

Anchoring of nematic liquid crystals on a thin polymeric film

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We analyze the influence of a thin polymer layer with lateral side groups on the anchoring of a nematic liquid crystal. We show that the effective anisotropic part of the anchoring energy depends on the coupling of the nematic with the polymer side groups, as well as on the coupling of the polymer side groups with the surface. The relaxation time for the nematic orientation induced by an external field is evaluated by considering the surface dissipation connected to the relative motion of the nematic director with respect to the polymer side groups.

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I. INTRODUCTION

The surface properties of nematic liquid crystals depend on the interaction of the nematic molecules with the supporting substrate and on the broken symmetry of the nematic phase due to the presence of the limiting surface [1]. The interaction with the substrate depends on the presence of surface layers since (a) the presence of a surface layer is responsible for a screening of the substrate [2], and (b) the presence of the surface layer can be responsible for new interactions. In the special case where the surface layer is an ordered medium particular effects are expected, because in addition to the physicochemical interactions, the steric interaction also has to be taken into account [3–5]. Theoretical models describing the effects of a Langmuir-Blodgett film on the surface properties have been proposed in the past [6–8]. In the present paper we investigate the anchoring of a nematic liquid crystal on a side-chain polymer. These nanostructured polymeric layers seem very promising for application in display technology because they allow a continuous control of the pretilt angle of nematic liquid crystals [9]. Our paper is organized as follows. In Sec. II we discuss the effective anchoring energy of a nematic liquid crystal in the framework of the Rapini-Papoular approximation [10] by considering simple configurations. In the same section we propose a mechanical model of the orienting effect of a layer made by a side-chain polymer on a nematic liquid crystal, and evaluate the anchoring energy strength. The analysis is performed in the presence and in the absence of an external distorting electric field. In Sec. III we consider the relaxation time in a nematic cell, with different degrees of approximation, taking into account the weak anchoring and the presence of the surface viscosity. Finally, in the same section, the relaxation time of a nematic liquid crystal oriented by means of a thin layer made of a side-chain polymer is considered. There we show that, due to the presence of the mechanical coupling between the nematic director and the surface orien-

tation of the side groups, an additional dissipation term has to be considered in the equilibrium of the surface torques. The effect of this term on the relaxation time is discussed. Section IV is devoted to the conclusions.

II. EFFECTIVE ANCHORING ENERGY

Let us consider a nematic sample in the shape of a slab of thickness d . The Cartesian reference frame used for the description has the z axis perpendicular to the limiting surfaces located at $z=0$ and d . We assume that the surface treatment is such to induce weak planar alignment on the surface at $z=0$, and strong tilted alignment on the surface at $z=d$. We assume that the nematic deformation is contained in a plane, which we choose as the (x, z) plane, and characterize the nematic deformation by means of the angle formed by the nematic director with the x axis. We indicate by $\varphi=\varphi(z)$ the tilt angle at the point of coordinate z , by $\phi_n=\varphi(0)$ the actual tilt angle on the surface characterized by weak anchoring, and by Φ the tilt angle imposed by the surface treatment on the limiting surface characterized by strong anchoring energy. We work in the framework of the one-constant approximation, where the elastic constants for the splay and bend deformations are assumed identical. In this situation the total energy of the nematic sample, per unit area, is given by

$$F = f_s + \int_0^d (k/2)(d\varphi/dz)^2 dz, \quad (1)$$

where f_s is the anisotropic part of the surface energy and k the elastic constant of the nematic liquid crystal. The profile of $\varphi(z)$ is the one minimizing F . Routine calculations give for the bulk differential equation satisfied by $\varphi(z)$ the expression $k d^2\varphi/dz^2=0$, which has to be solved with the boundary conditions [12]

$$-k \left(\frac{d\varphi}{dz} \right)_0 + \frac{df_s}{d\phi_n} = 0 \quad \text{and} \quad \varphi(d) = \Phi. \quad (2)$$

The bulk differential equation states that in the actual deformed state the bulk density of mechanical torque vanishes, with the boundary conditions that the torque due to the bulk is balanced by the surface torque connected to the aniso-

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tropic surface energy. By solving the bulk differential equation satisfied by $\varphi(z)$, taking into account the second of the boundary conditions (2), we get for the actual tilt angle the expression

$$\varphi(z) = \phi_n + \frac{\Phi - \phi_n}{d}z, \quad (3)$$

and the surface tilt angle ϕ_n is given by

$$-k \frac{\Phi - \phi_n}{d} + \frac{df_s}{d\phi_n} = 0. \quad (4)$$

We note that the boundary condition (4) can be obtained by substituting the expression for $\varphi(z)$ given by (3) into (1) and minimizing the resulting expression for F with respect to ϕ_n [12]. This means that the actual surface tilt angle ϕ_n is the one minimizing F .

A. Standard analysis

In the framework of the Rapini-Papoular approximation $f_s(\phi_n) = (w/2)\sin^2\phi_n$, where w is the anchoring energy strength [10]. By substituting this expression for $f_s(\phi_n)$ into Eq. (4) we get

$$-k \frac{\Phi - \phi_n}{d} + \frac{w}{2}\sin(2\phi_n) = 0, \quad (5)$$

which determines ϕ_n . Equation (5) is a transcendental equation that can have more than one solution. In this case, the actual ϕ_n is the one minimizing F given by

$$F = \frac{w}{2}\sin^2\phi_n + k \frac{(\Phi - \phi_n)^2}{2d}, \quad (6)$$

as discussed above. Equation (5) can be rewritten in the form

$$w = 2 \frac{k}{d} \frac{\Phi - \phi_n}{\sin(2\phi_n)}. \quad (7)$$

If w is such that $\phi_n \ll 1$, the analysis can be linearized. In this case $f_s(\phi_n) = (w/2)\phi_n^2$, and the equation determining ϕ_n reads

$$-k \frac{\Phi - \phi_n}{d} + w\phi_n = 0, \quad (8)$$

from which

$$\phi_n = \frac{\Phi}{1 + wd/k}. \quad (9)$$

The elastic problem to determine φ is well posed, and can be solved as soon as we know the expression for the anisotropic part of the surface energy.

B. Effective surface energy of a side-chain polymer layer

Let us consider the case where the aligning layer is a side-chain polymer. We assume that the surface energy is

$$f_s = \frac{\beta}{2}\phi_p^2 + \frac{\alpha}{2}\sin^2(\phi_p - \phi_n), \quad (10)$$

where ϕ_p is the angle formed by the lateral groups with the x axis. We suppose that in the absence of any imposed defor-

mation the polymer side group is parallel to the x axis. The parameter β is connected with the restoring torque of elastic origin acting on the lateral group. Assuming mesogenic side groups, the parameter α takes into account the tendency of the nematic molecules to be parallel, for sterical reasons, to the side-chain groups. In the case under consideration, the surface state is characterized by two mechanical coordinates: ϕ_p , related to the orientation of the polymer side group, and ϕ_n , related to the nematic orientation. Since the bulk energy depends just on the nematic deformation, the total energy per unit surface is given by

$$F = \frac{\beta}{2}\phi_p^2 + \frac{\alpha}{2}\sin^2(\phi_p - \phi_n) + k \frac{(\Phi - \phi_n)^2}{2d}. \quad (11)$$

The equations determining ϕ_p and ϕ_n are obtained by minimizing F given by Eq. (11). By imposing $\partial F / \partial \phi_p = \partial F / \partial \phi_n = 0$ we get

$$\beta\phi_p + \frac{\alpha}{2}\sin[2(\phi_p - \phi_n)] = 0, \quad (12)$$

$$-\frac{\alpha}{2}\sin[2(\phi_p - \phi_n)] - k \frac{\Phi - \phi_n}{d} = 0. \quad (13)$$

Let us consider first the case $|\phi_p - \phi_n| \ll 1$, where Eqs. (12) and (13) can be linearized. In this framework the equations determining the surface deformations are

$$\beta\phi_p + \alpha(\phi_p - \phi_n) = 0, \quad (14)$$

$$-\alpha(\phi_p - \phi_n) - (k/d)(\Phi - \phi_n) = 0, \quad (15)$$

from which we obtain

$$\phi_p = \frac{\alpha}{\alpha + \beta} \frac{1}{1 + (w_e d/k)} \Phi, \quad (16)$$

$$\phi_n = \frac{1}{1 + (w_e d/k)} \Phi, \quad (17)$$

where we have put $w_e = \alpha\beta/(\alpha + \beta)$. By comparing ϕ_n given by Eq. (17) with the one given by Eq. (9) we conclude that, in the linear approximation, the equivalent surface energy related to the expression for f_s given by (10) is w_e . From the definition of w_e it follows that

$$\frac{1}{w_e} = \frac{1}{\alpha} + \frac{1}{\beta}. \quad (18)$$

From Eq. (18) it follows that if $\beta \rightarrow \infty$, i.e., the side groups are fixed, $w_e \rightarrow \alpha$, as expected. Equation (18) has been discussed by other authors in a framework where several forces are responsible for the anisotropic part of the surface energy of the nematic liquid crystal [13–15].

If Eqs. (12) and (13) cannot be linearized, the angle formed by the lateral side groups with the x axis, ϕ_p , depends on the nematic surface orientation ϕ_n according to the relation

$$\phi_p = \frac{k}{\beta d}(\Phi - \phi_n), \quad (19)$$

and ϕ_n is given by the transcendental equation

$$2\frac{k}{\alpha d}(\Phi - \phi_n) + \sin\left[2\frac{k}{\beta d}\Phi - 2\left(1 + \frac{k}{\beta d}\right)\phi_n\right] = 0. \quad (20)$$

In this case the equivalent surface energy w_{eq} can be obtained by Eq. (7),

$$w_{\text{eq}} = 2\frac{k}{d}\frac{\Phi - \phi_n}{\sin(2\phi_n)}, \quad (21)$$

identifying ϕ_n with the solution of Eq. (20). In the limit of small ϕ_n , $w_{\text{eq}} \rightarrow w_e$, as expected.

In the case in which, in addition to the side mesogenic groups, there are present also aliphatic chains, which have the tendency to impose homeotropic alignment, the surface energy is

$$f_s = \frac{\beta}{2}\phi_p^2 + \frac{\alpha}{2}\sin^2(\phi_p - \phi_n) + \frac{g}{2}\cos^2\phi_n, \quad (22)$$

instead of (10). The coefficient g is connected to the orienting effect of the aliphatic chains. By operating as before, we find the equations determining ϕ_n and ϕ_p as

$$\beta\phi_p + \frac{\alpha}{2}\sin[2(\phi_p - \phi_n)] = 0, \quad (23)$$

$$\frac{\alpha}{2}\sin[2(\phi_p - \phi_n)] + \frac{g}{2}\sin(2\phi_n) + \frac{k}{d}(\Phi - \phi_n) = 0. \quad (24)$$

In the linear case, these equations read

$$\beta\phi_p + \alpha(\phi_p - \phi_n) = 0, \quad (25)$$

$$-\alpha(\phi_p - \phi_n) - g\phi_n - \frac{k}{d}(\Phi - \phi_n) = 0, \quad (26)$$

from which we get

$$\phi_p = \frac{\alpha}{\alpha + \beta} \frac{1}{1 + (w_{\text{eff}}d/k)} \Phi, \quad (27)$$

$$\phi_n = \frac{1}{1 + (w_{\text{eff}}d/k)} \Phi, \quad (28)$$

where we have put $w_{\text{eff}} = w_e - g$, where w_e has been defined above. By comparing Eq. (28) with Eq. (9), we conclude that the effective surface energy for the present case is w_{eff} . The presence of the aliphatic chains reduces the effective surface energy responsible for the planar alignment of the nematic liquid crystal. We observe that the planar easy axis is stable only if $w_{\text{eff}} > 0$, which implies $g < \alpha\beta/(\alpha + \beta)$. The effective anchoring energy relevant to the planar alignment tends to zero when $g \rightarrow \alpha\beta/(\alpha + \beta)$. In the special case where $\beta \rightarrow \infty$, $w_{\text{eff}} \rightarrow \alpha - g$, and the planar alignment is stable only if $\alpha > g$. In the opposite case where $\beta = 0$, from Eq. (22) we have $f_s = (\alpha/2)\sin^2(\phi_p - \phi_n) + (g/2)\cos^2\phi_n$. In this situation $\phi_p \rightarrow \phi_n$ to minimize f_s . Consequently $f_s = (g/2)\cos^2\phi_n$, and the

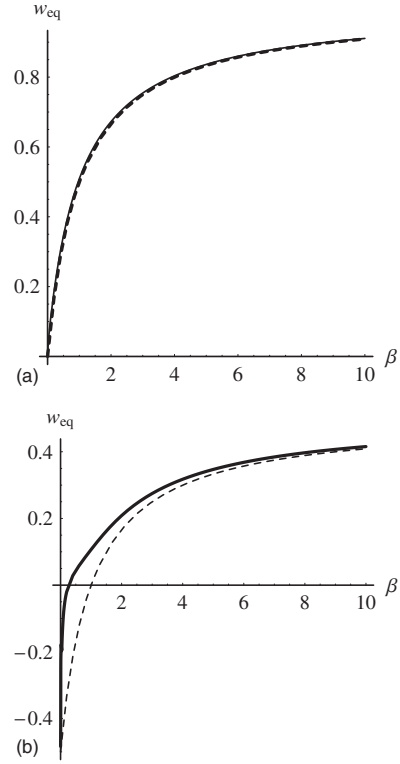


FIG. 1. w_{eq} versus β for different g , and $\Phi = \pi/3$. The energies are expressed in units of α . $\lambda = k/\alpha$, $u = \lambda/d = 0.1$. (a) $g = 0$ and (b) $g = \alpha/2$. The dotted lines represent $w_{\text{eff}} = \alpha\beta/(\alpha + \beta) - g$, valid in the linear approximation.

effective anchoring strength is $-g$, in agreement with the definition of w_{eff} reported above. According to the discussion reported above, the presence of the aliphatic chains allows the control of the effective anchoring energy strength. By controlling the surface densities of aliphatic chains and of the mesogenic side chains, we have a method to control the anchoring [11].

In the nonlinear case the basic equations of the problem are Eqs. (23) and (24), from which we obtain

$$\phi_p = \frac{1}{\beta} \left(\frac{k}{d}(\Phi - \phi_n) + \frac{g}{2}\sin(2\phi_n) \right), \quad (29)$$

for the angle formed by the polymer side group with the x axis. The transcendental equation determining ϕ_n is obtained by substituting the expression for ϕ_p into Eq. (23). The equivalent anchoring energy is then evaluated by means of Eq. (21), where ϕ_n is the one for the case under consideration. From Eq. (23) a simple calculation shows that, when $\phi_n \ll 1$, $w_{\text{eq}} \rightarrow w_{\text{eff}}$, as expected. We observe that in the limit of $\beta \rightarrow 0$ the easy axis tends to be homeotropic. Hence, the linear approximation seems not to be satisfactory for small β .

In Fig. 1 we show w_{eq} versus β for different g , and $\Phi = \pi/3$. In this figure the energies are expressed in units of α . We introduce $\lambda = k/\alpha$, which represents the extrapolation length when α is the anchoring energy strength, and $u = \lambda/d$. In Fig. 1(a) we consider the case $g = 0$, corresponding to the absence of the aliphatic chains. In this case, for β

$\rightarrow 0$, $w_{\text{eq}} \rightarrow 0$, and for $\beta \rightarrow \infty$, $w_{\text{eq}} \rightarrow \alpha$. In the same figure the dotted line represents $w_e = \alpha\beta/(\alpha + \beta)$ which is the anchoring energy strength in the linear approximation. In Fig. 1(b) is reported the case where $g = \alpha/2$. In this situation, for $\beta \rightarrow 0$, $w_{\text{eq}} \rightarrow -g = -\alpha/2$, as discussed above, and for $\beta \rightarrow \infty$, $w_{\text{eq}} \rightarrow \alpha - g = \alpha/2$. In this figure the dotted line represents $w_{\text{eff}} = \alpha\beta/(\alpha + \beta) - g$, valid in the linear approximation. As is evident from Fig. 1, the agreement between the linear approximation and the rigorous solution of the problem is rather poor for small β . As has been underlined above, this is due to the fact that for $g > \alpha\beta/(\alpha + \beta)$ the easy axis is perpendicular to the surface characterized by weak anchoring. Consequently the tilt angle cannot be considered as small. In this limit it is possible to obtain the dependence of w_{eq} versus β in a perturbative manner. Let us indicate by $\beta^* = \beta/\alpha$ and $g^* = g/\alpha$ the anchoring energies connected with the side chains and with the aliphatic chains, respectively, in units of α , and $u = \lambda/d = k/(ad)$. We limit our analysis to the case of $\beta^* \ll 1$, and use it as a small parameter. In the case of $\beta^* = 0$ from Eq. (23) we obtain $\phi_p^0 = \phi_n^0$, and from Eq. (24) the nematic orientation, in this limit, is the solution of the equation

$$g^* \sin(2\phi_n^0) + 2u(\Phi - \phi_n^0) = 0, \quad (30)$$

which minimizes the total energy per unit area, $F = f_s^0 + (k/2d)(\Phi - \phi_n^0)^2$, where $f_s^0 = (g/2)\cos^2 \phi_n^0$. Let us consider now the case of small β^* . We put $\phi_p^1 = \phi_n^0 + \beta^* \delta\phi_p$ and $\phi_n^1 = \phi_n^0 + \beta^* \delta\phi_n$. By substituting these expressions into Eqs. (23) and (24), and taking into account Eq. (30) we get, at the first order in β^* ,

$$\delta\phi_p = -\phi_n^0 - \frac{2\phi_n^0}{u - 2g^* \cos(\phi_n^0)}, \quad (31)$$

$$\delta\phi_n = -\frac{2\phi_n^0}{u - 2g^* \cos(\phi_n^0)}. \quad (32)$$

At the first order in β^* the equivalent anchoring w_{eq} given by Eq. (21) is found to be

$$w_{\text{eq}} = -g + \frac{2\phi_n^0}{\sin(2\phi_n^0)} \frac{u - g^* \cos(2\phi_n^0)}{u - 2g^* \cos(2\phi_n^0)} \beta. \quad (33)$$

From this equation it follows that when $\beta = 0$, $w_{\text{eq}} = -g$, and that

$$\left(\frac{dw_{\text{eq}}}{d\beta}\right)_{\beta=0} = \frac{2\phi_n^0}{\sin(2\phi_n^0)} \frac{u - g^* \cos(2\phi_n^0)}{u - 2g^* \cos(2\phi_n^0)}, \quad (34)$$

whereas in the linear limit $(dw_{\text{eq}}/d\beta)_0 = 1$. Since we are considering the nonlinear case, $2\phi_n^0/\sin(2\phi_n^0) > 1$, and for $\phi_n^0 \rightarrow \pi/2$, $2\phi_n^0/\sin(2\phi_n^0) \gg 1$, which implies $(dw_{\text{eq}}/d\beta)_0 \gg 1$. This result shows that for $\beta = 0$ the limit is correct, but the numerical values of w_{eq} close to $\beta = 0$ are not well approximated by the formula valid in the linear limit.

Another interesting case is the one where w_{eq} vanishes. According to Eq. (21) the condition $w_{\text{eq}} = 0$ implies $\phi_n = \Phi$. In this case the boundary conditions (23) and (24) read

$$\beta\phi_p + \frac{\alpha}{2}\sin[2(\phi_p - \Phi)] = 0, \quad (35)$$

$$\frac{\alpha}{2}\sin[2(\phi_p - \Phi)] + \frac{g}{2}\sin(2\Phi) = 0. \quad (36)$$

From these equations we obtain $\phi_p = (g/2\beta)\sin(2\Phi)$, and

$$g \sin(2\Phi) + \sin[(g/\beta)\sin(2\Phi) - 2\Phi] = 0, \quad (37)$$

which defines the relation among g , β , and Φ for which $w_{\text{eq}} = 0$. In the particular case where $g = \alpha/2$ and $\Phi = \pi/3$, this equation gives $\beta_c = 0.26\alpha$, whereas the linear approximation gives $\beta_c = \alpha g/(\alpha - g)$, which here gives $\beta_c = 0.26\alpha$, in good agreement with the value derived from Fig. 1(b).

C. Anchoring energy and Fredericksz transition

In the analysis reported above we have evaluated the effective anchoring energy of a polymer layer with side groups by comparing the profile of the nematic tilt angle in the cell under consideration with the one in a cell having strong tilted anchoring on one limiting surface, and weak anchoring on the other, where the anchoring energy is assumed of the type proposed by Rapini and Papoular [10]. In this section we evaluate the effective anchoring energy by assuming that the imposed deformation is due to an external electric field and that the anchoring energy is weak on the two limiting surfaces. We assume that the dielectric anisotropy of the liquid crystal is positive ($\epsilon_a > 0$), and the external electric field is parallel to the z axis, $\mathbf{E} = E\mathbf{z}$. The Cartesian reference frame used in this section has the origin of the z axis in the middle of the sample, and the limiting surfaces are located at $z = \pm d/2$. In the framework of the Rapini-Papoular approximation, the energy per unit surface of the nematic cell submitted to an external field is given by [16]

$$F = \frac{1}{2} \left\{ w_- \sin^2 \varphi(-d/2) + w_+ \sin^2 \varphi(d/2) + \int_{-d/2}^{d/2} [k(d\varphi/dz)^2 - \epsilon_a E^2 \sin^2 \varphi] dz \right\}, \quad (38)$$

where w_{\pm} are the anchoring energy strengths on the surfaces at $z = \pm d/2$, respectively. By minimizing F given by Eq. (38) we get

$$k(d^2\varphi/dz^2) + (1/2)\epsilon_a E^2 \sin(2\varphi) = 0 \quad (39)$$

for the bulk differential equation, and

$$\mp k(d\varphi/dz) + (w_{\mp}/2)\sin(2\varphi) = 0 \quad (40)$$

for the boundary conditions, at $z = \mp d/2$, respectively [12]. In the following we consider a symmetric sample, for which $w_- = w_+ = w$, and hence $\varphi(z) = \varphi(-z)$. In this framework the fundamental equations of the problem, which are Eqs. (39) and (40), read

$$2\xi^2(d^2\varphi/dz^2) + \sin(2\varphi) = 0 \quad \text{for } -d/2 \leq z \leq d/2, \quad (41)$$

and

$$2b(d\varphi/dz) - \sin(2\varphi) = 0 \quad \text{for } z = -d/2, \quad (42)$$

where $\xi = \sqrt{k/\varepsilon_a E^2}$ is the coherence length and $b = k/w$ the extrapolation length [12].

We are interested in the critical field E_c , such that for $E < E_c$ the stable configuration is the undistorted one, whereas for $E > E_c$ the stable configuration is distorted. For $E \sim E_c$, if the order-disorder transition is continuous, φ is very small, and the total free energy per unit surface of the sample is

$$F = w\phi^2 + (k/2) \int_{-d/2}^{d/2} [(d\varphi/dz)^2 - (1/\xi^2)\varphi^2] dz, \quad (43)$$

where $\phi = \varphi(-d/2) = \varphi(d/2)$, and Eqs. (41) and (42) become

$$\xi^2(d^2\varphi/dz^2) + \varphi = 0, \quad (44)$$

$$b(d\varphi/dz) - \phi = 0, \quad (45)$$

respectively. From Eq. (44) we obtain $\varphi(z) = A \cos(z/\xi)$. By substituting this expression for $\varphi(z)$ into Eq. (45) we get

$$A\{b \sin[d/(2\xi)] - \xi \cos[d/(2\xi)]\} = 0. \quad (46)$$

In the deformed state $A \neq 0$, and from Eq. (46) we have that the threshold field is defined by

$$\tan[d/(2\xi_c)] = \xi_c/b, \quad (47)$$

where $\xi_c = \sqrt{k/\varepsilon_a E_c^2}$, and E_c is the threshold field we are looking for. To analyze the stability of the deformed state we have to substitute the expression $\varphi(z) = A \cos(z/\xi)$ into F given by (43). We obtain

$$F = (k/\xi)\{(\xi/b) - \tan[d/(2\xi)]\}A^2 \cos^2[d/(2\xi)]. \quad (48)$$

It follows that

$$\frac{dF}{dA} = 2(k/\xi)\{(\xi/b) - \tan[d/(2\xi)]\}A \cos^2[d/(2\xi)], \quad (49)$$

$$\frac{d^2F}{dA^2} = 2(k/\xi)\{(\xi/b) - \tan[d/(2\xi)]\}\cos^2[d/(2\xi)]. \quad (50)$$

Since the actual profile has to minimize F , $dF/dA = 0$ and $d^2F/dA^2 > 0$. Consequently $A = 0$, which corresponds to the undeformed state, minimizes F if $\tan[d/(2\xi)] < \xi/b$. On the contrary, if $\tan[d/(2\xi)] > \xi/b$, the stable state is the distorted one.

Let us consider now the case in which the aligning layer is a polymer side chain. We do not take into account the presence of aliphatic chains, imposing homeotropic alignment. The total energy, per unit surface, for a symmetric sample submitted to an external electric field of amplitude E directed along the z axis is given by

$$F = \beta\phi_p^2 + \alpha \sin^2(\phi_p - \phi_n) - \Delta E^2 \sin^2 \phi_p + (k/2) \int_{-d/2}^{d/2} [(d\varphi/dz)^2 - (1/\xi^2)\sin^2 \varphi] dz, \quad (51)$$

where $\Delta = \varepsilon_{ap}\ell$, ε_{ap} being the dielectric anisotropy of the polymer side group, and ℓ the length of the chain connecting the lateral group to the surface. Close to the threshold ϕ_p and

ϕ_n are very small, and the expression for F given by (51) can be rewritten as

$$F = (\beta - \Delta E^2)\phi_p^2 + \alpha(\phi_p - \phi_n)^2 + (k/2) \int_{-d/2}^{d/2} [(d\varphi/dz)^2 - (1/\xi^2)\varphi^2] dz. \quad (52)$$

By operating as before we get again $\varphi(z) = A \cos(z/\xi)$, and F given by (52) becomes

$$F = (\beta - \Delta E^2)\phi_p^2 + \alpha\{\phi_p - A \cos[d/(2\xi)]\}^2 - [k/(2\xi)]A^2 \sin(d/\xi). \quad (53)$$

Now $F = F(\phi_p, A)$. The stable state is such that

$$\frac{\partial F}{\partial \phi_p} = \frac{\partial F}{\partial A} = 0, \quad \frac{\partial^2 F}{\partial A^2} > 0, \quad \frac{\partial^2 F}{\partial A^2} \frac{\partial^2 F}{\partial \phi_p^2} - \left(\frac{\partial^2 F}{\partial A \partial \phi_p}\right)^2 > 0. \quad (54)$$

Using (53) we have that the relations $\partial F/\partial \phi_p = \partial F/\partial A = 0$ give

$$(\beta - \Delta E^2 + \alpha)\phi_p - \alpha \cos[d/(2\xi)]A = 0, \quad (55)$$

$$2\alpha \cos[d/(2\xi)]\phi_p + \{k \sin(d/\xi) - 2\alpha \cos^2[d/(2\xi)]\}A = 0, \quad (56)$$

which form a homogeneous system. The solution $\phi_p = A = 0$, corresponding to the undistorted state, is stable if

$$2\alpha \cos^2[d/(2\xi)] - (k/\xi)\sin(d/\xi) > 0, \quad (57)$$

$$4\alpha \cos^2[d/(2\xi)]\{(\beta - \Delta E^2 + \alpha)(1 - (k/\alpha\xi)\tan[d/(2\xi)]) - \alpha\} > 0. \quad (58)$$

Since ℓ is a molecular dimension $\Delta E^2 \ll \beta$, and relations (57) and (58) can be rewritten as

$$\frac{k}{\alpha\xi} \tan[d/(2\xi)] < 1, \quad (59)$$

$$\frac{k}{w_e\xi} \tan[d/(2\xi)] < 1, \quad (60)$$

respectively, where $w_e = \alpha\beta/(\alpha + \beta)$, as before. The most restrictive inequality between (59) and (60) is the second one. Consequently the threshold we are seeking is given by $(k/w_e\xi)\tan[d/(2\xi)] = 1$. By comparing Eq. (60) with (47) we conclude that the effective anchoring energy is w_e , in agreement with the calculation reported above relevant to the case in which one of the surfaces was imposing strong anchoring.

Let us consider now the situation where aliphatic chains, inducing homeotropic alignment, are present. In this case, in Eq. (51) there is also the term $(g/2)\cos^2 \phi_n \sim (g/2)(1 - \phi_n^2)$, taking into account the surface energy related to the aliphatic chains. An analysis of the same type reported above gives again that the undistorted configuration is stable when $(k/w_{\text{eff}}\xi)\tan[d/(2\xi)] < 1$, where $w_{\text{eff}} = w_e - g$ as before.

It follows from the discussion reported above that the equivalent anchoring energy w_{eq} is smaller than α and β .

Consequently, the presence of the side chains reduces the anchoring energy, and hence the threshold voltage. The electric coherence length, indicating the zone where the distortion of the nematic liquid crystal is localized, is proportional to the inverse of the electrical field inducing the distortion. It follows that in the presence of a side-chain polymer, at the threshold, the electric coherence length is larger than the one when the side chains are absent.

III. RELAXATION TIME

We are interested now in the relaxation of an imposed deformation, when the distorting field is removed. We consider again a nematic cell in the shape of a slab of thickness d . The surface treatment is such as to induce planar alignment, and the nematic liquid crystal has a positive dielectric anisotropy. If the nematic cell is submitted to an electric field $E > E_c$, where E_c is the threshold field for the Fredericksz transition, the nematic tilt angle is not constant across the sample, as discussed in the previous section. If the external electric field is switched off, the nematic orientation relaxes toward the planar orientation, imposed by the surface treatment. The evolution of the nematic tilt angle $\varphi(z, t)$ is governed by the differential equation

$$k \frac{\partial^2 \varphi}{\partial z^2} - \eta \frac{\partial \varphi}{\partial t} = 0, \quad (61)$$

where η is the bulk viscosity. Equation (61) states that the bulk density of elastic torque, $k \partial^2 \varphi / \partial z^2$, is balanced by the viscous bulk density of viscous torque, $-\eta \partial \varphi / \partial t$. The temporal boundary conditions on $\varphi(z, t)$ are $\varphi(z, 0) = \Phi_0(z)$, and $\lim_{t \rightarrow \infty} \varphi(z, t) = 0$, where $\Phi_0(z)$ represents the initial deformation of the nematic liquid crystal induced by the external field. The boundary conditions on the coordinate z for $\varphi(z, t)$ depend on the surface treatment.

A. Strong anchoring

If the surface treatment is such as to give strong anchoring, the relevant boundary conditions are $\varphi(\pm d/2, t) = 0$. Let us consider first this simple case. The symmetry of the problem imposes that $\varphi(z, t) = \varphi(-z, t)$. We look for a solution of Eq. (61) of the type $\varphi(z, t) = Z(z)T(t)$. By substituting this expression into Eq. (61) we obtain

$$\left(\frac{1}{Z(z)} \frac{d^2 Z(z)}{dz^2} \right) - \frac{\eta}{k} \left(\frac{1}{T(t)} \frac{dT(t)}{dt} \right) = 0. \quad (62)$$

From Eq. (62) it follows that

$$\frac{1}{Z_a(z)} \frac{d^2 Z_a(z)}{dz^2} = -a^2 \quad \text{and} \quad \frac{\eta}{k} \left(\frac{1}{T_a(t)} \frac{dT_a(t)}{dt} \right) = -a^2, \quad (63)$$

where a is a constant to be determined. We note that a is real because $\lim_{t \rightarrow \infty} \varphi(z, t) = 0$. A simple calculation, taking into account the symmetry of the problem, gives $Z_a(z) = R_a \cos(az)$, and $T_a(t) = S_a \exp(-t/\tau_a)$, where R_a and S_a are constants, and $\tau_a = (1/a^2)(\eta/k)$ plays the role of the relaxation time. In this case a is the wave vector of the deforma-

tion. Note that in this framework the relaxation time coincides with the diffusion time for the initial deformation, since Eq. (61) is a diffusion equation for the tilt angle $\varphi(z, t)$. The actual deformation, related to the mode a , is then

$$\varphi_a(z, t) = A_a \cos(az) \exp(-t/\tau_a), \quad (64)$$

where $A_a = R_a S_a$. Using the boundary conditions $\varphi(\pm d/2, t) = 0$, we obtain that the possible values of a are given by $a_n = (2n+1)(\pi/d)$, where n is an integer. The relevant relaxation times, using $\tau_a = (1/a^2)(\eta/k)$, are then $\tau_n = \tau_0 / (2n+1)^2$, with $\tau_0 = (\eta/k)(d/\pi)^2$. Since Eq. (61) is linear, the complete solution is

$$\varphi(z, t) = \sum_a \varphi_a(z, t) = \sum_{n=0}^{\infty} A_n \cos(a_n z) \exp(-t/\tau_n). \quad (65)$$

The amplitudes A_n are determined by the initial condition $\varphi(z, 0) = \Phi_0(z)$, which reads

$$\Phi_0(z) = \sum_{n=0}^{\infty} A_n \cos(a_n z). \quad (66)$$

The set of functions $u_n(z) = \cos(a_n z) = \cos[(2n+1)(\pi z/d)]$ form an orthogonal basis in $(-d/2, d/2)$. Consequently, the inversion of Eq. (66) is simple. The problem is then solved. The longest relaxation time is $\tau_0 = (\eta/k)(d/\pi)^2$ introduced above.

B. Weak anchoring

In this case, in the Rapini-Papoular approximation [10], the boundary conditions are

$$\mp k \frac{\partial \varphi}{\partial z} + \frac{w}{2} \sin(2\varphi) = 0 \quad (67)$$

at $z = \mp d/2$. Equation (67) states the equilibrium of the torques at the surfaces. We limit our analysis to the linear case, where Eq. (67) can be written, at the surface $z = -d/2$, as

$$-k \frac{\partial \varphi}{\partial z} + w\varphi = 0. \quad (68)$$

By operating as before, from Eq. (68) we get the eigenvalue equation in the form

$$(ad/2) \tan(ad/2) = d/(2b), \quad (69)$$

where $b = k/w$ is the extrapolation length. Equation (69) has infinite solutions a_n . We have again that Eqs. (65) and (66) hold. The inversion of Eq. (66) is not simple as before because the set of eigenfunctions $u_n = \cos(a_n z)$ is no longer orthogonal. However, the problem can be solved following the procedure discussed in [17].

In the simple case where the anchoring energy is very weak, $b = k/w \gg d$, and from Eq. (69) we get $a^2 = 2/(bd)$. It follows that the longest relaxation time is found to be $\tau_w = \eta d / (2w)$, i.e., it is proportional to the thickness of the sample and to the inverse of the anchoring energy [18]. Consequently, for a given thickness of the nematic sample, the

lower the anchoring energy, the longer the relaxation time.

C. Surface viscosity

In the case where in the boundary conditions there is also a viscous torque, due to the surface viscosity, Eq. (68) reads

$$-k \frac{\partial \varphi}{\partial z} + w\varphi + \eta_s \frac{\partial \varphi}{\partial t} = 0, \quad (70)$$

where η_s is the coefficient of surface viscosity introduced by Derzhanski and Petrov [19] and discussed, among others, by [20–24]. By operating as before we obtain for the eigenvalue equation the expression

$$(ad/2)[a(\eta_s/\eta) + \tan(ad/2)] = d/(2b). \quad (71)$$

From now on to obtain the full solution of the problem it is necessary to do as described in the previous section.

In the limit of weak anchoring, from Eq. (71) we obtain

$$a^2 = \frac{2}{bd} \frac{1}{1 + 2\eta_s/(\eta d)}. \quad (72)$$

The relevant relaxation time is then $\tau_{sv} = \tau_w[1 + 2\eta_s/(\eta d)]$, where $\tau_w = \eta d/(2w)$ has been defined before. From the expression for τ_{sv} it follows that $\tau_{sv} > \tau_w$, as expected.

D. Surface layer

If a side-chain polymer is responsible for the nematic orientation, the surface energy, in the linear approximation, is

$$f_s = \frac{\beta}{2} \phi_p^2 + \frac{\alpha}{2} (\phi_p - \phi_n)^2, \quad (73)$$

where $\phi_n = \varphi(-d/2)$. In (73) we have neglected the presence of aliphatic chains imposing a homeotropic alignment on the nematic liquid crystal. The most general quadratic dissipation function for the two angles ϕ_n and ϕ_p is

$$\mathcal{R} = \frac{1}{2} \gamma_1 \phi'^2 + \gamma_2 \phi'_n \phi'_p + \frac{1}{2} \gamma_3 \phi_p'^2, \quad (74)$$

where the prime means a time derivative, and γ_1 , γ_2 , and γ_3 are phenomenological coefficients such that $\mathcal{R} \geq 0$. In the following we consider the special case $\gamma_1 = \gamma_3 = -\gamma_2 = \gamma$, where $\mathcal{R} = (\gamma/2)(\phi'_p - \phi'_n)^2$. In this framework the surface viscous torque on the side groups of the polymer is $\tau_{v,p} = -\delta \mathcal{R} / \delta \phi'_p = -\gamma(\phi'_p - \phi'_n)$, where γ is the viscosity relevant to the dissipation occurring at the interface between the nematic and the side groups of the polymer. The viscous torque on the liquid crystal is $\tau_{v,n} = -\tau_{v,p}$. According to this model, the dissipation in the surface layer is related to the relative motion of the liquid crystal director with respect to the side groups of the polymer. It is not the dissipation function responsible for the surface viscosity introduced in [19], but a kind of viscosity between two ordered media. The boundary conditions for the present case are

$$\beta \phi_p + \alpha(\phi_p - \phi_n) + \gamma(\phi'_p - \phi'_n) = 0, \quad (75)$$

$$-k \left(\frac{\partial \varphi}{\partial z} \right)_{-d/2} - \alpha(\phi_p - \phi_n) - \gamma(\phi'_p - \phi'_n) = 0. \quad (76)$$

From Eqs. (75) and (76) we obtain

$$\phi_p(t) = \frac{k}{\beta} \left(\frac{\partial \varphi}{\partial z} \right)_{-d/2}, \quad (77)$$

which, by taking into account Eq. (64), can be rewritten as

$$\phi_p(t) = \frac{k}{\beta} a A_a \sin(ad/2) \exp(-t/\tau_a). \quad (78)$$

By substituting Eqs. (64) and (78) into Eq. (75) we get for the eigenvalue equation the expression

$$\frac{k}{\beta} \frac{\alpha + \beta - (\gamma/\tau_a)}{\alpha - (\gamma/\tau_a)} a \tan(ad/2) = 1. \quad (79)$$

For $\gamma=0$ from Eq. (79) we get

$$k \frac{\alpha + \beta}{\alpha \beta} a \tan(ad/2) = 1, \quad (80)$$

which is equivalent to

$$(ad/2) \tan(ad/2) = d/(2L), \quad (81)$$

where $L = k/w_e$, with $w_e = \alpha\beta/(\alpha + \beta)$, as obtained before.

In the limit $\beta \rightarrow \infty$ Eq. (79) gives Eq. (71), if b is identified with k/α , and η_s with γ . These limits are expected because in the considered case of $\beta \rightarrow \infty$ the effective anchoring energy is α , and the surface dissipation is related just to the movement of the nematic liquid crystal.

For a numerical calculation we assume $k \sim 10^{-11}$ N, $\eta \sim 10^{-1}$ N s/m² [24], $\alpha \sim 10^{-5}$ J/m² [21], and $\beta \sim 4\alpha$. The thickness of the sample is supposed to be $d \sim 10^{-5}$ m. We consider the case where $\gamma \sim 2 \times 10^{-6}$ N s/m, which is a value in the range of the surface viscosity measured for nematic liquid crystals [20,21,24]. The influence of the viscosity related to the surface coupling between the side groups of the polymer and the nematic liquid crystal can be investigated by considering the function

$$\Psi(a) = \frac{k}{\beta} \frac{\alpha + \beta - (\gamma/\tau_a)}{\alpha - (\gamma/\tau_a)} a \tan(ad/2) - 1, \quad (82)$$

whose zeros define the relaxation times of the phenomenon under consideration. A simple analysis shows that the surface viscosity increases the longer relaxation time, as shown in Fig. 2. Using the numerical values reported above, the longest relaxation time is $\tau_{\max}(\gamma=0) = 0.156$ s, defined by the largest zero of the function $\Psi(a)$. In the case of $\gamma = 2 \times 10^{-6}$ N s/m, $\tau_{\max} = 0.279$ s. In Fig. 2 are reported the functions $\Psi(a)$ for $\gamma=0$ (dotted), and 2×10^{-6} N s/m (continuous). As is evident from Fig. 2, the two curves are coincident for large values of τ , and negative. We underline that the surface viscosity in nematic liquid crystals is assumed of the order of $\eta \ell_m$, where ℓ_m is on the nanometer scale [21]. Other values for this parameter have been reported in [20] and in [24]. The parameter γ introduced by us takes into account the dissipation connected to the coupling between the side groups and the nematic liquid crystal. It depends not

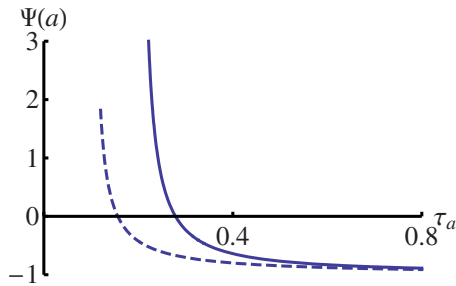


FIG. 2. (Color online) Eigenvalue function $\Psi(a)$ versus the relaxation time $\tau_a=1/a$. The actual relaxation times are the ones determined by the intersection of $\Psi(a)$ with the horizontal axis. The numerical values used in the calculation are the ones reported in the text. Dotted line $\gamma=0$, continuous curve $\gamma=2 \times 10^{-6}$ N s/m.

only on the liquid crystal, but also on the coupling at the interface between the two media. In our analysis we consider just the influence of γ on the longer relaxation time. However, the presence of γ influences all the characteristic times involved in the relaxation of the initial deformation, in particular, the shorter one. An analysis of this influence requires the solution of the complete problem and the determination of all the modes necessary to describe the initial deformation of the nematic liquid crystal, and will be the subject of a further investigation.

IV. CONCLUSIONS

We have considered the aligning properties of a polymer with side chains on a nematic liquid crystal. The equivalent anchoring energy of the surface polymer, w_{eq} , depends on the anchoring energy of the side chains and on the steric interaction of the side chains with the nematic liquid crystal. It has been derived by comparing the nematic tilt angle profile with that in a cell having a strong tilted anchoring on one surface, and weak anchoring on the other surface. We considered also the Freedericksz transition in a symmetric nematic cell. In this case, from the expression for the threshold field we obtain an expression for w_{eq} in agreement with the one determined with the previous calculation. Finally, we have considered the relaxation time of an imposed deformation in a nematic cell oriented by means of a polymer with side chains. In this case, the dissipation taking place at the interface between the nematic liquid crystal and the polymer is equivalent to a surface viscosity connected to a dissipation function quadratic in the relative angular velocity. In our analysis the surface energy connected to the deformation of the side chains has been assumed proportional to the square of the deformation, in agreement with the usual elastic theory. Our model can be easily generalized to more realistic surface energy and dissipation for the polymer side chains.

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