Fluctuation modes in confined nematic liquid crystals in a regime of critical wetting

N. B. Ivanov
Institute for Solid State Physics, Bulgarian Academy of Sciences, Tzarigradsko chaussee-72, 1784 Sofia, Bulgaria
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Analytic solutions are obtained for the energies of normal fluctuation modes in confined nematic liquid crystals in a regime of critical wetting. The expressions are valid close enough to the nematic-isotropic phase-transition temperature and demonstrate that the spectra of local director modes give direct information about the nature of presurface forces and the criticality by itself. The possible changes in the spectra imposed by interface-position fluctuations and order-electricity effects are also discussed. [S1063-651X(99)10711-6]

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Recently, Žumer and co-workers have studied the dynamics of normal fluctuations near the nematic-isotropic phase-transition temperature T_{NI} in nematic liquid crystals sandwiched between two parallel ordering (or disordering) substrates [1]. Apart from the well-known soft scalar order-parameter modes, reflecting the interface position fluctuations, their numerical analysis also indicated a few director modes restricted to the boundary layers: uniaxial director modes in the case of ordering substrates, and biaxial director modes in the case of disordering substrates. In a regime of critical wetting both types of local director modes exhibit pretransitional slowdown. In this Brief Report we present analytic results valid close enough to T_{NI} for the energies of local director modes and discuss the role of order electricity and critical interface-position fluctuations.

In a macroscopic Landau–de Gennes description [2] the surface free-energy potential in a single elastic-constant approximation can be recasted to the following form:

$$F_s[\mathbf{S}]=LQ_c^2\int dxdy\int_0^\infty dz\left\{\frac{1}{2}(\partial_\alpha S_{\beta\gamma})^2+\frac{1}{\xi_0^2}[f(\mathbf{S})-f(\mathbf{S}_b)]+\delta(z)f_0(\mathbf{S})\right\}, \tag{1}$$

where $f(\mathbf{S})=(1+\tau)\mathrm{tr}\,\mathbf{S}^2/2-\sqrt{6}\,\mathrm{tr}\,\mathbf{S}^3+[\mathrm{tr}\,\mathbf{S}^2]^2/2$ is the uniform free-energy potential. The following reduced quantities are used in the above expression: (i) the reduced tensor order parameter $\mathbf{S}\equiv\mathbf{Q}/Q_c$, where $Q_c=2b/3\sqrt{6}c$ is the value of the scalar order parameter Q at $T_{NI}=T^*+b^2/27\alpha c$; (ii) the reduced temperature $\tau=(T-T_{NI})/(T_{NI}-T^*)$. The liquid crystal is assumed to occupy the semi-infinite space $z>0$, z being the coordinate normal to the surface. $\mathbf{S}_b=\mathbf{S}_b(\tau)$ is the order parameter deeply in the bulk ($z\to\infty$). $\xi_0=\sqrt{L/\alpha(T_{NI}-T^*)}$ is the correlation length of the isotropic phase at coexistence. L is an elastic constant, and $a\equiv\alpha(T-T^*)$. The material constants α, b, and c are positive and temperature independent. T^* is the supercooling temperature for the bulk isotropic phase. The short-ranged substrate potential $f_0(\mathbf{S})$ is modeled by the expression $f_0(\mathbf{S})=a_s\,\mathrm{tr}(\mathbf{S}-\mathbf{S}_s)^2/2$ [3], where $\mathbf{S}_s=u_s(3\mathbf{n}_s\otimes\mathbf{n}_s-1)/\sqrt{6}$ is a symmetric traceless second-rank tensor characterizing the substrate, and a_s is a phenomenological constant. u_s and $\mathbf{n}_s$ are the scalar order parameter and the director orientation preferred at the surface. We consider uniform director configurations, i.e., $\mathbf{S}_0(z)=u(z)(3\mathbf{n}_0\otimes\mathbf{n}_0-\mathbf{1})/\sqrt{6}$, where $\mathbf{n}_0$ is the constant nematic director (normal to the substrate) and $u(z)$ is the scalar order-parameter profile. Above T_{NI} the function $u(z)$ is known to be [4]

$$u(z)=\frac{1+\tau}{1+\sqrt{\tau}\sinh(z/\xi_I+\alpha_I)}, \tag{2}$$

where $\alpha_I=\mathrm{arcsinh}\{[(1+\tau)/u_0-1]/\sqrt{\tau}\}$. $\xi_I=\xi_0/\sqrt{1+\tau}$ is the correlation length in the isotropic phase, $u_0\equiv u(0)$. On the other hand, below T_{NI} one finds

$$u(z)=u_b-\frac{3u_b-2(1+\tau)}{2u_b-1-\sqrt{u_b-1}\sinh[\mathrm{sgn}(u_0-u_b)z/\xi_N+\alpha_N]}, \tag{3}$$

where $\alpha_N=\mathrm{arcsinh}\{[2u_b-1+(3u_b-2\tau-2)/(u_0-u_b)]/\sqrt{u_b-1}\}$ and $u_b(\tau)=3/4+\sqrt{1-8\tau}/4$. $\xi_N\equiv d^2f(u_b)/du_b^2=\xi_0/\sqrt{3u_b-2(1+\tau)}$ is the correlation length in the nematic phase.

For $\tau>0$ the profile $u(z)$ describes a paranematic layer, whereas the bulk is occupied by the isotropic phase (Fig. 1). For large enough u_0, $u(z)$ has an inflection point at $z=d_I$ marking the center of the nematic-isotropic interface. Below

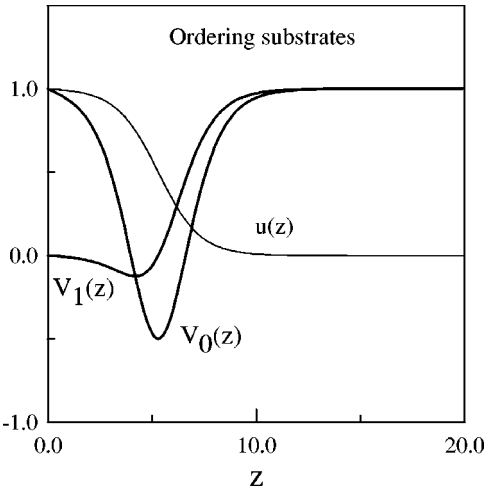

FIG. 1. Potentials from Eq. (4) for ordering substrates at $\tau=0.0001$. ξ_0 is used as a unit length for the z coordinate.

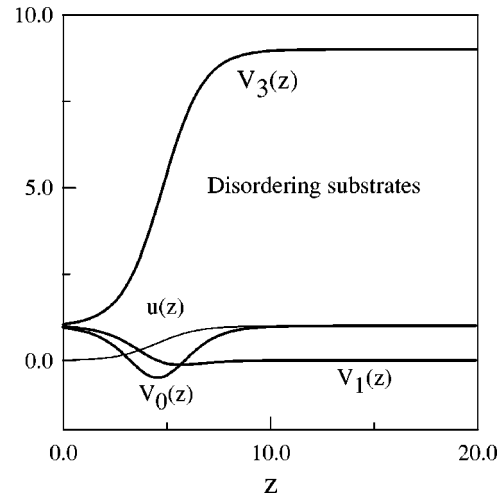

FIG. 2. Potentials from Eq. (4) for disordering substrates at $\tau = -0.0001$. ξ_0 is used as a unit length for the z coordinate.

T_{NI} and for $u_0 < u_b$ the surface layer is less ordered as compared to the bulk. The profile has an inflection point at $z = d_N$ marking the interface position (Fig. 2). The above profile functions can be used to describe the surface phase diagrams [5]. Here we just note that for the special cases of ordering substrates, which are described by the condition $a_s \to +\infty$, a complete wetting regime is realized for $u_s \geqslant 1$ and $\tau \to 0^+$, whereas for the special case of disordering substrates, described by the condition $u_s = 0$, the isotropic phase wets completely the wall for $a_s \geqslant \xi_0^{-1}$ and $\tau \to 0^-$. The latter case is more interesting in the sense that now the surface order parameter u_0 is not pinned by the surface forces and it changes with the temperature as $u_0(\tau) = |\tau|^{1/2}/\sqrt{\xi_0^2 a_s^2 - 1} + O(|\tau|)$. This additional surface criticality takes place simultaneously with the critical interface delocalization.

Fluctuation modes. Using the decomposition $\mathbf{S}(\mathbf{r}) = \mathbf{S}_0(z) + \boldsymbol{\phi}(\mathbf{r})$, and the parametrization of the tensor fluctuation field by the base tensors $\mathbf{g}_i$, $i = 0, \ldots, 4$ [6], i.e., $\boldsymbol{\phi}(\mathbf{r}) = \Sigma_{i=0}^{4} \phi_i(\mathbf{r}) \mathbf{g}_i$, one obtains the following Schrödinger-type eigenmode equations:

$$\left[-\xi_0^2 \frac{d^2}{dz^2} + V_i(z) \right] \phi_i(z) = E_i \phi_i(z), \quad i = 0, \ldots, 4, \quad (4)$$

where the functions $V_0(z) = 1 + \tau - 6u(z) + 6u(z)^2$, $V_1(z) = V_2(z) = 1 + \tau - 3u(z) + 2u(z)^2$, and $V_3(z) = V_4(z) = 1 + \tau + 6u(z) + 2u(z)^2$ may be thought of as potential energies in a related quantum-mechanical problem. The profile function $u(z)$ is defined by Eqs. (2) and (3). The variable $\phi_0(\mathbf{r})$ describes *longitudinal* scalar order-parameter fluctuations, whereas the pair variables $[\phi_1(\mathbf{r}), \phi_2(\mathbf{r})]$ and $[\phi_3(\mathbf{r}), \phi_4(\mathbf{r})]$ are connected to the *transverse* uniaxial and biaxial director fluctuations, respectively.

In what follows we study the eigenvalue problem just for the special cases of ordering and disordering substrates specified above. In the first case the fluctuation modes are pinned at the surface, i.e., $\phi_i(z)|_{z=0} = 0$, $i = 1, \ldots, 4$, and there are two types of local excitations related to the potential wells shown in Fig. 1. The first one is the lowest soft mode $\phi_0^{(0)}(z)$ characterized by an energy $E_0^{(0)}(\tau) \propto \tau$ and related to the scalar order-parameter field. This mode describes fluctuations of the mean-field interface position located at $z = d_I$. Physically, this excitation appears as a result of the broken translational symmetry $[u(z) \neq 0]$ and its existence is a typical feature of the critical wetting transition. The second type of localized modes discussed in Ref. [1] is connected with the uniaxial director fluctuation fields $\phi_1(z)$ and $\phi_2(z)$. In a vicinity of T_{NI} the uniaxial modes soften and become gapless at T_{NI}. These features of the local uniaxial director excitations can easily be obtained analytically in the limit $\tau \to 0^+$. At a mean-field level the interface width is much smaller than the layer thickness $d_I \simeq \xi_0 \ln(1/\tau)$, so that the region $0 < z < d_I$ can be thought of as a nematic plate of width d_I. In the same limit $\tau \to 0^+$ for the low-energy excitations one can use the following square-well potential $V_1(z)$ (see Fig. 1): $V_1(z) = 0$, if $0 < z < d_I$, and $V_1(z) = 1$, if $z > d_I$. Thus, using the continuity of the logarithmic derivative of the field $\phi_1(z)$ at $z = d_I$, one finds the excitation energies $E_1^{(n)} = \xi_0^2 k_n^2$. The parameters k_n satisfy the implicit equation

$$k_n d_I = \pi n - \arcsin(k_n \xi_0), \quad n = 1,2, \ldots, n_{max}, \quad (5)$$

where the number of localized modes n_{max} is finite and fixed by the condition $0 \leqslant k_n \xi_0 \leqslant 1$: it depends on the reduced temperature τ since $d_I = d_I(\tau)$. In the limit $\tau \to 0^+$, when $d_I \simeq \xi_0 \ln(1/\tau)$, the excitation energies $E_1^{(n)}$ take the following asymptotic form:

$$E_1^{(n)} \simeq \frac{\pi^2 n^2}{\ln^2(1/\tau)}, \quad n = 1,2, \ldots, n_{max}. \quad (6)$$

This expression is in agreement with the numerical results of Ref. [1] and reproduces, in particular, the observed cusplike behavior of the low-lying energy levels. We see that the low-energy levels give a direct information about the logarithmically divergent interface position, $d_I \simeq \xi_0 \ln(1/\tau)$. The latter critical behavior is characteristic for short-range substrate interaction, and in the case of long-range presurface forces it is, in principle, changed (see Ref. [7] and the references therein). Therefore, the above excitation spectra can give a valuable information about both the nature of presurface forces and the criticality by itself.

In the second limiting case of disordering substrates the complete wetting regime is realized for $a_s \geqslant \xi_0^{-1}$ as $\tau \to 0^-$. Now it is the isotropic phase which wets the wall and the presurface layer of thickness $d_N = d_N(\tau)$ may be considered as a plate occupied by the isotropic phase. Due to the fact that biaxial director fluctuations are strongly suppressed in the bulk nematic phase, there is a well in the potential function $V_3(z)$ (see Fig. 2). The potential well is located in the presurface quasi-isotropic domain with a characteristic thickness d_N. Thus, in the case of disordering substrates bound biaxial director modes appear. On the other hand, the uniaxial director modes, being gapless Goldstone modes in the bulk nematic phase, are controlled by the monotonically decreasing potential $V_1(z)$ so that they will be delocalized all over the sample. In a vicinity of T_{NI} the low-energy levels of the local biaxial modes can easily be obtained by use of the same procedure. Now the potential $V_3(z)$ is simplified as $V_3(z) = 1$ for $0 < z < d_N$, and $V_3(z) = 9$ for $z > d_N$. The

boundary condition at $z=0$ for the biaxial field $\phi_3(z)$ reads $d\phi_3(0)/dz=a_s\phi_3(0)$. One finds the excitation energies $E_3^{(n)}=1+\xi_0^2k_n^2$, where the parameters k_n now satisfy the equation

$$k_n d_N=\pi n-\arcsin\left(\frac{\xi_0 k_n}{2\sqrt{2}}\right)-\arcsin\left(\frac{k_n}{\sqrt{k_n^2+a_s^2}}\right), \qquad (7)$$

where $n=1,2,\ldots,n_{max}$. The number of localized modes n_{max} is fixed by the condition $0\leqslant k_n\xi_0/2\sqrt{2}\leqslant 1$. Using $d_N\simeq\xi_0\ln(1/|\tau|)$, one gets for $\tau\to 0^-$

$$E_3^{(n)}=1+\frac{\pi^2n^2}{\ln^2(1/|\tau|)}, \quad n=1,2,\ldots,n_{max}. \qquad (8)$$

We see that in the limit $\tau\to 0^-$ the local biaxial modes are strongly softened as compared to the bulk biaxial fluctuations in the nematic phase. For every n the energies $E_3^{(n)}$ change from $E_3^{(n)}=9$ (the gap in the bulk nematic phase) to $E_3^{(n)}=1$ (the gap in the bulk isotropic phase).

Role of the interface-position fluctuations. Since the upper critical spatial dimension for a critical wetting transition is $D=3$, higher order fluctuation effects are not excluded. Indeed, the singular part of the mean-field free energy in a regime of complete wetting behaves like $f_s^{sing}\propto-\tau\ln(\tau)$. On the other hand, the one-loop fluctuation contribution to the free energy is related to the lowest soft mode $\phi_0^{(0)}(z)$ since the energies of the excited states of Eq. (4) are separated from $E_0^{(0)}$ with a finite gap. Using this fact, it is easy to see that the fluctuation part of the free energy is $f_s^{fl}(\tau)\propto -E_0^{(0)}\ln(E_0^{(0)})\sim-\tau\ln(\tau)$, so that it compares to the singular part of the mean-field free energy [8,9]. Since for uniform-director configurations the scalar order-parameter field $\phi_0(\mathbf{r})$ is decoupled from the director fields, most of the results known from the scalar theory [10] can be applied to nematic systems without changes. However, the fluctuation mode $\phi_0^{(0)}$ can effectively disturb the studied local director excitations. It is easy to see this qualitatively if we remember some of the fluctuation effects connected to the soft mode $\phi_0^{(0)}(z)$, originally obtained in a context of the scalar order-parameter theory. At the first place, it can be shown that this mode produces singularities in the correlation function $\langle\phi_0(\mathbf{r}_\perp,z_1)\phi_0(\mathbf{0},z_2)\rangle\sim\exp(-r_\perp/\xi_\parallel)\phi_0^{(0)}(z_1)\phi_0^{(0)}(z_2)$, where $\xi_\parallel=1/\sqrt{E_0^{(0)}}\propto 1/\sqrt{\tau}$ is the characteristic length of the scalar order-parameter correlations parallel to the surface. Thus, there are critical long-range correlations of the scalar order-parameter fluctuations parallel to the surface (capillary waves). Another criticality connected to $\phi_0^{(0)}(z)$ is the predicted divergence of the interfacial width. Denoting by $d_I(\mathbf{r}_\perp)=d_I+\zeta(\mathbf{r}_\perp)$ the local interface position, it can be shown that the characteristic interface thickness $\xi_\perp\equiv\sqrt{\langle\zeta^2\rangle}$ diverges as $\tau\to 0^+$ according to the asymptotic form $\xi_\perp\propto\ln\xi_\parallel\propto\sqrt{d_I}$ [9]. The critical increase of the effective interface width will effectively change the potential $V_1(z)$ which controls the director excitation spectrum. On the other hand, the treatment of the local fluctuation modes used throughout the paper remains valid, since close enough to T_{NI} the effective interfacial width will be much smaller than the characteristic domain thickness.

Order-electricity effects. There is a series of issues which might invalidate the uniform-director appoximation suggested in the above analysis [11]. The order electricity [12,13] belongs to this series. Since the nematic-isotropic interface is characterized by a strong variation of the scalar order parameter, one can expect that the order electricity will play an important role in the wetting phenomena. Let us concentrate on the case of ordering substrates when the nematic director is strongly anchored along the normal to the surface. The inhomogeneity in the profile function $u(z)$, Eq. (2), generates along the axis z the electric polarization field $P_o^z=(r_1n_{0z}^2+r_2)(du/dz)$, where r_1 and r_2 are the order-electric coefficients [13]. Denoting by θ the polar angle of the director $\mathbf{n_0}=(\sin\theta,0,\cos\theta)$, it is easy to see that $\theta=\theta(z)$, since the free-energy density term f_o, connected with P_o^z, mixes $\mathbf{n_0}$ and du/dz:

$$f_o=-\frac{1}{2}P_o^zE_o^z=\frac{2\pi}{\epsilon_{zz}(\theta)}(r_1\cos^2\theta+r_2)^2\left(\frac{du}{dz}\right)^2. \qquad (9)$$

Here $\epsilon_{zz}(\theta)=\epsilon_\perp+(\epsilon_\parallel-\epsilon_\perp)\cos^2\theta$ is the zz component of the dielectric tensor and E_o^z is the z component of the induced electric field. Combining the last equation with the elastic term in Eq. (1), one finds that the elastic constant L in Eq. (1) is effectively renormalized as $L\to L_{eff}(\theta)=L+[4\pi/\epsilon_{zz}(\theta)](r_1\cos^2\theta+r_2)^2$. To find the function $\theta(z)$ we will follow the arguments of Ref. [13], applicable in our case for $\tau\to 0^+$. The Euler-Lagrange equation for the polar angle θ, as obtained from Eq. (1), reads

$$\frac{d^2\theta}{dz^2}=\frac{1}{6Lu^2}\frac{dL_{eff}}{d\theta}\left(\frac{du}{dz}\right)^2. \qquad (10)$$

Since du/dz is a δ-like function centered at $z=d_I$, the function $\theta(z)$ can be approximated with a linear function in the region $0<z<d_I$, excluding the vicinity of the interface and, possibly, of the surface. Since the interfacial energy is proportional to $L_{eff}^{1/2}$, the minimum condition for this energy $dL_{eff}/d\theta=0$ also defines the average polar angle at the interface θ_0 [14]. We do not consider here possible deviations from the linear behavior of $\theta(z)$ close to the substrate [15]. Therefore, as $\tau\to 0^+$ the inhomogeneous director state is characterized by the polar angle

$$\theta(z)=\theta_0\frac{z}{d_I}\simeq\theta_0\frac{z}{\xi_0}\frac{1}{\ln(1/\tau)}, \quad \tau\to 0^+, \quad z\leqslant d_I. \qquad (11)$$

The inhomogeneous director state described above can generate several changes in the fluctuation mode dynamics. Since the local base tensors are now coordinate dependent, $\mathbf{g}_i=\mathbf{g}_i(z)$, the normal mode equations (4) are coupled. In particular, there is a coupling between the longitudinal scalar order-parameter field $\phi_0(z)$ and the transverse director fluctuations $\phi_2(z)$ and $\phi_3(z)$. The mode coupling is, however, asymptotically small, as it is controlled by the small parameter $\xi_0/d_I\propto\ln^{-1}(1/\tau)$. Since the interaction decreases logarithmically , the mode coupling due to order-electricity effects can play an important role in real experiments.

In conclusion, the above analysis shows that the spectra of local director modes can give a direct information about the nature of presurface forces and the criticality by itself. In

principle, the role of interface-position fluctuations can be neglected only close enough to T_{NI}, when the effective interface width is smaller than the presurface layer thickness. The fluctuation effects in $D=3$ are known to depend on the value of the dimensionless parameter $\omega=T/4\pi\xi\sigma$, where ξ is the bulk correlation length of the phase attracted to the wall, and σ is the surface tension of the free interface [9]. It wiil be interesting to study the role of this parameter in different liquid crystal materials. Finally, it was shown that the order-electricity effects can importantly change the local excitation spectra, as they effectively couple the normal director modes to the ''dangerous'' scalar order-parameter mode $\phi_0(z)$.

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