

## Nematic surface transitions induced by anchoring competition

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(Received 21 September 1995; revised manuscript received 2 January 1996)

The interface properties of a nematic liquid crystal in contact with a solid substrate are investigated by considering the effect of a position dependent external field on a short range nematic-substrate interaction. Such a field could be due, for instance, to the van der Waals interaction between the substrate and the nematic, or to the electrostatic interaction due to selective ion adsorption. In all cases a transition from homeotropic to planar orientation is expected. This phenomenon is interpreted in terms of different aligning effects, by invoking the competition between a stabilizing short range term and a destabilizing long range term. We show that, according to the value of the short range anchoring energy strength, the stable nematic state in the presence of the position dependent external field can be homeotropic, distorted, or planar. The thresholds and the order of the corresponding transitions are obtained. Temperature induced surface transitions can be also interpreted in this framework. [S1063-651X(96)00406-0]

PACS number(s): 61.30.Cz, 61.30.Gd

### I. INTRODUCTION

Nematic liquid crystals are anisotropic fluids formed by rodlike molecules [1]. They behave like uniaxial materials whose optical axis  $\vec{n}$  coincides with the statistical average of the molecular directions  $\vec{a}$ , parallel to the major axis of molecules.  $\vec{n}$  is known as the nematic director. The physical properties of a nematic sample depend on the director field  $\vec{n}$ . As is well known,  $\vec{n}$  can be oriented by means of surface treatments [2] or by external fields [1].

In special symmetrical arrangements, the nematic-external-field interaction is a threshold phenomenon. This means that, if the field is lower than a critical value  $E_c$ , the stable orientation is the undeformed one. On the contrary, if the field is larger than  $E_c$ , the deformed state is stable [1,3,4]. This effect is known as the Fréedericksz transition. The value of the critical field depends on the elastic properties of the nematic liquid crystal and on the surface anchoring energy characterizing the anisotropic part of the nematic-substrate interaction [5]. In the past, this effect has been used to measure the elastic constants of nematics [6] and the anchoring energy strength [7].

Long ago, the effect of the van der Waals interaction between a nematic and a solid substrate was analyzed by Dubois-Violette and de Gennes [8,9]. More recently, the electrostatic interaction between a surface field, due to selective ion adsorption, and a nematic has been investigated in order to study the thickness dependence of the effective anchoring energy [10,11]. In both these interesting cases, the nematic-external-field interaction is similar to a Fréedericksz transition in which the external field is position dependent.

Usually, the analysis of the Fréedericksz transition is performed by supposing that the external field is homogeneous [1,3,4]. In our paper we reconsider the Fréedericksz effect in the framework of a strongly position dependent external field. This study is important for two reasons: (i) to analyze the anchoring competition between short range and long

range nematic-substrate interactions [12,13]; (ii) to interpret the temperature induced surface transitions in nematics [14–16].

This paper is organized as follows. The theoretical model is presented in Sec. II. We consider a simple planar and one-dimensional problem in which a nematic sample, having the shape of a slab of thickness  $d$ , is submitted to a position dependent external field. The short range nematic-substrate interaction is supposed to give homeotropic alignment. The stability of the homogeneous homeotropic and planar configurations is analyzed by means of the Ritz method [17]. The real situation in which the external field responsible for the distorting effect is localized in a microscopic surface layer is discussed in Sec. III. In Sec. IV, we obtain the same result using an alternative simplified approach based on the presence of a particular surface field. Finally, Sec. V is devoted to the analysis of the order of the homeotropic→distorted and distorted→planar transitions for the theoretical model presented.

### II. THEORETICAL MODEL

We analyze the planar and one-dimensional problem of a nematic sample submitted to a position dependent external field. In this case the nematic director lies in a vertical plane and it depends only on the  $z$  coordinate (Fig. 1). The total energy per unit surface of a nematic slab of thickness  $d$ , in one constant approximation [1], is given by

$$F = \frac{1}{2} w \sin^2 \phi_0 + \frac{1}{2} \int_{-d/2}^{d/2} [k \phi'^2 - u(z) \sin^2 \phi] dz, \quad (1)$$

where  $w$  is the anchoring strength,  $k$  is the nematic bulk elastic constant,  $\phi(z) = \cos^{-1}(\vec{n} \cdot \vec{k})$  is the tilt angle,  $\vec{k}$  is the surface normal,  $\phi'(z) = (d\phi/dz)$ ,  $\phi_0 = \phi(\pm d/2)$ . The bulk term  $u(z) \sin^2 \phi(z)$  represents the coupling between the nematic liquid crystal and the surface field. Hence it is connected with some kind of nematic anisotropy.

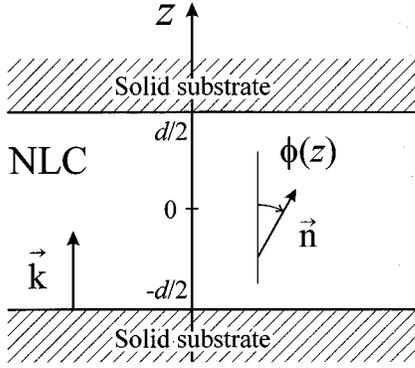


FIG. 1. Geometry of the analyzed problem. A nematic sample of thickness  $d$  is considered.  $\vec{n}$  is the nematic director,  $\phi$  is the tilt angle, and  $\vec{k}$  is the geometrical normal to the surface.

The sign of the external field interaction term is chosen to destabilize a starting homeotropic orientation. In (1), the first elasticlike surface aligning term is in competition with the term connected to the position dependent external field. In the following  $u(z)$  will be assumed to be of the kind

$$u(z) = u(-z) = u_0 \frac{\cosh(z/\lambda)}{\cosh(d/2\lambda)}. \quad (2)$$

This choice allows us to analyze a general problem connected with the presence of a surface field and to simplify the mathematical aspect of the analysis. We introduce the characteristic length  $\lambda$ , i.e., the thickness of the layer close to the surface in which the field is present and  $u_0$  is a parameter connected with the anisotropy of the nematic. When the van der Waals forces are considered  $\lambda \approx 10^3 \text{ \AA}$  [9]. In the case in which the external field is due to the selective ion adsorption,  $\lambda$  coincides with the Debye length [10]. If  $d \gg \lambda$ ,  $u(z)$  differs from zero only in two surface layers of thickness  $\lambda$ , as shown in Fig. 2.

If one wants to take into account also the coupling of the quadrupolar properties of the nematic liquid crystal with the gradient of the surface field, he has to add, in the expression of the bulk energy, a term of the kind  $Q\nabla E$ , where  $Q$  is the tensor order parameter of the nematic. By assuming for the surface field an exponential decay as in Refs. [10,11], simple calculations show that this term is equivalent to change  $u_0$  in

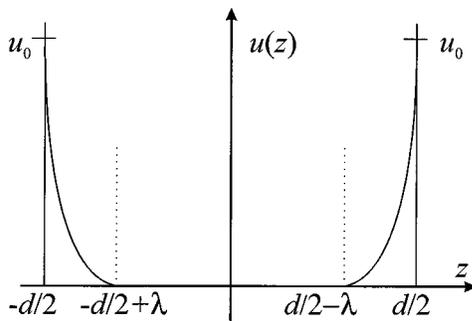


FIG. 2. Dependence of the anisotropic interaction energy  $u$  strength vs  $z$ .  $u(z)$  is different from zero in a microscopic layer of thickness  $\lambda$ .

$u_0 + \alpha$ , where  $\alpha = [(4\pi\sigma)/\epsilon](\epsilon_a/2\epsilon_{\parallel})(\lambda_D\sigma + 2e)$  [18]. In this last expression  $\epsilon$  is an average dielectric permittivity,  $\lambda_D$  is the Debye length,  $e$  is the flexoelectric coefficient, and  $\sigma$  is the charge surface density. Hence our analysis can be extended to take into account also quadrupolar properties only by changing  $u_0 \rightarrow u_0 + \alpha$ .

From (1) it follows that the nematic configuration  $\phi(z) = 0$ ,  $\forall z \in (-d/2, d/2)$ , is characterized by a total energy

$$F_0 = 0, \quad (3)$$

whereas the total energy of the state  $\phi(z) = \pi/2$ ,  $\forall z \in (-d/2, d/2)$  is

$$F_{\pi/2} = \frac{1}{2}w - \frac{1}{2} \int u(z) dz = \frac{1}{2}w - \frac{1}{2}A, \quad (4)$$

where

$$A = \int_{-d/2}^{d/2} u(z) dz = 2u_0\lambda \tanh\left(\frac{d}{2\lambda}\right). \quad (5)$$

The state  $\phi=0$  is stable with respect to the state  $\phi=\pi/2$  if

$$F_0 < F_{\pi/2}. \quad (6)$$

From Eqs. (3) and (4) one obtains that

$$w > A, \quad (7)$$

which represents the condition of stability of the state  $\phi=0$  with respect to the state  $\phi=\pi/2$ .

By means of the variational calculus, it is possible to analyze the stability of the state  $\phi=0$  with respect to other possible distorted states. The extremizing functions of (1) are solutions of the differential equation

$$k\phi'' + \frac{1}{2}u(z)\sin(2\phi) = 0, \quad (8)$$

satisfying the boundary conditions

$$-k\phi' + \frac{1}{2}w \sin(2\phi_0) = 0. \quad (9)$$

Since  $u$  depends on  $z$ , it is difficult to obtain a first integral representing the total energy of the system. However, it is possible to solve the problem in an alternative manner by considering the two limits  $\phi \rightarrow 0$  and  $\phi \rightarrow \pi/2$ .

In the case  $\phi \rightarrow 0$ , at the second order in  $\phi$ , Eq. (1) writes

$$F = \frac{1}{2}w\phi_0^2 + \frac{1}{2} \int_{-d/2}^{d/2} [k\phi'^2 - u(z)\phi^2] dz. \quad (10)$$

Since  $u(z) = u(-z)$ , the tilt angle  $\phi(z)$  is expected to be an even function of  $z$ . In the considered limit, we will assume for  $\phi(z)$  the following expression:

$$\phi(z) = \psi + \Phi \frac{\cosh(z/\xi)}{\cosh(d/2\xi)}, \quad (11)$$

where  $\psi + \Phi = \phi_0 \neq 0$  because we consider a weak anchoring.  $\xi$  is the typical length connected to the distortion and is expected to be of the order of  $\lambda$ . In the following we will consider  $\xi \neq \lambda$ , whereas in Sec. III the particular case  $\xi = \lambda$  will be analyzed.

By substituting (11) into (10) one obtains

$$F = \frac{1}{2}(w - A)\psi^2 - B\psi\Phi + \frac{1}{2}(D - C)\Phi^2, \quad (12)$$

where  $A$  is defined in Eq. (5),

$$\begin{aligned} B &= \frac{1}{\cosh(d/2\xi)} \int_{-d/2}^{d/2} u(z) \cosh(z/\xi) dz \\ &= \frac{\xi \lambda u_0}{(\xi^2 - \lambda^2) \cosh(d/2\xi) \cosh(d/2\lambda)} \left[ \sinh\left(\frac{d}{2\xi} + \frac{d}{2\lambda}\right) \right. \\ &\quad \left. \times (\xi - \lambda) - \sinh\left(\frac{d}{2\xi} - \frac{d}{2\lambda}\right) (\xi + \lambda) \right], \quad (13) \end{aligned}$$

$$\begin{aligned} C &= \frac{1}{\cosh^2(d/2\xi)} \int_{-d/2}^{d/2} u(z) \cosh^2(z/\xi) dz \\ &= \frac{\lambda u_0}{2(\xi^2 - 4\lambda^2) \cosh(d/2\xi) \cosh(d/2\lambda)} \left\{ \xi^2 \left[ \sinh\left(\frac{d}{\xi} + \frac{d}{2\lambda}\right) \right. \right. \\ &\quad \left. \left. - \sinh\left(\frac{d}{\xi} - \frac{d}{2\lambda}\right) + 2 \sinh\left(\frac{d}{2\lambda}\right) \right] - 2\lambda \xi \left[ \sinh\left(\frac{d}{\xi} + \frac{d}{2\lambda}\right) \right. \right. \\ &\quad \left. \left. + \sinh\left(\frac{d}{\xi} - \frac{d}{2\lambda}\right) \right] - 8\lambda^2 \sinh\left(\frac{d}{2\lambda}\right) \right\}, \quad (14) \end{aligned}$$

and

$$\begin{aligned} D &= \frac{k}{\xi^2} \frac{1}{\cosh^2(d/2\xi)} \int_{-d/2}^{d/2} \sinh^2(z/\xi) dz \\ &= \frac{k}{\xi^2} \frac{1}{\cosh^2(d/2\xi)} \left[ \frac{\xi}{2} \sinh\left(\frac{d}{\xi}\right) - \frac{d}{2} \right]. \quad (15) \end{aligned}$$

Since the stable state is the one minimizing  $F$ ,  $\psi$  and  $\Phi$  are given by the system

$$\begin{cases} \frac{\partial F}{\partial \psi} = (w - A)\psi - B\Phi = 0, \\ \frac{\partial F}{\partial \Phi} = (D - C)\Phi - B\psi = 0, \end{cases} \quad (16)$$

and they have to satisfy the conditions

$$\frac{\partial^2 F}{\partial \psi^2} > 0, \quad (17)$$

and

$$H = \frac{\partial^2 F}{\partial \psi^2} \frac{\partial^2 F}{\partial \Phi^2} - \left( \frac{\partial^2 F}{\partial \psi \partial \Phi} \right)^2 > 0. \quad (18)$$

The system (16) always has the solution  $\psi = \Phi = 0$ , corresponding to the homogeneous homeotropic state. This configuration is stable if

$$\begin{aligned} w &> w_1 = A, \\ w &> w_2 = A + \frac{B^2}{D - C}. \end{aligned}$$

In the case  $D > C$ , since  $w_2 > w_1$ , we conclude that the homeotropic state becomes unstable in the sense that some other state has a lower energy when

$$w^* = w_2 = A + \frac{B^2}{D - C}. \quad (19)$$

In this case  $w^*$  is larger than the threshold evaluated in (7). When  $D < C$ , this transition occurs for  $w^* = w_1 = A$ .

In the opposite limit, in which  $\phi \rightarrow \pi/2$ , we can write  $\phi = \pi/2 - \vartheta$  and consider the limit  $\vartheta \rightarrow 0$ . The total energy per unit surface is

$$F = \frac{1}{2} w \cos^2 \vartheta_0 + \frac{1}{2} \int_{-d/2}^{d/2} [k \vartheta'^2 - u(z) \cos^2 \vartheta] dz, \quad (20)$$

which, by using Eq. (4), in the limit  $\vartheta \rightarrow 0$ , is

$$F = F_{\pi/2} - \frac{1}{2} w \vartheta_0^2 + \frac{1}{2} \int_{-d/2}^{d/2} [k \vartheta'^2 - u(z) \vartheta^2] dz. \quad (21)$$

By considering

$$\vartheta(z) = \omega + \Theta \frac{\cosh(z/\xi)}{\cosh(d/2\xi)}, \quad (22)$$

where  $\omega + \Theta = \vartheta_0$ , Eq. (21) becomes

$$F = F_{\pi/2} + \frac{1}{2} (-w + A) \omega^2 + \frac{1}{2} (C + D) \Theta^2 + B \omega \Theta. \quad (23)$$

The stable states are given by

$$\begin{cases} \frac{\partial F}{\partial \omega} = (-w + A) \omega + B \Theta = 0, \\ \frac{\partial F}{\partial \Theta} = (C + D) \Theta + B \omega = 0, \end{cases} \quad (24)$$

and they have to satisfy the conditions

$$\frac{\partial^2 F}{\partial \omega^2} > 0, \quad (25)$$

and

$$H = \frac{\partial^2 F}{\partial \omega^2} \frac{\partial^2 F}{\partial \Theta^2} - \left( \frac{\partial^2 F}{\partial \omega \partial \Theta} \right)^2 > 0. \quad (26)$$

The system (24) always has the solution  $\omega = \Theta = 0$ , corresponding to the homogeneous planar orientation. This solution is stable if

$$\begin{aligned} w &< w_1 = A, \\ w &< w_3 = A - \frac{B^2}{D + C}. \end{aligned}$$

Since  $w_3 < w_1$ , the planar homogeneous state is stable for

$$w < w^{**} = A - \frac{B^2}{D + C}. \quad (27)$$

Note that  $w^{**}$  is smaller than the threshold evaluated in (7). Hence we obtain the solution shown in Fig. 3. The first

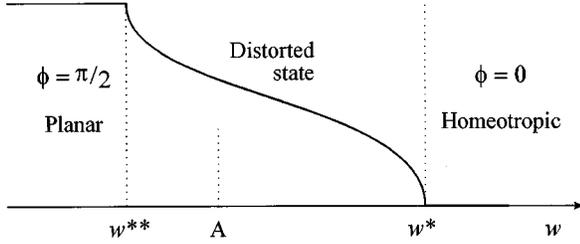


FIG. 3. Nematic liquid crystal tilt angle  $\phi$  vs anchoring energy strength  $w$ .  $w^*$  and  $w^{**}$  are the critical values of the anchoring energy for the stable homeotropic and planar orientations, respectively.

conclusion is that two transitions appear at  $w^*$  and  $w^{**}$ , which are, in general, different from  $w_1 = A$ . When  $w = w^*$ , there is a transition from the homeotropic state to the distorted one. At  $w = w^{**}$ , another transition appears from the distorted configuration to the planar one. For  $w^{**} < w < w^*$  the stable state is a distorted one. To study the order of these transitions, it is necessary to expand  $F$  up to the fourth order in  $\phi$ . This will be done in Sec. V.

Note that the anchoring energy, written in the form  $W = 1/2w \sin^2 \phi_0$ , takes origin from the short range interactions. According to Berreman [19],  $w$  is expected to be proportional to the elastic constant  $k$ . As it is well known,  $k \propto S^2$  [1].  $u(z)$  depends on the nematic anisotropy with respect to the surface field and this anisotropy is proportional to the scalar order parameter  $S$  [1]. Consequently  $A$ ,  $B$ , and  $C$  are also proportional to  $S$ . It follows that Eqs. (19) and (27) define particular values of  $S$ ,  $S^*$  and  $S^{**}$ , at which the homeotropic state becomes unstable ( $S^*$ ), and at which the planar state becomes stable ( $S^{**}$ ). In this sense, the competing action of the short range stabilizing term and of the long range destabilizing one may explain the temperature induced surface transitions observed by different groups [14–16].

### III. CASE IN WHICH $\lambda \ll d$

To evaluate the physical parameters introduced in the previous discussion, the following analysis will be performed considering a particular case when the sample thickness  $d$  is very large with respect to surface layer thickness  $\lambda$ . Furthermore, we will assume that  $\lambda \approx \xi = \delta$ . In the limit  $\delta/d \ll 1$ , one obtains

$$A = 2\delta u_0, \quad B = \delta u_0, \quad C = \frac{2}{3}\delta u_0, \quad D = \frac{k}{\delta}. \quad (28)$$

The expressions for  $w^*$  and  $w^{**}$  contain the quantities

$$Q_{\pm} = D \pm C, \quad (29)$$

which in the above mentioned limit become

$$Q_{\pm} = \frac{k}{d} \left\{ 1 \pm \frac{2}{3} \frac{\delta^2}{k} u_0 \right\}. \quad (30)$$

In order to compare the term  $(2/3)(\delta^2/k)u_0$  with respect to 1, we will consider the system analyzed by Dubois-Violette and de Gennes, in which the effects of the long

range van der Waals forces on the nematic anchoring are considered [9]. According to them, for a semi-infinite sample,  $u(z)$  is of the kind

$$u(z) = \frac{\tilde{C}}{(z + \lambda)^3}, \quad (31)$$

where  $\tilde{C}$  is the Hamaker constant [20] and  $\lambda$  is a microscopic length having the same meaning as before. In our symmetrical arrangement, (31) writes

$$u(z) = \tilde{C} \left\{ \frac{1}{(d/2 + \lambda - z)^3} + \frac{1}{(d/2 + \lambda + z)^3} \right\}. \quad (32)$$

For  $z = \pm d/2$ , Eq. (32) gives

$$u\left(\pm \frac{d}{2}\right) \approx \frac{\tilde{C}}{\lambda^3}. \quad (33)$$

This quantity corresponds to  $u_0$ , introduced in (2). Hence we assume

$$u_0 = \frac{\tilde{C}}{\lambda^3}. \quad (34)$$

By substituting (34) into (30), we obtain

$$1 \pm \frac{2}{3} \frac{\delta^2}{k} u_0 = 1 \pm \frac{2}{3} \frac{\tilde{C}}{\delta k}.$$

As discussed in [20],  $\tilde{C}$  is of the order of  $10^{-12}$  cgs whereas  $k \approx 10^{-6}$  cgs [1]; we have for the intrinsic length  $\tilde{C}/k \approx 100$  Å. Since  $\delta$ , considered in the nonretardation limit, is of the order of  $10^3$  Å [8,9], we obtain

$$\frac{2}{3} \frac{\tilde{C}}{\delta k} \approx 0.1$$

that is not negligible with respect to 1. Consequently, in this limit the transition homeotropic  $\rightarrow$  distorted  $\rightarrow$  planar seems to be a cascade of two second order transitions, as will be demonstrated in Sec. V.

### IV. ALTERNATIVE APPROACH TO THE HOMEOTROPIC $\rightarrow$ DISTORTED $\rightarrow$ PLANAR TRANSITIONS

The analysis presented for the general case of Sec. II may be performed in a simplified way, by considering a particular surface field  $E_S$  of the kind shown in Fig. 4, i.e., different from zero in  $-d/2 < z < -d/2 + \lambda$  and zero elsewhere. Note that this is a reasonable approximation for the surface field in the case of ion adsorption.

For  $z = -d/2$ , the surface energy is  $W = (1/2)w \sin^2 \phi_0$ , whereas for  $z = -d/2 + \lambda$  the anchoring strength vanishes. The functional to be considered now is

$$G_T = \int_{-d/2}^{-d/2 + \lambda} \left( \frac{1}{2} k \phi'^2 - \frac{1}{2} \epsilon_a E^2 \phi^2 \right) dz + \frac{1}{2} w \phi_0^2, \quad (35)$$

in the limit of small  $\phi$  (near the threshold), and

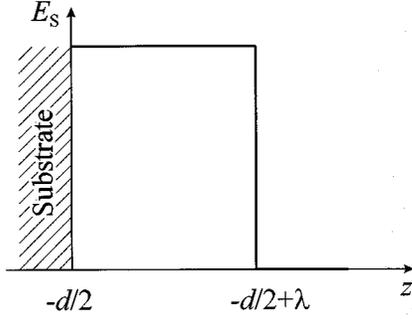


FIG. 4. Surface field  $E_s$  vs  $z$ .  $E_s$  is different from zero only in a layer of thickness  $\lambda$ .

$$G_S = \int_{-d/2}^{-d/2+\lambda} \left( \frac{1}{2} k \vartheta'^2 + \frac{1}{2} \epsilon_a E^2 \vartheta^2 \right) dz - \frac{1}{2} w \vartheta_0^2, \quad (36)$$

in the limit of large  $\phi$  (near the saturation).

$G_T$  and  $G_S$  represent the total energy (per surface unit) of the surface layer of thickness  $\lambda$  in the harmonic approximation. The total energy of the nematic sample is given by  $F_T = 2G_T$ , in the limit of small  $\phi$ , or  $F_S = 2G_S$ , in the limit of large  $\phi$ . This comes from the hypothesis that, in the bulk, the nematic follows the orientation imposed by the surface layer. This is equivalent to the fact that in the bulk,  $-d/2 + \lambda \leq z \leq d/2 - \lambda$ , the nematic energy is zero because (i) the orientation is supposed homogeneous and the elastic contribution, proportional to  $\phi'$ , is identically zero; and (ii) the distorting field responsible for  $u(z)$  is absent.

The trend of  $\phi(z)$  vs  $z$  is of the kind shown in Fig. 5. Note also that in Eqs. (35) and (36) the term  $\epsilon_a E^2$  represents a kind of average of  $u(z)$ . In fact, from Eq. (1) written in the limit  $\phi \rightarrow 0$ , the term representing the interaction with the surface field is

$$-\frac{1}{2} \int_{-d/2}^{d/2} u(z) \sin^2 \phi(z) dz = - \int_{-d/2}^0 u(z) \sin^2 \phi(z) dz,$$

because  $u(z) = u(-z)$ , which means  $\phi(z) = \phi(-z)$ . Since  $\phi(z) \rightarrow 0$  and  $u(z) \neq 0$  only for  $-d/2 \leq z \leq -d/2 + \lambda$ , we have, furthermore,

$$- \int_{-d/2}^0 u(z) \sin^2 \phi(z) dz \cong - \int_{-d/2}^{-d/2+\lambda} u(z) \phi^2(z) dz.$$

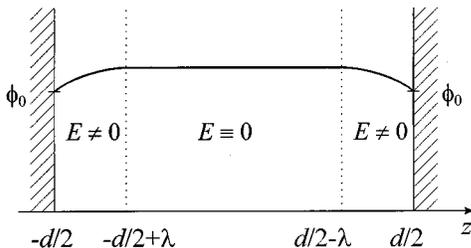


FIG. 5. Nematic liquid crystal orientation vs the distorting field in the case of weak anchoring. In the first approximation, the surface tilt angle is proportional to the maximum tilt angle.

By taking into account that  $u(z) \geq 0$  and  $\phi^2(z) \geq 0$ ,  $\forall z \in (-d/2, -d/2 + \lambda)$ , we can apply the average theorem of the integral calculus to the last expression. Hence

$$-\frac{1}{2} \int_{-d/2}^{d/2} u(z) \phi^2(z) dz = -u(z^*) \int_{-d/2}^{-d/2+\lambda} \phi^2(z) dz.$$

The quantity  $u(z^*)$  depends also on  $\phi(z)$ , which is unknown. However near the threshold or near the saturation it is possible to assume  $\phi = 0$  or  $\phi = \pi/2$ , respectively. This means that  $u(z^*)$  depends only on the  $u(z)$  profile.

In this analysis, we consider that  $u(z^*) = u_0 = (1/2) \epsilon_a E^2$ , where  $\epsilon_a$  is the nematic anisotropy with respect to the surface field itself (in the range of frequency in which the van der Waals interactions are important) and  $E^2$  is a positive and constant parameter.

By minimizing (35) and (36) one obtains

$$\begin{cases} k \phi'' + \epsilon_a E^2 \phi = 0, & -d/2 \leq z \leq -d/2 + \lambda \\ k \phi' - w \phi_0 = 0, & z = -d/2 \\ k \phi' = 0, & z = -d/2 + \lambda \end{cases} \quad (37)$$

and

$$\begin{cases} k \vartheta'' - \epsilon_a E^2 \vartheta = 0, & -d/2 \leq z \leq -d/2 + \lambda \\ k \vartheta' + w \vartheta_0 = 0, & z = -d/2 \\ k \vartheta' = 0, & z = -d/2 + \lambda. \end{cases} \quad (38)$$

From (37), we deduce

$$\phi = M \cos\left(\frac{z+d/2}{\Lambda}\right) + N \sin\left(\frac{z+d/2}{\Lambda}\right), \quad (39)$$

where  $M$  and  $N$  are integration constants and

$$\frac{1}{\Lambda^2} = \frac{\epsilon_a E^2}{k}.$$

By substituting (39) into the boundary conditions (37), we obtain

$$\begin{cases} \frac{N}{\Lambda} - \frac{w}{k} M = 0, \\ M \sin\left(\frac{\lambda}{\Lambda}\right) - N \cos\left(\frac{\lambda}{\Lambda}\right) = 0, \end{cases} \quad (40)$$

which admits a solution different from zero for  $M$  and  $N$  only if

$$\tan\left(\frac{\lambda}{\Lambda}\right) = \Lambda \frac{w}{k}. \quad (41)$$

From this last condition, we deduce that the state  $\phi = 0, \forall z$ , is stable when

$$w > w_H = \frac{k}{\Lambda} \tan\left(\frac{\lambda}{\Lambda}\right). \quad (42)$$

Let us consider now Eq. (38). By operating as above, we deduce

$$\vartheta = R \cosh\left(\frac{z+d/2}{\Lambda}\right) + S \sinh\left(\frac{z+d/2}{\Lambda}\right), \quad (43)$$

and the boundary conditions become

$$\begin{cases} S \frac{1}{\Lambda} + R \frac{w}{k} = 0, \\ R \sinh\left(\frac{\lambda}{\Lambda}\right) + S \cosh\left(\frac{\lambda}{\Lambda}\right) = 0. \end{cases} \quad (44)$$

This system has a solution different from the trivial one only if

$$\tanh\left(\frac{\lambda}{\Lambda}\right) = \Lambda \frac{w}{k}, \quad (45)$$

which defines the saturation field. The state  $\phi = \pi/2, \forall z$ , is stable for

$$w < w_p = \frac{k}{\Lambda} \tanh\left(\frac{\lambda}{\Lambda}\right). \quad (46)$$

To compare with the results of Sec. III, we have just to observe that  $\lambda/\Lambda \ll 1$ . Hence

$$w_H \cong \frac{k\lambda}{\Lambda^2} = k\lambda \frac{\epsilon_a E^2}{k} \cong 2u_0\lambda,$$

$$w_p \cong \frac{k\lambda}{\Lambda^2} \cong 2u_0\lambda.$$

In conclusion, as  $w_H$  and  $w_p$  are very close, the homeotropic-planar transition could be considered of the first order.

## V. ON THE KIND OF THE ORDER OF THE TRANSITION HOMEOTROPIC→DISTORTED STATE

In the theoretical model presented in Sec. II, the hypothesis made on  $\phi$  implies that at  $w = w^*$  or  $w = w^{**}$  the transitions are of the second order. To prove this assumption, let us remember that a phase transition, in the Landau formalism, is of the second order if, near the transition, the free energy may be written in the form [1]

$$F = F_0 + \frac{1}{2}\alpha(T - T_C)y^2 + \frac{1}{4}\beta y^4.$$

Here  $y$  is the order parameter and  $\alpha > 0$ . The phase transition is of the second order at  $T = T_C$  if  $\beta > 0$ .

To show that the transitions we analyzed are of the second order, we have to consider the development at the fourth order of the total free energy. Let us evaluate (1) in the limit  $\phi \rightarrow 0$  (the other case in which  $\phi \rightarrow \pi/2$  may be treated in a similar way).

For  $\phi \rightarrow 0$  one obtains

$$\sin\phi = \phi - \frac{1}{6}\phi^3, \quad \sin^2\phi = \phi^2 - \frac{1}{3}\phi^4. \quad (47)$$

In the case of weak anchoring, the surface tilt angle  $\phi_0$  is nearly proportional to the maximum tilt angle having the same sign. This means that if  $\phi(z)$  is of the kind (11),  $\phi_0$  is expected to be of the kind

$$\phi_0 = \gamma\Phi, \quad \gamma > 0. \quad (48)$$

At the fourth order in  $\Phi$ , by using (47) and (48), Eq. (1) rewrites as

$$F = \frac{1}{2}[(w-A)\gamma^2 - 2\gamma B + D - C]\Phi^2 + \frac{1}{6}[(-w+A)\gamma^4 + (4\gamma^3 B + 6\gamma^2 C + 4\gamma E + G)]\Phi^4, \quad (49)$$

where  $A, B, C, D$  are given by (5), (13), (14) and (15),

$$\begin{aligned} E &= \frac{1}{\cosh^3(d/2\xi)} \int_{-d/2}^{d/2} u(z) \cosh^3(z/\xi) dz \\ &= \frac{1}{\cosh^3(d/2\xi)} \frac{1}{\cosh(d/2\lambda)} \frac{3u_0\xi\lambda}{4(\xi^4 - 10\xi^2\lambda^2 + 9\lambda^4)} \\ &\quad \times \left[ \sinh\left(\frac{d}{2\xi} - \frac{d}{2\lambda}\right) (-\xi^3 - \xi^2\lambda + 9\xi\lambda^2 + 9\lambda^3) \right. \\ &\quad + \sinh\left(\frac{3d}{2\xi} - \frac{d}{2\lambda}\right) \left( -\frac{1}{3}\xi^3 - \xi^2\lambda + \xi\lambda^2 + \lambda^3 \right) \\ &\quad + \sinh\left(\frac{d}{2\xi} + \frac{d}{2\lambda}\right) (\xi^3 - \xi^2\lambda - 9\xi\lambda^2 + 9\lambda^3) \\ &\quad \left. + \sinh\left(\frac{3d}{2\xi} + \frac{d}{2\lambda}\right) \left( \frac{1}{3}\xi^3 - \xi^2\lambda - \xi\lambda^2 + \lambda^3 \right) \right] \quad (50) \end{aligned}$$

and

$$\begin{aligned} G &= \frac{1}{\cosh^4(d/2\xi)} \int_{-d/2}^{d/2} u(z) \cosh^4(z/\xi) dz \\ &= \frac{1}{\cosh^4(d/2\xi)} \frac{1}{\cosh(d/2\lambda)} \frac{4u_0\lambda}{8(\xi^4 - 20\xi^2\lambda^2 + 64\lambda^4)} \\ &\quad \times \left[ \sinh\left(\frac{d}{\xi} - \frac{d}{2\lambda}\right) (-\xi^4 - 2\xi^3\lambda + 16\xi^2\lambda^2 + 32\xi\lambda^3) \right. \\ &\quad + \sinh\left(\frac{2d}{\xi} - \frac{d}{2\lambda}\right) \left( -\frac{1}{4}\xi^4 - \xi^3\lambda + \xi^2\lambda^2 + 4\xi\lambda^3 \right) \\ &\quad + \sinh\left(\frac{d}{\xi} + \frac{d}{2\lambda}\right) (\xi^4 - 2\xi^3\lambda - 16\xi^2\lambda^2 + 32\xi\lambda^3) \\ &\quad + \sinh\left(\frac{2d}{\xi} + \frac{d}{2\lambda}\right) \left( \frac{1}{4}\xi^4 - \xi^3\lambda - \xi^2\lambda^2 + 4\xi\lambda^3 \right) \\ &\quad \left. + \sinh\left(\frac{d}{2\lambda}\right) \left( \frac{2}{3}\xi^4 - 30\xi^2\lambda^2 + 96\lambda^4 \right) \right]. \end{aligned}$$

The transition homeotropic→distorted configuration implies that the coefficient of  $\Phi^2$  in (49) is negative. When this coefficient vanishes, the coefficient of  $\Phi^4$  is

$$\frac{1}{6}[2\gamma^3 B + \gamma^2(4C + D) + 4\gamma E + G] > 0,$$

i.e., it is positive and the transition is actually of the second order.

## VI. CONCLUSIONS

The surface orientational transitions induced in a nematic liquid crystal submitted to an inhomogeneous external field have been theoretically analyzed. The starting nematic surface orientation is determined by the short range nematic-substrate interaction. The position dependent external field may be due to long range anisotropic nematic-substrate interactions. The competition between these two anchoring sources determines the actual state for the nematic.

In a simple one-dimensional and planar problem, we evaluate the critical values of the anchoring energy strength for the cases in which the stable orientation of the nematic liquid crystal is the homeotropic or the planar one. When a destabilizing surface field is present, a homeotropic→planar

transition takes place. A detailed analysis shows that a distorted state, intermediate between the homogeneous homeotropic and planar ones, can be stable in a very narrow region of the surface anchoring energy strength. In the framework of the Landau formalism, the homeotropic-distorted and the distorted-planar transitions result to be of the second order. The physical parameters entering in the model were evaluated in the case of  $\lambda \ll d$  and long range van der Waals interactions. The same result was obtained for a simplified surface field, valid in the case of selective ion adsorption, giving two very close threshold values. Possible applications of this description to the temperature induced surface transitions are also discussed.

## ACKNOWLEDGMENT

Many thanks are due to G. Barbero for very fruitful discussions.

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- [1] P. G. de Gennes and J. Prost, *The Physics of Liquid Crystals* (Clarendon, Oxford, 1993).
  - [2] B. Jérôme, Rep. Prog. Phys. **54**, 391 (1991).
  - [3] H. J. Dueling, in *Solid State Physics*, Suppl. 14 (Academic, New York, 1976).
  - [4] S. Chandrasekhar, *Liquid Crystals* (Clarendon, Oxford, 1977).
  - [5] R. Rapini and M. Papoular, J. Phys. (Paris) Colloq. **30**, (1969).
  - [6] I. Haller, J. Chem. Phys. **57**, 1400 (1972).
  - [7] G. Barbero and A. Strigazzi, Nuovo Cimento B **64**, 101 (1981).
  - [8] E. Dubois-Violette and P. G. de Gennes, J. Phys. (Paris) Lett. **36**, L 255 (1975).
  - [9] E. Dubois-Violette and P. G. de Gennes, J. Colloid Interface Sci. **57**, 403 (1976).
  - [10] G. Barbero and G. Durand, J. Phys. (Paris) **51**, 281 (1990).
  - [11] G. Barbero and G. Durand, J. Appl. Phys. **67**, 2678 (1990).
  - [12] A. L. Alexe-Ionescu, R. Barberi, M. Giocondo, G. Cnossen, and T. H. van der Donk, Appl. Phys. Lett. **66**, 1701 (1995).
  - [13] A. L. Alexe-Ionescu, R. Barberi, G. Barbero, J. J. Bonvent, and M. Giocondo, Appl. Phys. A **60**, 104 (1995).
  - [14] G. Barbero, T. Beica, A. L. Alexe-Ionescu, and R. Moldovan, Liq. Cryst. **14**, 877 (1992).
  - [15] R. Barberi, G. Barbero, M. Giocondo, and R. Moldovan, Phys. Rev. E **50**, 2093 (1994).
  - [16] A. L. Alexe-Ionescu, R. Barberi, G. Barbero, and M. Giocondo, Phys. Lett. A **195**, 227 (1994).
  - [17] L. Elsgolts, *Differential Equations and Variational Calculus* (Mir, Moscow, 1976).
  - [18] A. L. Alexe-Ionescu, G. Barbero, and A. G. Petrov, Phys. Rev. E **48**, R1631 (1993).
  - [19] D. W. Berreman, Phys. Rev. Lett. **28**, 1683 (1972).
  - [20] J. N. Israelachvili, *Intermolecular and Surface Forces* (Academic, New York, 1985).