and dashed verticals denote the ''supercooling'' and the structural transition film thickness, respectively ($\theta=0.9$, $a_S=1.1$, $g\rightarrow\infty$).

which is characterized by directors $\mathbf{e}_x$ and $\mathbf{e}_z$, respectively. This can be easily understood if we consider that $\beta_{\pm 2}$ represent amplitudes of the projection of the tensor order parameter along the base tensors $\mathsf{T}_{\pm 2}$ which couple directions *y* and *z* or *y* and *x*, respectively. That means that β_2 refers to director fluctuations in the $\mathbf{n}=\mathbf{e}_z$ part of the film but to biaxial fluctuations in the other part, and vice versa for the β_{-2} fluctuation modes. Since in the uniaxial nematic phase director fluctuations are much more favorable than biaxial fluctuations [8], $\beta_{\pm 2}$ fluctuations tend to be localized at the appropriate half of the film only. Higher modes are spread over the whole film whereas the unfavorable manner of biaxial fluctuations is compensated by the shorter wave vector of a deformation. In addition, it is well known that the higher the modes, the smaller the effect of the shape of the potential on them.

The biaxial relaxation rates are higher than the rates of other fluctuation modes, therefore the biaxial fluctuations do not play any important role in the structural transition discussed (Fig. 14).

V. CONCLUSIONS

The analysis of nematic liquid crystals confined to highly constrained hybrid films with a biaxial structure has revealed a soft-mode or soft-mode-like dynamics in the vicinity of the structural transition toward hybridly aligned (bent-director) structure. The soft fluctuation manner is related to the bending director fluctuations which deform the undistorted director profile (in biaxial configuration) toward the continuously bent-director field in a usual hybridly distorted structure. In addition to this fluctuation mode the lowest order parameter mode exhibits similar slowdown of the relaxation rate, however, the relaxation rate remains finite even at the ''supercooling'' limit of the biaxial configuration. Yet, this mode being related to fluctuations of the position of the interface between the two uniaxial parts of the film (characterized by mutually perpendicular directors), its relaxation rate becomes even more softened if the film thickness is increased or if the surface anchoring is weaker. Other fluctuation modes do not contribute to the structural transition. However, low biaxial modes are interesting because they are localized in one-half of the film only.

Studying temperature and film thickness dependence of the structural transition the upper limit for the tricritical point of the structural transition was found. Above the tricritical values of the temperature ($T_{NI}-T_{\mathrm{TP}}\gtrsim 0.28$ K) and film thickness ($d_{\mathrm{TP}}\lesssim 34$ nm) the structural transition becomes progressively discontinuous.

Phenomena similar to the one discussed in this paper have already been studied experimentally [11], e.g., the structural transition between distorted and undistorted structure. However, our discussion has been focused on the structural transition from the undistorted biaxial configuration, whereas in the experimental study mentioned above the studied undistorted configuration was the one with the uniform director field. If our formalism, taking into account the tensorial nature of the nematic order parameter, is applied to the conditions examined in the experimental setup of Wittebrood *et al.* the critical thickness for the hybridly aligned director field is comparable to the one they determined. However, the main object of our study was to determine the regions of stability of different ordered structures in systems where the anchorings of different confining substrates are comparable (equal). Therefore, the validity and limitations of our model could be proven by an experiment designed to probe the dynamics in very thin samples, which could be based on, for example, the evanescent light wave scattering technique [33,22].

The studied behavior of the nematic ordering and pretransitional dynamics of a liquid crystal in a hybrid film is certainly not limited to the simple planar geometry discussed in this paper. A similar phenomenon is expected in systems where the hybrid manner of confinement is induced by topological constraints imposed by curved walls, such as in cylindrical cavities. It seems possible that the results obtained here can explain some experimentally detected effects [34,35]. However, in the cylindrical geometry the liquid crystal is confined by only one solid substrate whereas the other substrate is substituted by a topological singularity. Therefore, if one wants to go beyond a qualitative comparison of experimental and theoretical results the effect of defects should be carefully taken into account.

ACKNOWLEDGMENTS

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