

## Collective fluctuations and wetting in nematic liquid crystals

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The role of wetting in the dynamics of collective orientational fluctuations in confined nematic liquid crystals is examined by analyzing the spectrum of normal modes in planar geometry bounded either by disordering or ordering substrates. The heterophase nature of the equilibrium configurations occurring in the vicinity of the nematic-isotropic phase transition gives rise to a localized slow mode, which corresponds to fluctuations of thickness of the (dis)ordered boundary layer and becomes soft if the wetting is complete. In addition, a few modes restricted to the boundary layer—director modes in case of ordering substrate, and biaxial modes in case of disordering substrate—also exhibit pretransitional slowdown provided that the surface interaction is strong enough. Analogous behavior of fluctuations is expected in other wetting geometries, e.g., in the case of a substrate-stabilized smectic boundary layer in nematic and isotropic samples.

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### I. INTRODUCTION

The variation of material properties of liquid crystals in the vicinity of phase transitions has attracted the attention of both experimentalists and theorists for a long time, mainly because it can offer an insight into the evolution of the order characteristic for the low-temperature phase. In the isotropic phase, for example, the onset of short-range orientational ordering is observed on cooling towards the nematic-isotropic phase transition [1]. On a large temperature scale, the pretransitional behavior can usually be explained quite accurately by a mean-field theory, such as the Landau–de Gennes model of the nematic-isotropic transition. However, in the immediate proximity of the phase transition the mean-field theory fails to provide a correct description of the system, the discrepancy being due to fluctuations of the order parameter [1,2]. Should the pretransitional behavior be interpreted consistently, a detailed analysis of fluctuations is, therefore, imperative.

For over a decade, considerable scientific efforts have been focused on confined liquid crystals, which are already recognized as one of the cornerstones of present and future display technologies. Regardless of the geometry of the host medium, these systems are characterized by high surface-to-volume ratio and thus very susceptible to any interaction between the constituent molecules and the surrounding walls. This interaction may result in aligning power of the walls, and in an earlier study it has been shown that an ordering substrate with a prescribed nematiclike degree of order at the surface results in a critical slowdown of fluctuations as the nematic-isotropic phase transition temperature is approached from above [3]. The slow modes have been found to be closely related to the existence of the quasine-matic wetting layer induced by the ordering action of the substrate [4].

However, the surface coupling encountered in actual confined systems is usually not strong enough to be describable by a fixed value of the degree of order at the wall, and requires a more realistic model. Second, the surface interaction may also have a disordering effect if, for example, the

inner surface of the host medium is rough [5,6]: in this case a reduction of the degree of order in the boundary layer is expected below the phase transition temperature, and the substrate induces wetting by the isotropic phase.

There are, therefore, a number of parameters of wetting in liquid-crystalline systems that seem to be pertinent to the behavior of collective excitations of the ordering in the vicinity of the nematic-isotropic phase transition. In order to provide a more complete account of the phenomenon first discussed in a preliminary study [3], some of them are elaborated theoretically in this paper by (i) comparing the spectra of fluctuations in geometries with surface-induced order and disorder, and (ii) by extending the analysis to substrates with finite strength of the surface interaction.

The phenomenological theory of the liquid-crystalline ordering used in the analysis is described in Sec. II, and in Sec. III the two relevant mean-field configurations are presented. Section IV deals with the fluctuations of the ordering in the complete wetting regime and in its vicinity. The results are summarized and discussed in Sec. V.

### II. THEORETICAL FRAMEWORK

One of the difficulties encountered in any theoretical description of confined liquid crystals is the curved or even irregular and random internal geometry of the host material, which is often not easy to model. However, in case of wetting the anchoring effect of the confining surface is either partly or completely screened, and thus the actual topology of walls is not really important: it can be expected that the basic physics of these systems can be captured by a model planar geometry consisting of a nematic liquid crystal sandwiched between two parallel substrates, which is adopted in the present analysis. Two types of walls are considered: the *disordering substrate* gives rise to an isotropic boundary layer below the nematic-isotropic phase transition temperature, where the largest part of the sample is nematic, and to perfectly isotropic phase above the transition. In case of *ordering substrate* the equilibrium configuration is nematic below  $T_{NI}$ , and above  $T_{NI}$  it remains nematic within the

boundary layer whereas the core melts into isotropic phase. The forthcoming analysis, based on the Landau–de Gennes model of the phase transition, is concentrated on the two wetting geometries, i.e., the disordering substrate below the clearing point and the ordering substrate above it.

The nematic ordering can be described by a macroscopic order parameter  $\mathbf{Q}$ , which is mathematically an irreducible tensor of rank two. As suggested by de Gennes [7], a Landau theory of the nematic-isotropic phase transition can be constructed by expanding the free energy density of the ordered phase in terms of scalar invariants of the order parameter

$$f = \frac{1}{2}A(T-T^*) \operatorname{tr} \mathbf{Q}^2 - \frac{1}{3}B \operatorname{tr} \mathbf{Q}^3 + \frac{1}{4}C(\operatorname{tr} \mathbf{Q}^2)^2 + \frac{1}{2}L \nabla \mathbf{Q} : \nabla \mathbf{Q}, \quad (1)$$

where  $A$ ,  $T^*$ ,  $B$ ,  $C$ , and  $L$  are temperature-independent material constants, and  $T$  is the temperature. (Being represented by a single elastic term, the deformational free energy is treated within the one constant approximation.) The surface free energy is modeled by

$$f_s = \frac{1}{2}G \operatorname{tr} (\mathbf{Q} - \mathbf{Q}_s)^2, \quad (2)$$

where  $G$  is the strength of the interaction and  $\mathbf{Q}_s$  is the preferred value of the order parameter tensor at the substrate, which is assumed to be homeotropic and uniaxial [8].

It is appropriate to rewrite the quantities involved into a dimensionless form. From now on, the temperature will be controlled by  $\theta = (T - T^*) / (T_{NI} - T^*)$ , where  $T_{NI} = T^* + B^2 / 27AC$  is the phase transition temperature;  $\theta = 0$  and 1 thus correspond to  $T^*$  and  $T_{NI}$ , respectively. The rescaled order parameter is measured in units of the degree of order in nematic phase at  $T_{NI}$ ,  $2B/3\sqrt{6}C$ , and the dimensionless spatial coordinates are expressed in terms of sample thickness  $d$ . The dimensionless free energy density then reads

$$f = \frac{1}{2}[\theta \operatorname{tr} \mathbf{Q}^2 - 2\sqrt{6} \operatorname{tr} \mathbf{Q}^3 + (\operatorname{tr} \mathbf{Q}^2)^2 + \zeta^2 \nabla \mathbf{Q} : \nabla \mathbf{Q}], \quad (3)$$

where  $\zeta = \sqrt{27CL/B^2d^2}$  and the gradient operator  $\nabla$  now refers to dimensionless coordinates  $x$ ,  $y$ , and  $z$ . The dimensionless surface interaction is given by  $f_s = g \operatorname{tr} (\mathbf{Q} - \mathbf{Q}_s)^2 / 2$ , where  $g = (27C/B^2d)G$ . (In the following, the reduced quantities are used exclusively; they can, therefore, be denoted by the original symbols.)

The temporal evolution of the orientational order in liquid crystals is, in principle, coupled to the translational motion of the molecules. However, the characteristic time scales of the two types of dynamics differ by two orders of magnitude, the hydrodynamic degrees of freedom being faster than the orientational ones [1]. It is, therefore, reasonable to derive an effective equation of motion of the slow variables based on the adiabatic elimination of the fast ones, and within this approximation the dissipative dynamics of the order parameter is described by the time-dependent Ginzburg-Landau model

$$-\Gamma \frac{\partial \mathbf{Q}}{\partial t} = \frac{\delta f}{\delta \mathbf{Q}}, \quad (4)$$

where  $\Gamma$  is the effective kinetic coefficient, proportional to the rotational viscosity of the material [9,10]. If spelled out,

$$\frac{\partial \mathbf{Q}}{\partial t} = -\theta \mathbf{Q} + 3\sqrt{6}\widetilde{\mathbf{Q}^2} - 2\mathbf{Q} \operatorname{tr} \mathbf{Q}^2 + \zeta^2 \nabla^2 \mathbf{Q}, \quad (5)$$

where the tilde denotes the traceless part of the tensor in question, and the kinetic coefficient has been disposed of by introducing the dimensionless time  $t \leftarrow t/\tau_a$  with  $\tau_a = (27C/B^2)\Gamma \sim 10^{-8}$  s [10].

In order to study the harmonic excitations around the equilibrium,  $\mathbf{Q}$  should be split into a mean-field and a fluctuating part

$$\mathbf{Q}(\mathbf{r}, t) = \mathbf{A}(\mathbf{r}) + \mathbf{B}(\mathbf{r}, t), \quad (6)$$

where  $\mathbf{A}$  corresponds to a (local) minimum of the total free energy of the system, whereas  $\mathbf{B}$  is governed by a linearized form of the equation of motion [Eq. (5)], which reads

$$\frac{\partial \mathbf{B}}{\partial t} = -\theta \mathbf{B} + 3\sqrt{6}(\mathbf{A} \cdot \mathbf{B} + \mathbf{B} \cdot \mathbf{A}) - 2\mathbf{B} \operatorname{tr} \mathbf{A}^2 - 4\mathbf{A} \operatorname{tr} (\mathbf{A} \cdot \mathbf{B}) + \zeta^2 \nabla^2 \mathbf{B}. \quad (7)$$

If the liquid-crystalline ordering is uniaxial, a suitable tensorial base corresponding to the five degrees of freedom of the order parameter is given by

$$\begin{aligned} \mathbf{T}_0 &= \frac{3 \mathbf{n} \otimes \mathbf{n} - \mathbf{I}}{\sqrt{6}}, \\ \mathbf{T}_1 &= \frac{\mathbf{e}_1 \otimes \mathbf{e}_1 - \mathbf{e}_2 \otimes \mathbf{e}_2}{\sqrt{2}}, \quad \mathbf{T}_{-1} = \frac{\mathbf{e}_1 \otimes \mathbf{e}_2 + \mathbf{e}_2 \otimes \mathbf{e}_1}{\sqrt{2}}, \\ \mathbf{T}_2 &= \frac{\mathbf{e}_1 \otimes \mathbf{n} + \mathbf{n} \otimes \mathbf{e}_1}{\sqrt{2}}, \quad \mathbf{T}_{-2} = \frac{\mathbf{e}_2 \otimes \mathbf{n} + \mathbf{n} \otimes \mathbf{e}_2}{\sqrt{2}}, \end{aligned} \quad (8)$$

where  $\mathbf{n}$  (the nematic director),  $\mathbf{e}_1$ , and  $\mathbf{e}_2$  form an orthonormal triad, and  $\mathbf{I}$  is the unit second rank tensor [11]. The base tensors can be interpreted as follows: the component of  $\mathbf{Q}$  along  $\mathbf{T}_0$  is equal to the sum of mean-field profile and fluctuations of the degree of order, the projections of the order parameter onto  $\mathbf{T}_{\pm 1}$  correspond to fluctuations of the degree of biaxiality and to fluctuations of the biaxial director, respectively, and their  $\mathbf{T}_{\pm 2}$  complements represent director fluctuations (Fig. 1).

The material parameters enter the above formalism through the reduced temperature  $\theta$  and through  $\zeta$ , the ratio of the bare correlation length and the sample thickness. Since the study is focused on the pretransitional behavior of fluctuations, the relevant range of  $\theta$  is centered around 1, and by setting  $\zeta$  to 0.01 the forthcoming analysis corresponds to an approximately 800 nm thick film of a typical liquid-crystalline material such as 5CB ( $A = 0.13 \times 10^6$  J/m<sup>3</sup> K,  $B = 3.89 \times 10^6$  J/m<sup>3</sup>,  $C = 3.92 \times 10^6$  J/m<sup>3</sup>,  $L = 9 \times 10^{-12}$  N [12,13]).

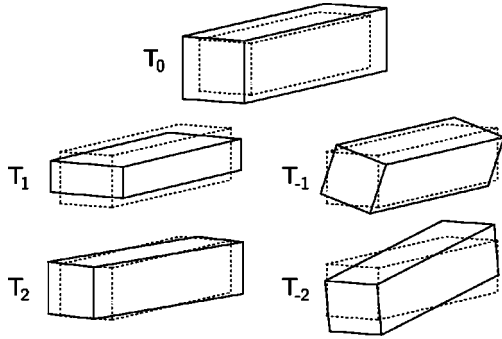


FIG. 1. A schematic representation of the five types of fluctuations of the orientational ordering visualized by a block such that the anisotropy of its sides is proportional to the eigenvalues of the order parameter. Fluctuations of the degree of order correspond to a breathing mode ( $T_0$ ); fluctuations of the degree of biaxiality simultaneously decrease one of the short sides and increase the other by the same amount ( $T_1$ ); and fluctuations of the biaxial and nematic director are identified by rotations of the box about the long ( $T_{-1}$ ) and the two short axes ( $T_{\pm 2}$ ), respectively.

### III. MEAN-FIELD STRUCTURES

To make the analysis as transparent as possible, the equilibrium director field is assumed to be uniform and homeotropic in both geometries in question. In case of disordering substrate, the orientation of the director is supposed to be maintained by the aligning action of the magnetic field. The only external force the field has to compete with is the anchoring at the nematic-isotropic interface, which induces oblique alignment of the molecules [14]. However, the strength of this interaction is very small,  $\sim 10^{-5}$  J/m<sup>2</sup>, and the director configuration can be reoriented even by a weak magnetic field ( $\sim 0.01$  T), which need not be included in the analysis explicitly. On the other hand, the homeotropic alignment in the quasineumatic boundary layer at the order-inducing wall is fixed by the anchoring.

For a uniform director field with  $\mathbf{n} = \mathbf{e}_z$ , the base tensors are uniform themselves provided that the orientation of the two arbitrary vectors  $\mathbf{e}_1$  and  $\mathbf{e}_2$  are also position-independent, e.g., identified by  $\mathbf{e}_x$  and  $\mathbf{e}_y$ . Being uniaxial, both wetting structures are thus characterized by an inhomogeneous profile of the degree of order ( $a_0$ ), which depends only on the distance from (one of) the substrates and is symmetric, whereas the other four coefficients in the expansion  $\mathbf{A} = \sum_{i=-2}^2 a_i(\mathbf{r}) \mathbf{T}_i$  are all equal to 0. The Euler-Lagrange equation, which determines the mean-field profile of  $a_0$ , reduces to

$$\zeta^2 a_0'' - \theta a_0 + 3a_0^2 - 2a_0^3 = 0, \quad (9)$$

where prime denotes  $d/dz$ . Since  $\mathbf{Q}_S$  is assumed uniaxial and homeotropic, the boundary conditions at  $z=0$  and  $z=1/2$  read

$$a_0' = g \zeta^2 (a_0 - a_{0S}) / \zeta^2 \quad (10)$$

(where  $a_{0S}$  is the preferred degree of order at the substrate) and  $a_0' = 0$ , respectively. The disordering wall is described by  $a_{0S} = 0$ , and the order-inducing substrate should be characterized by  $a_{0S} > 1$ , say,  $a_{0S} = 1.1$ .

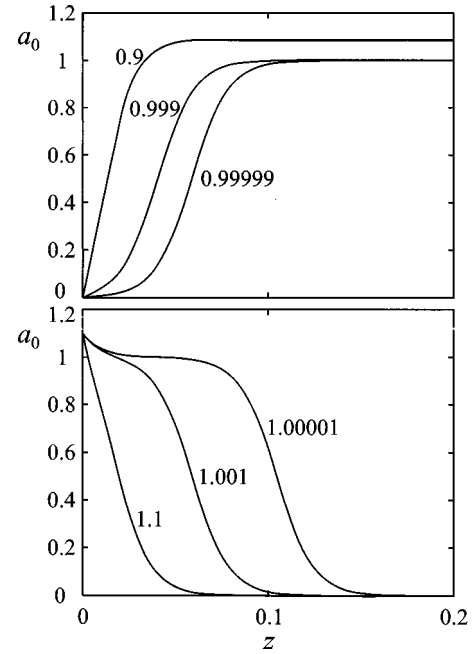


FIG. 2. Mean-field profiles of the degree of order in the vicinity of a disordering substrate at  $\theta = 1 - 10^{-1}$ ,  $1 - 10^{-3}$ , and  $1 - 10^{-5}$  (top), and an ordering substrate at  $\theta = 1 + 10^{-1}$ ,  $1 + 10^{-3}$ , and  $1 + 10^{-5}$  (bottom). In both cases, the surface interaction is modeled by a prescribed degree of order (equal to 0 and 1.1, respectively).

In both wetting geometries the mean-field profile of the degree of order exhibits a substrate-induced variation in the boundary layer and levels off at the bulk value in the center of the sample (Fig. 2). On approaching the nematic-isotropic phase transition, the thickness of the wetting layer increases and if it diverges at  $\theta_{NI}$ —which can, of course, only occur in a semi-infinite sample—the wetting is referred to as complete. On the other hand, the wetting is partial if the thickness of the substrate-induced phase remains finite at the clearing point [12].

Although the wetting behavior of liquid crystals can be quite complex [15,16], complete wetting is generally related to substrates with large (dis)ordering power, whereas otherwise partial wetting is to be expected. For the quadratic surface interaction used in the present study, complete wetting of the disordering wall occurs only if  $a_{0S} = 0$  and  $g \geq 0.02$ . In case of an order-inducing substrate the critical value of  $g$  depends on the preferred degree of order, which must exceed 1: for example,  $g_c(a_{0S} = 1.1) = 0.0053$ . These figures correspond to  $G_c \approx 0.002$  and  $6.1 \times 10^{-4}$  J/m<sup>2</sup> and are consistent with the results of an earlier study [12], based on a somewhat different type of surface interaction. To illustrate the role of the strength of the surface interaction in the wetting behavior, some mean-field profiles of the degree of order in the two geometries are shown in Fig. 3.

In a confined geometry, the transition between a surface-induced heterophase ordering and a homophase structure occurs at a temperature somewhat different from the clearing point. In case of disordering walls, the transition from the low-temperature phase characterized by molten boundary layer to the high-temperature isotropic phase is shifted below the nematic-isotropic phase transition temperature. Conversely, in the order-inducing geometry the transition from

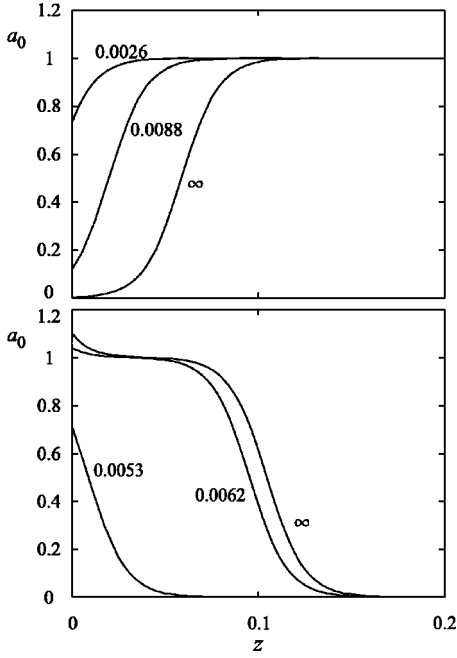


FIG. 3. Some profiles of the degree of order in the finite anchoring model: a disordering substrate at  $\theta = 1 - 10^{-5}$  (top), and an ordering substrate at  $\theta = 1 + 10^{-5}$  (bottom); the preferred degrees of order are equal to 0 and 1.1, respectively. The profiles are labeled by the reduced anchoring strength  $g$ .

nematic to paranematic phase takes place above  $\theta_{NI}$ . The actual magnitude of the shift depends on the size of the sample and on the parameters of the surface interaction, and is practically negligible in micrometer-size cavities: for example, for  $\zeta = 0.01$  and perfectly disordering (ordering) wall with  $g \rightarrow \infty$  and  $a_{0S} = 0$  (1.1), the transition occurs at  $\theta = 0.99274$  (1.0073), which indicates that the two shifts do not exceed 0.01 K. However, in smaller cavities the effect can be far more prominent [17,18].

#### IV. FLUCTUATIONS

Once the relevant mean-field structures in the two wetting geometries have been described, the scene is set for the analysis of fluctuations. The dynamics of the five scalar components of collective excitations—introduced by the expansion  $\mathbf{B}(\mathbf{r}, t) = \sum_{i=-2}^2 b_i(\mathbf{r}, t) \mathbf{T}_i$ —is derived by projecting the equation of motion [Eq. (7)] onto the base tensors. The two biaxial modes turn out to be degenerate and so are the two director modes, and since the mean-field profiles depend on the  $z$ -coordinate only, the normal modes can be factorized as follows:

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

where  $\mu_i$ 's are the dimensionless relaxation rates of the eigenmodes. Their normal components  $\beta_i$  are uncoupled and determined by

$$\begin{aligned} \zeta^2 \beta_0'' - (\theta - 6a_0 + 6a_0^2 - \lambda_0) \beta_0 &= 0, \\ \zeta^2 \beta_{\pm 1}'' - (\theta + 6a_0 + 2a_0^2 - \lambda_{\pm 1}) \beta_{\pm 1} &= 0, \\ \zeta^2 \beta_{\pm 2}'' - (\theta - 3a_0 + 2a_0^2 - \lambda_{\pm 2}) \beta_{\pm 2} &= 0, \end{aligned} \quad (12)$$

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; the in-plane components of the wave vector,  $k_x$  and  $k_y$ , are assumed to be subjected to periodic boundary conditions. In case of finite anchoring strength, the corresponding boundary condition at the substrate is given by

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

and otherwise  $\beta_i(z=0) = 0$ . Due to symmetry arguments, the normal modes must be either even [ $\beta_i'(1/2) = 0$ ] or odd [ $\beta_i(1/2) = 0$ ] with respect to the center of the sample.

Before proceeding with the analysis of fluctuations in the two wetting geometries, it is instructive to outline their behavior in homophase samples [19].

#### A. Homophase structures

In a nematic layer bounded by the walls characterized by strong surface interaction and a bulklike value of the preferred degree of order,  $\beta_i$ 's reduce to sine waves, and their relaxation rates may be cast into

$$\tilde{\lambda}_i = \xi_{N,i}^{-2} + \zeta^2[(n+1)\pi]^2, \quad (14)$$

where  $\xi_{N,i}$ 's are the (dimensionless) correlation lengths of a particular type of excitations given by

$$\begin{aligned} \xi_{N,0}^{-2} &= \frac{9}{4} \sqrt{1 - 8\theta/9} (1 + \sqrt{1 - 8\theta/9}), \\ \xi_{N,\pm 1}^{-2} &= \frac{27}{4} (1 + \sqrt{1 - 8\theta/9}), \end{aligned} \quad (15)$$

$$\xi_{N,\pm 2}^{-2} = 0.$$

The correlation length of the fluctuations of the degree of order diverges at  $\theta^* = 9/8$ , the superheating limit, whereas  $\xi_{N,\pm 1}$  remains finite in the entire range of (meta)stability of the nematic phase. On the other hand, the director modes, which are related to the broken orientational symmetry of the ordered phase, are characterized by infinite correlation length. In the vicinity of the nematic-isotropic phase transition,  $\xi_{N,0}^{-2} \approx 6 - 5\theta$  and  $\xi_{N,\pm 1}^{-2} \approx 18 - 9\theta$ .

Above the clearing point, a disordering wall produces a perfectly isotropic phase. In this case, all five types of fluctuations are degenerate, and their (dimensionless) correlation length is determined by

$$\xi_I^{-2} = \theta. \quad (16)$$

Obviously,  $\xi_I$  diverges at the supercooling limit,  $\theta^* = 0$ , where the local minimum of the free energy corresponding to the isotropic phase ceases to exist.

The hardness of a given type of fluctuations can be characterized by its correlation length: the shorter the correlation length, the higher the energy of fluctuations. To understand the pretransitional behavior of the system, it is important to know how the energy levels of excitations in nematic phase compare with those in isotropic phase. In the vicinity of the phase transition, fluctuations of the degree of order are equally hard in both phases; in nematic phase, the biaxial

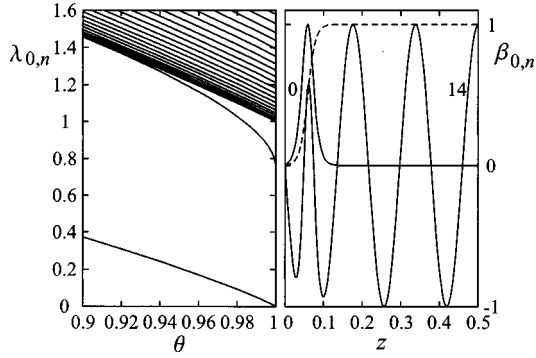


FIG. 4. Disordering substrate: spectrum of fluctuations of the degree of order (left), illustrated by the portraits of a few typical modes labeled by the number of nodes (right;  $\theta = 1 - 10^{-5}$ ). The lowest mode characterized by soft dispersion of the relaxation rate corresponds to fluctuations of the thickness of the wetting layer, whereas the upper part of the spectrum is basically the same as in the purely nematic sample and disturbs the whole of the sample. Dashed line: mean-field profile of the degree of order;  $g \rightarrow \infty$ .

modes are energetically far more costly than in isotropic phase — as opposed to the director modes, which are characterized by an infinite correlation length in nematic phase, whereas  $\xi_l$  is finite at the phase transition temperature.

## B. Heterophase ordering

Due to surface-induced inhomogeneity of the profile of the degree of order, the eigenmodes of fluctuations in the two wetting geometries can only be determined numerically. In the following the spectra of collective excitations in nematic phase with molten boundary layers and in paranematic phase are interpreted simultaneously.

### 1. Fluctuations of degree of order

In both systems, the primary effect of wetting is related to the existence of a slow mode characterized by soft dispersion of its relaxation rate, whereas the upper part of the spectrum remains more or less the same as in homophase system (Figs.

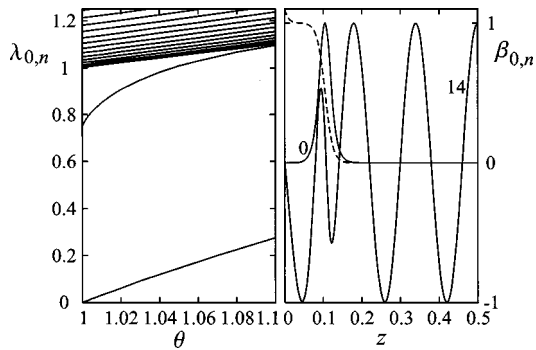


FIG. 5. Ordering substrate: relaxation rates of fluctuations of the degree of order in paranematic phase (left), and some typical modes (right;  $\theta = 1 + 10^{-5}$ ). As in Fig. 4, the soft mode represents fluctuations of the thickness of the wetting layer, and the upper part of the spectrum is more or less the same as in perfectly isotropic sample, which is also reflected in the sinusoidal behavior of  $\beta_{0,n>1}(z)$ . Again, the mean-field profile of the degree of order is plotted with the dashed line;  $g \rightarrow \infty$ .

4 and 5). The elementary mode of fluctuations of the degree of order is localized at the phase boundary between the wetting layer and the bulk phase, and since it is even with respect to the center of the sample, it corresponds to fluctuations of thickness of the central part of the slab. Similarly, the lowest odd mode—also localized at the nematic-isotropic interface—represents fluctuations of position of the core. However, the relaxation rates of these two modes are the same within numerical accuracy, indicating that the two wetting layers are effectively uncoupled. This is directly related to the thickness of the sample, which is much larger than  $\xi_{N,0}$ , the typical length scale of the variation of the degree of order. Were the system thinner, the correlation between the (dis)ordered regions induced by the two substrates would be stronger and the degeneracy of the lowest two normal modes would be removed.

In the complete wetting regime, the relaxation rate of the elementary excitations of the degree of order exhibits a linear critical temperature dependence typical for soft modes:

$$\lambda_{0,0} = \pm C_{\pm}(\theta - 1), \quad (17)$$

where “−” and “+” correspond to nematic phase with molten boundary layer and paranematic phase, respectively. (The difference between the coefficients  $C_-$  and  $C_+$ , which are approximately equal to 5.6 and 3.0, can be attributed to the fact that the thickness of the isotropic wetting layer at the disordering wall at  $\theta = 1 - \delta$  is half of the thickness of the nematic wetting layer at the ordering substrate at  $\theta = 1 + \delta$  [20].) The slowdown of the relaxation rates of the surface-induced soft modes (i.e., the divergence of their relaxation times) at the phase transition temperature is a well-known and clear signature of the continuity of the transition, which is actually just another face of the advancing phase boundary in any complete wetting geometry [4,21]. In a finite system, however, a wetting-driven phase transition can never be truly continuous, because the heterophase configuration eventually becomes unstable in the immediate vicinity of the clearing point—but in samples of thickness  $\geq 100$  nm this effect is detectable only if the temperature resolution of the experimental method is better than, say, 0.01 K.

In both wetting geometries, the upper part of the spectrum is more or less the same as its homophase (i.e., nematic and isotropic) counterpart, which is reflected in its regularity as well as in the sinusoidal profiles of the normal modes (Figs. 4 and 5). This also means that the upper, quasihomophase modes are more or less independent on the strength of the surface interaction (which has been verified numerically). On the other hand, the behavior of the wetting-induced elementary mode does depend strongly on the magnitude of  $g$ : if the wetting is partial instead of complete, the pretransitional decrease of the localized modes’ relaxation rates is less pronounced. They do not drop to 0 but remain finite at  $\theta_{NI} = 1$ , so that the transition from surface-molten nematic to isotropic phase (or from nematic to paranematic phase) is discontinuous even in semi-infinite systems, although the corresponding latent heat may be reduced considerably compared to the bulk nematic-isotropic transition. However, the temperature variation of the relaxation rates of the lowest modes remains linear, implying that the underlying mechanism is basically the same as in the complete wetting geometry.

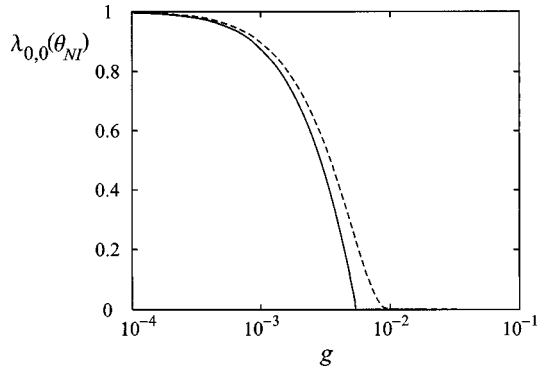


FIG. 6. Relaxation rate of fluctuations of the thickness of the boundary layer in disordering (dashed line) and ordering wetting geometry (solid line) as a function of the strength of the surface interaction. In both cases,  $\lambda_{0,0}$  is finite for  $g < g_c$  (partial wetting) and 0 otherwise (complete wetting), the critical values of  $g$  being equal to 0.018 (disordering substrate) and 0.0053 (order-inducing wall). Note that the two geometries differ in the type of the behavior of  $\lambda_{0,0}$  in the vicinity of  $g_c$ .

These findings are quantitatively summarized in Fig. 6, where the lowest mode's relaxation rate at the nematic-isotropic phase transition temperature is plotted as a function of the anchoring strength. In the partial wetting regime, which corresponds to small  $g$ 's,  $\lambda_{0,0}$  is finite; in the complete wetting regime, on the other hand, it is (within numerical accuracy) equal to 0. The two geometries give rise to slightly different behavior of  $\lambda_{0,0}$  in the vicinity of the critical strength of the surface interaction: in the case of a disordering wall,  $\lambda_{0,0}$  approaches 0 somewhat more slowly than in the case of an order-inducing wall.

In addition to the two elementary modes corresponding to fluctuations of thickness of the boundary layers, there are actually two more localized modes with relaxation rates that do depart from the quasihomophase spectrum—although not as distinctly as the soft dispersion of  $\lambda_{0,0}$ . These modes represent fluctuations of the shape of the phase boundaries: the even one is related to simultaneous sharpening/flattening of the phase boundaries, whereas the odd one describes out-of-phase fluctuations of their slope. The relaxation rates of these two modes are degenerate, which is, as it has already been established, related to the fact that the system considered is rather thick, so that the correlation between the two wetting layers is very weak.

There are, therefore, two localized modes associated to each interface between nematic and isotropic phase: one of them corresponds to fluctuations of the position of the phase boundary, and the other one changes its profile. Since the theoretical approach used in this analysis is quite universal in its very nature, it seems that the same should hold true for any interface that can be described by a scalar variable. However, in case of a phase boundary with a more complex structure, additional and more sophisticated localized modes are expected.

## 2. Biaxial and director fluctuations

As the mean-field structures discussed are characterized by inhomogeneous profiles of the degree of order and homogeneous profiles of the degree of biaxiality and director

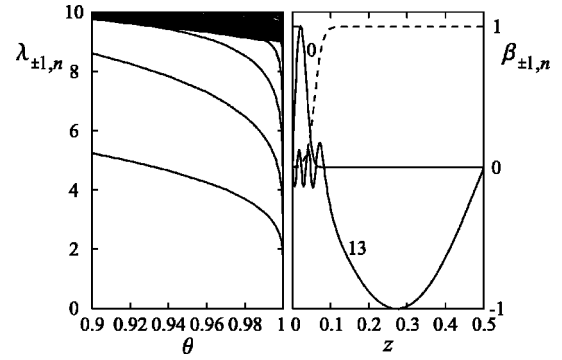


FIG. 7. Biaxial modes in a nematic sample bounded by disordering substrates: the lowest modes exhibit pretransitional slow-down on approaching the clearing point (left) and are confined to the isotropic wetting layer (right;  $\theta = 1 - 10^{-5}$ ). The upper part of the spectrum is more or less nematiclike, the modes being spread over the whole slab.

fields, the wetting-specific dynamics must be primarily related to fluctuations of the degree of order. On the other hand, any critical behavior of the biaxial and director modes should be merely an indirect effect of the surface-induced heterophase ordering.

*Biaxial modes* are the hardest type of fluctuations in uniaxial nematic phase, which is related to the fact that thermal excitations of transverse molecular order have to compete with the existing uniaxial alignment. (In systems with intrinsic biaxiality, biaxial fluctuations are expected to be much softer.) At the phase transition temperature, the lower limit of their relaxation rates in nematic phase is nine times larger than in isotropic phase [Eqs. (15) and (16)], and this considerable difference in the energy levels of biaxial modes in the two phases is reflected in their spectra in the two wetting geometries.

In the case of nematic phase confined by a disordering wall, the lowest modes are bounded to the isotropic wetting layer; obviously, a strong elastic deformation of the modes in the thin isotropic region of the sample is energetically more favorable than a moderate deformation in the thick nematic core (Fig. 7). The number of these modes depends on the thickness of the wetting layer and, thus, on temperature: as the sample is heated towards the clearing point, more and more levels depart from the upper, nematiclike part of the spectrum, which corresponds to modes that disturb the whole of the sample.

In paranematic phase induced by the ordering substrate, biaxial fluctuations are, conversely, expelled from the ordered boundary layer (Fig. 8), so that the allowed wavelengths of the normal modes are determined by the thickness of the central isotropic part, not by the actual thickness of the sample. The difference between these two is not significant except in the vicinity of the phase transition temperature, where the nematic wetting layers squeeze the isotropic core and speed up the relaxation rates of the biaxial modes.

*Director modes* are, as opposed to biaxial fluctuations, excited very easily in nematic phase, where their Hamiltonian is purely elastic, whereas in isotropic phase they are characterized by finite correlation length [Eq. (16)]. This implies that their wetting-induced behavior should be quite the inverse of what is predicted for the biaxial modes.

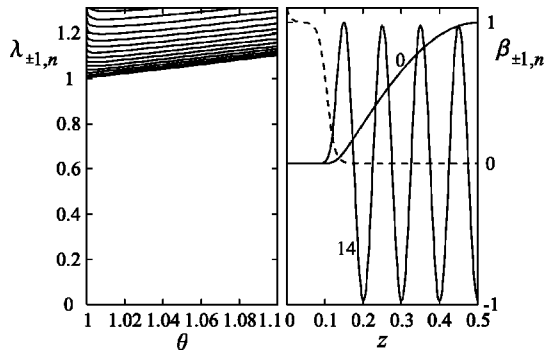


FIG. 8. Biaxial modes in paranematic phase are all expelled from the quasinematic boundary layer (right;  $\theta = 1 + 10^{-5}$ ), and in the immediate vicinity of  $\theta_{NI}$  their relaxation rates must therefore increase along with the thickness of the boundary layer (left).

In the disordering geometry, for example, the director modes are forced out of the substrate-induced isotropic boundary layer into the nematic core (Fig. 9) just like the biaxial modes are expelled from the nematic boundary layer into the isotropic core of the paranematic phase induced by the ordering substrate. Far from the phase transition temperature, their relaxation rates are temperature-independent, whereas in the vicinity of the clearing point they all increase because of rapid growth of the wetting layer.

In paranematic phase a few lowest director modes are confined to the nematic boundary layer, whereas the upper ones extend over the whole sample and are more or less the same as in perfectly isotropic phase (Fig. 10). The relaxation rates of the lowest modes exhibit a cusplike slowdown similar to that observed in biaxial modes in a disordering geometry (Fig. 7). Moreover, their pretransitional slowdown resulting from the increase of the thickness of the wetting layer is actually critical, since in this case the fluctuations confined to the wetting layer are Goldstone modes.

The results discussed correspond to infinitely strong surface interaction. How do they change if this constraint is relaxed, i.e.,  $g < \infty$ ? For  $g$ 's which are large enough to induce complete wetting, the spectra of fluctuations remain qualitatively the same, whereas otherwise the slow modes are no longer critical. Eventually, if the strength of the surface interaction is very weak, all fluctuations become cosinelike and their spectrum is described by Eqs. (14), (15), and (16).

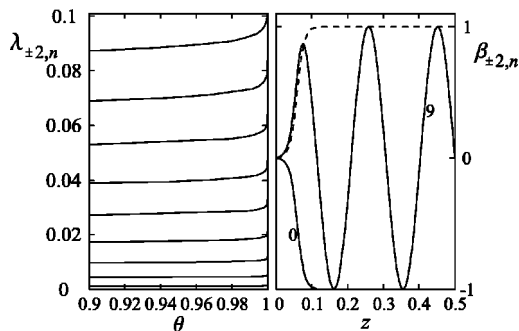


FIG. 9. Director modes in a nematic sample bounded by disordering substrates: director fluctuations are forced out of the boundary layer (right;  $\theta = 1 - 10^{-5}$ ) and must speed up on approaching the clearing point (left), just like the biaxial modes in paranematic phase (Fig. 8).

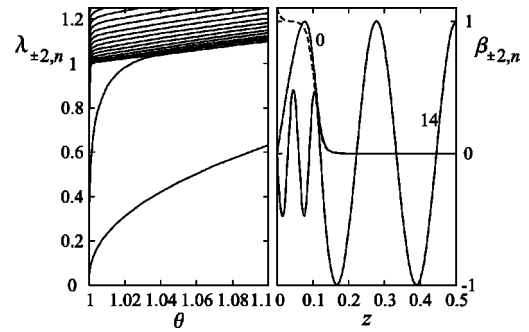


FIG. 10. Director modes in paranematic phase: the relaxation rates of the lowest modes, which are restricted to the nematic wetting layer (right;  $\theta = 1 + 10^{-5}$ ), decrease to 0 as  $\theta \rightarrow 1$  (left) due to the growth of the wetting layer (cf. Fig. 8).

## V. CONCLUSION

The analysis has revealed a close relationship between the wetting regime induced by (dis)ordering substrates and the pretransitional behavior of thermal fluctuations of the ordering in confined liquid crystals. In case of disordering action of the bounding surface, a heterophase structure consisting of an isotropic wetting layer and a nematic core occurs below the nematic-isotropic phase transition temperature, whereas a substrate with an ordering power stabilizes a quasinematic boundary layer even at temperatures well above the clearing point where the central part of the sample is isotropic. Both geometries are characterized by a wetting-induced interface between nematic and isotropic phase, which gives rise to two localized normal modes: the first one represents fluctuations of the position of the phase boundary and is characterized by a soft dispersion of its relaxation rate (provided that the wetting is complete), and the second one corresponds to fluctuations of the shape of the interface. Moreover, there are a few additional slow modes, which are restricted to the wetting layer and whose pretransitional behavior is related to its growth: an isotropic boundary layer accommodates the lowest biaxial modes, whereas the lowest director modes are constrained within the nematic boundary layer. If the wetting is partial, the slowdown of the localized modes is not as pronounced as in the complete wetting regime, but the underlying physics remains the same.

The wetting-induced pretransitional behavior of the fluctuations of the liquid-crystalline ordering is certainly not limited to geometries discussed in this study. For example, a similar phenomenon is expected in nematic and isotropic samples with substrate-stabilized smectic boundary layer [22,23], which should exhibit critical slowdown in the vicinity of the smectic-nematic and smectic-isotropic phase transition, respectively. This effect is probably quite ubiquitous because some smectic order is induced by any solid wall — at least by its impenetrability and the corresponding broken translational symmetry of nematic or isotropic phase. But the analogy with the substrate-stabilized nematic layer above the nematic-isotropic phase transition is not complete due to layered structure of the smectic ordering, which presumably gives rise to nontrivial features of the wetting-induced fluctuations in this system.

It seems possible that the effect described here has already been detected experimentally in some microconfined liquid-crystalline systems, where a huge increase of the de-

cay time of fluctuations has been observed in the vicinity of nematic-isotropic [24] and smectic *A*–nematic phase transition [25]. However, conclusive evidence can only be provided by a detailed and comprehensive analysis of the existing data or by an experiment designed to probe the dynamics within the boundary layer, which could be based on, for example, the evanescent light scattering technique [26].

The results of the study can be extrapolated beyond the geometries discussed once it has been realized that the slow dynamics of the localized modes is actually directly related to the existence of the phase boundary and that the wetting itself is merely a mechanism that introduces a heterophase structure—and, therefore, a phase boundary—into the system. In confined liquid crystals, heterophase ordering is very often induced by topological constraints imposed by curved walls, which result in singularities of the director field, where very strong elastic deformation of the nematic phase is

avoided by reducing the degree of order. Since the disordered regions called defects are more complex than the planar nematic-isotropic interface [27–29], they should be accompanied by several localized modes related to fluctuations of their structure as well as those corresponding to fluctuations of their size, position, and shape. This indicates that the defects should be considered as possible generators of slow nondirector fluctuations in confined liquid crystals.

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