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Surface energy of a nematic liquid crystal in contact with structured surfaces

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A generalization of the functional form of the anchoring energy of a nematic liquid crystal in contact with a structured surface is proposed. The structured surface is represented by side-chain polymer, containing only aliphatic or aliphatic and mesogenic side groups, deposited as a thin alignment film onto a solid substrate. The basic assumption in the model developed in the present work is that the coupling between the polymer side groups and the nematic liquid crystal molecules is responsible for the elastic deformation and compression of the orienting groups taking place in the alignment film. We show that in the limit of small deformations, the surface energy is the same as the one given by the Rapini-Papoular approximation. In this limit, the effective anchoring strength is weak and is due to the elastic deformation of the orienting side groups, which is proportional to the inverse of the length of the aliphatic groups and the length of the linkage group of the mesogens, respectively. In the limit of large deformation, however, the term accounting the film compression is predominant which results in a nonzero torque facilitating the relaxation process of an imposed deformation when the applied electric field is switched off. Good agreement is found between the prediction of our model and the experimental data of the anchoring energy of a nematic liquid crystal aligned by means of Langmuir-Blodgett monolayers of fatty acids as a function of the length of their alkyl chains.

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I. INTRODUCTION

The anisotropic interaction of a nematic liquid crystal with a solid surface is, usually, described by introducing a surface field. The coupling of the surface field with the anisotropic properties of the nematic liquid crystal is responsible for the anisotropic part of the surface tension of the nematic liquid crystal-solid surface interface. In the Rapini-Papoular's approximation [1] this contribution is written in the form $f_s=-(w/2)(\mathbf{n}\cdot\mathbf{n_e})^2$. The coefficient w is known as anchoring energy strength and $\mathbf{n_e}$ as the easy direction. Their meaning has been extensively discussed by Faetti [2]. The anchoring energy strength w is an important parameter for technological applications of nematic liquid crystals because the threshold voltage for the transition of Freedericksz in uniformly oriented samples depends on w [3]. The expression written above for f_s has been proposed by means of symmetry considerations, in analogy with the coupling of an external field with the anisotropic properties of a nematic liquid crystal. In fact, the coupling of a nematic liquid crystal with an electric field of modulus E directed along $\mathbf{n_E}$, $\mathbf{E}=E\mathbf{n_E}$, is described by a bulk energy density $f_E=-(\varepsilon_a/2)E^2(\mathbf{n}\cdot\mathbf{n_E})^2$, where $\varepsilon_a=\varepsilon_\parallel-\varepsilon_\perp$ is the dielectric anisotropy of the liquid crystal, and $\parallel$ and $\perp$ refer to the nematic director $\mathbf{n}$, coinciding with the average molecular orientation [4]. By comparing the expressions for f_s and f_E it follows that w is related to the anisotropy of the nematic liquid crystal with respect to the surface field, oriented along $\mathbf{n_e}$, and to the strength of the surface field. The expression for f_s reported above is valid in the case where the liquid crystal is in contact with a solid substrate [5]. In the case where the solid substrate is nematic like, the functional form for f_s has to be generalized because also the orienting layer participate to the reorientation phenomenon induced by external fields on the nematic liquid crystal [6–8]. This aspect of the problem has been recently discussed by considering the temperature transitions in nematic liquid crystal samples oriented with a new type of polymer containing mesogenic side groups [9]. The importance of the substrate surface structure for the interfacial energy has been discussed also in connection with the relaxation time of an imposed deformation in a nematic sample [10]. In this paper we consider the orienting effect of a structured surface on a nematic liquid crystal. The surface can be a Langmuir-Blodgett film, as the one considered in [11,12], or a film made from side-chain polymers, as those recently proposed for technological applications [13]. In our analysis we investigate the orienting effect of the side groups of a side-chain polymer. These groups are only aliphatic chains and aliphatic chains and mesogenic molecules, attached to the main polymer chain via spacers. In the case where a Langmuir-Blodgett film is considered [11], the orienting groups are just flexible chains. The orienting groups are assumed uniformly distributed on the surface of the sample, with a surface density σ per unit area, close to the value of saturation, where σ is of the order of $1/S$, where S is the area of a transversal section of the chains. The coupling between the nematic molecules and the orienting film is supposed strong, in such a manner that the orientation of the nematic director at the interface with the orienting film coincides with the one of the orienting groups. In this framework, a deformation of the nematic liquid crystal orientation can induce a bend deformation (see Fig. 1) and a compression in the orienting film (see Fig. 2). Both deformation effects in the film are source of nematic surface energy, as it is shown in the following. A description of the model is presented in the next section. In Sec. III the elastic deformation of the orienting groups is presented. The contribution to the surface energy related to the compression of the orienting groups is evaluated in Sec. IV, and the total elastic deforma-

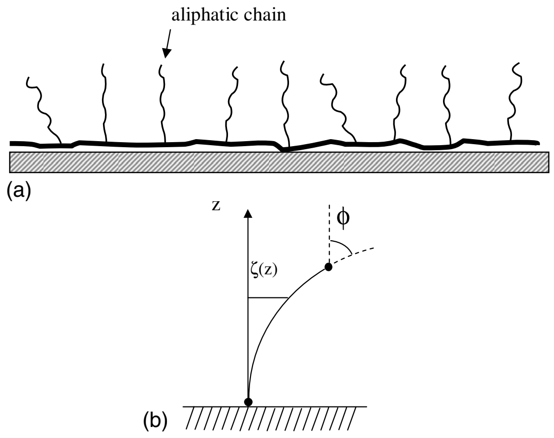

FIG. 1. (a) Schematic presentation of alignment layer made by side-chain polymer containing aliphatic orienting groups. (b) Orienting molecule of the surface layer. H is the length of the undeformed molecule, assumed of cylindrical shape of radius r. ξ is the molecular deformation induced by a localized torque, due to the coupling with the nematic molecules. The extremity of the orienting molecule in contact with the solid substrate is assumed fixed by short-range forces, such that $\xi(0)=0$ as well as $(d\xi/dz)_0=0$.

tion of the orienting film is discussed in Sec. V. The comparison of the theoretical predictions of the model with the experimental data is presented in Sec. VI. Section VII is devoted to the conclusions.

II. MODEL

When two phases are in contact, as in a junction, the total energy of the system is given by the sum of three terms. Two terms are the bulk energies of the two phases, and the remaining term is due to the direct interaction of one phase with the other. In the case where the molecular interactions are short range, the bulk energy densities of the two phases can be written in the elastic approximation, where each phase is described by phenomenological parameters, termed elastic constants. In this framework, the energy related to the direct interaction between the two phases, is a surface contribution, known as surface energy. In our analysis, one of the phases is a structured medium, whose thickness is in the molecular scale, in contact with a nematic liquid crystal. The energy of structured medium, G, is due to its direct interaction with the substrate over which it has been deposited, to the interaction among the atoms forming the chain, and to the interaction among the chains forming the surface film. We assume that these interactions are such to induce on the aliphatic chains, or aliphatic chains and mesogenic side groups, an easy axis normal to the solid substrate, assumed flat at molecular level. The surface energy, due to the direct interactions between the two media, W, depends on the relative orientation of the molecules of the liquid crystal and of the mesogenic side groups [14]. We indicate by $\mathbf{m}$ and $\mathbf{n}$ the statistical average of the mesogenic side group and of the nematic molecules at the geometrical interface. In a first approximation we assume that the interactions among the atoms forming the aliphatic chain and among the aliphatic chains forming the surface film can be described by an elastic energy related to the deviation of the aliphatic chain from the linear configuration. For simplicity we assume that the chain has a one-dimensional structure, and its energy, related to the deformation induced but the coupling with the nematic liquid crystal in contact with it, is equivalent to the elastic energy of a rigid rod. In this case $G=G(\ell,\mathbf{m})$, where ℓ is a parameter describing the structure of the aliphatic chain, and $\mathbf{m}$ is the orientation of the attached mesogenic side group. The surface energy depends on the relative orientation of $\mathbf{n}$ and $\mathbf{m}$, and can be written as $W=W(\mathbf{n}\cdot\mathbf{m})$. Since the interacting molecules at the interface are nematic liquid crystal like, for steric reasons the minimum of W is reached for $\mathbf{n}\parallel\mathbf{m}$. In a first approximation $W=(\beta/2)(\mathbf{n}\cdot\mathbf{m})^2$, where β is a phenomenological parameters describing the coupling between the two phases, a part an inessential term independent of the orientation of $\mathbf{n}$ and $\mathbf{m}$. The energy of the structured surface in contact with the nematic liquid crystal is then $f_s=G(\ell,\mathbf{m})+(\beta/2)(\mathbf{n}\cdot\mathbf{m})^2$. In a real problem, a deformation imposed on the nematic liquid crystal by means of an external field produces a deformation at the interface between the two media. The actual nematic and surface layer deformations are evaluated by minimizing the total energy of the system, as described in

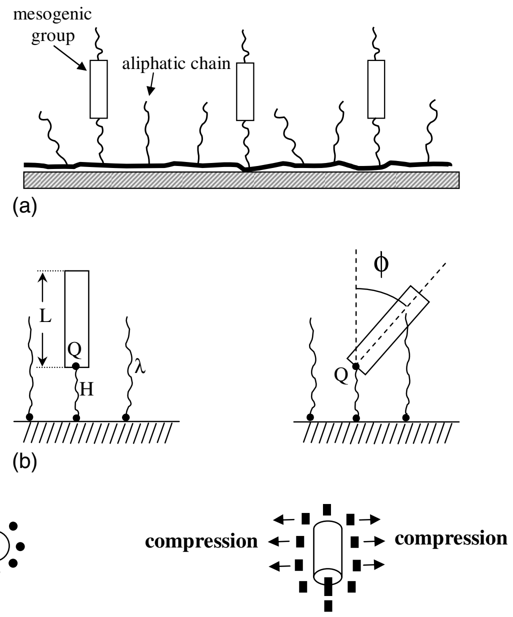

FIG. 2. (a) Schematic presentation of aligning layer made by side-chain polymer containing aliphatic chains and mesogenic groups. (b) Compression of a polymer side mesogenic group on a film of aliphatic chains. The tilt of the mesogenic group increases its volume in the aliphatic film, which is equivalent to a compression. The initial volume of the mesogenic group inside the aliphatic film is $V(\phi=0)=\pi r^2(\lambda-H)$, where λ and H are the length of aliphatic molecule and of the tail connecting the mesogenic group with the solid substrate. When the tilt of the mesogenic group is ϕ and the rotation around the point Q is free, the volume of the mesogenic group inside the aliphatic film is $V(\phi)=\pi r^2(\lambda-H)/\cos\phi$. The compression induced by the tilt is then $\delta=[V(\phi)-V(0)]/V(0)=(1-\cos\phi)/\cos\phi$. (c) Top view of the film containing aliphatic chains and mesogenic groups (left) before imposing the deformation and (right) under deformation.

[10]. In the simple case where $W(\mathbf{n}\cdot\mathbf{m}) \gg G(\ell,\mathbf{m})$, at the interface $\mathbf{n}=\mathbf{m}$. We limit our analysis to this case. In the more general case, the effective anchoring energy of the liquid crystal in contact with the structured surface depends also on the parameter β, as discussed in [15].

III. ELASTIC DEFORMATION OF THE ORIENTING GROUPS

If the orienting groups are stuck at the surface of the film, the coupling with the nematic molecules induces a deformation on these groups. In the high coverage limit of aliphatic chains, for the steric interaction connected to the excluded volume the orienting groups can be described as elastic rods of elastic modulus E and momentum of inertia of the section of the rods, assumed circular, I, the deformation induced by the torque τ, due to the coupling with the nematic liquid crystal, is

$$\xi(z) = \frac{\tau}{2\kappa} z^2, \tag{1}$$

where $\kappa = EI$ is the rigidity of the rod to the flexion, ξ is the deformation of the rod, and z is the Cartesian coordinate along the nondeformed position, as shown in Fig. 1 [16]. This assumption is justified from the hypothesis that the surface density of orienting groups is close to the saturation value. In this framework, even if the aliphatic chain is not completely rigid, due to the steric interactions among the aliphatic chains, the chains behave, in a first approximation, as rigid rods. As discussed by Landau and Lifchitz [16], Eq. (1) holds in the case where the rod has a circular section and the boundary conditions on the extremity of the molecular tail, in contact with the solid substrate, are such that $\xi(0)=0$ and $(d\xi/dz)_0=0$. From Eq. (1) it follows that the angle formed by the tangent to the rod with the z axis at $z=H$, ϕ, where H is the length of the tail, is given by

$$\tan \phi = \left(\frac{d\xi}{dz}\right)_{z=H} = \frac{H}{\kappa}\tau. \tag{2}$$

In our framework ϕ coincides with the nematic tilt angle at the interface. The torque τ is defined in terms of the surface energy of the nematic molecules, $U_1(\phi)$, by $\tau = -dU_1/d\phi$ [17]. By taking into account Eq. (2) we get that the surface energy, per molecule, is

$$U_1(\phi) = -j \log[\cos \phi], \tag{3}$$

where $j=\kappa/H$. The case of flexible rods corresponds to low value of κ, and thus to weak anchoring energy, whereas the case of $\kappa \to \infty$ gives strong anchoring. Hence, by tuning the flexibility of the orienting groups, it is possible to control the anchoring energy. The same considerations are valid in the case in which the elastic rod is bearing a mesogenic group at its end.

IV. ELASTIC COMPRESSION OF THE ORIENTING GROUPS

For orienting films made from side-chain polymers containing aliphatic chains and mesogenic side groups, the tilt of the orienting groups, induced by the coupling with the nematic molecules, can induce also a compression in the surface film. The mechanism is illustrated in Fig. 2, where a mesogenic group is shown, surrounded by aliphatic chains. We consider first the simple case where the mesogenic groups can freely rotate around the point Q, representing its connection with the tail stuck at the solid surface. In this framework a tilt of an angle ϕ of the mesogenic group induces a relative variation in the volume occupied by the mesogenic groups in the film given by $\delta = (1-\cos\phi)/\cos\phi$. The elastic energy per mesogenic molecule, due to the corresponding compression of the aliphatic chains in the film, is proportional to δ^2 [16], and hence it is given by

$$U_2(\phi) = R\left(\frac{1-\cos\phi}{\cos\phi}\right)^2, \tag{4}$$

for $\phi < \phi^*$, where $\cos\phi^* = (\lambda - H)/L$, with λ, H, and L being the length of the aliphatic chain, that of the tail, and that of the mesogenic group, respectively. The parameter R depends on the compressibility of the film β, and it is given by $R = (1/2)\beta$. On the contrary, for $\phi > \phi^*$, $U_2(\phi > \phi^*) = U_2(\phi^*)$, and the compression energy related to the tilt of the mesogenic group is independent of ϕ.

If the nematic anchoring energy strength is due to the compression of the film, the strong anchoring case corresponds to $R \to \infty$.

V. TOTAL ELASTIC DEFORMATION IN THE ORIENTING FILM

When the two mechanisms discussed above are present at the same time, the surface energy per unit area for a nematic liquid crystal having homeotropic easy axis is $f_s(\phi) = \sigma_A U_{1A}(\phi) + \sigma_M [U_{1M}(\phi) + U_2(\phi)]$, where σ_A and σ_M are the surface densities of aliphatic chains and of the mesogenic side groups, U_{1A} and U_{1M} are the elastic energies for the bend deformations of the aliphatic chains and of the mesogenic groups, respectively, and U_2 is the elastic energy for the compression of the aliphatic chains by the mesogenic groups in the orienting film. The dependence of f_s on ϕ is shown in Fig. 3.

As it is evident from the figure, f_s presents a minimum for $\phi=0$, indicating that the surface energy f_s under consideration is characterized by an easy direction perpendicular to the solid surface (homeotropic). In the limit of small ϕ, $U_1 \sim (j/2)\phi^2$ and $U_2 \sim (R/6)\phi^4$. It follows that, for small deformations around $\phi \to 0$, the anchoring energy is mainly due to the elastic deformation of the orienting groups, whereas for large ϕ, the leading term in f_s is the compression of the aliphatic side groups due to the tilt of the mesogenic groups. The peculiarity of the effective anchoring energy proposed above is that in the limit of $\phi \to \pi/2$, f_s does not present a maximum. This is the most important difference from the functional form proposed by Rapini-Rapoular [1]. In fact, according to [1] when f_s presents a maximum for $\phi = \pi/2$ it is possible to define the saturation field E_{sat}, such that for $E > E_{\text{sat}}$ the sample is in the planar orientation. If the deforming field is now removed, the imposed deformation relaxes to the initial homeotropic orientation under the effect of an ini-

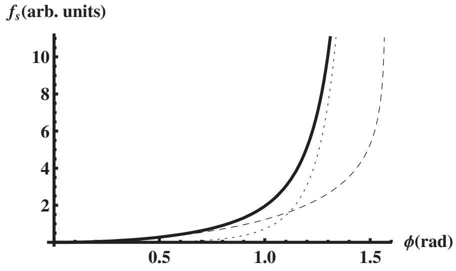

FIG. 3. Tilt angle dependence of the surface energy, f_s, of a nematic liquid crystal in contact with a structured surface. Dashed line: contribution related to the bend deformation of the orienting groups (U_1). Dotted line: contribution due to the compression of the orienting film (U_2). $f_s=\sigma(U_1+U_2)$ is the total surface energy. f_s presents a well-defined minimum for $\phi=0$, indicating that the easy axis is along the geometrical normal of the surface (homeotropic). Around $\phi=0$ the main contribution to the surface energy is related to the deformation of the surface molecule induced by the coupling of the surface molecules with the nematic liquid crystal. For large ϕ the more important contribution is the one due to the compression of the surface layer. The curves are drawn assuming that the bend deformation energy for the mesogenic side groups and the aliphatic chains have the same rigidity κ. The numerical values of the parameters entering into the model are: $j=2r$, $\sigma_A=\sigma_M$, $H=L$, and $\lambda=1.5L$, giving $\phi^*=1.04$ rad.

tial torque due to the surface treatment which is zero. On the contrary, according to the functional form of the surface energy due to the presence of a structured surface layer, the initial torque is large, and the relaxation toward the homeotropic orientation begins under the action of a large noncompensated torque. Hence, the presence of the structured surface layer may result in a reduction in the effective relaxation time of an imposed deformation. From an application point of view, this possibility seems very promising.

VI. DISCUSSION

To investigate the validity of the model presented above we analyze the experimental data reported in [11]. In that paper the anchoring energy strength of the nematic liquid crystal *N*-(*p*-methoxibenzyllidene)-*p*-butylaniline (MBBA) on Langmuir-Blodgett monolayers of fatty acids was studied as a function of the length of the fatty acid alkyl chain. In this case the orienting effect is due only to the fatty acid, and in the surface energy for the nematic only the term U_1 due to their elastic energy connected with the bend deformation appears. The monolayer was deposited onto the inner surfaces of the glass plates forming a sandwich cell filled with MBBA. The anchoring strength of MBBA on fatty acid Langmuir-Blodgett monolayers was measured by means of the Freedericksz transition technique [18]. According to this method only small deformations are involved since the anchoring energy is evaluated via the critical voltage to induce the transition of Freedericksz in a homeotropic sample of a nematic liquid crystal with a negative dielectric anisotropy. Consequently, the experimental values of w are connected only to the deformation of the fatty acids, related to the parameter $j=\kappa/H$ by the relation $w=\sigma_A j=a/H$, where $a=\sigma_A\kappa=\sigma_A EI$. In Fig. 4 we show the dependence of w on the length of the chain H. The best fit has been obtained by assuming that the length of the fatty acids is proportional to the number of carbon atoms, n, according to $H=nu$, where $u\sim 1$ Å. In this framework $a/u\sim 9.2\times 10^{-5}$ J/m^2. By taking into account that $\sigma_A\sim 1/A$, where $A\sim 0.25$ nm^2 is of the order of the surface per molecule [11], and $I=(\pi/4)r^4$, where $r\sim 2u$ is the radius of the cylinder by means of which we approximate the molecule of the fatty acid, we get $E\sim 2\times 10^6$ J/m^3. This value is a little bit smaller than the one expected by a simple estimation $E\sim K_BT/V$, where V is the volume of an aliphatic chain. By assuming $V\sim A\times H\sim 0.25\times 10^{-18}\times 20\times 10^{-10}\sim 5\times 10^{-28}$ m^3, we get $E\sim 2\times 10^7$ J/m^3. This discrepancy could be due to the crude approximation where the aliphatic chains are described as rigid rods.

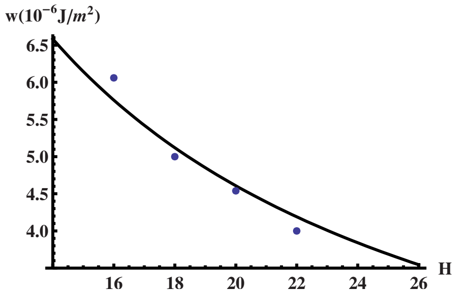

FIG. 4. (Color online) Comparison between the anchoring energy strength of the nematic liquid crystal MBBA on Langmuir-Blodgett monolayers of fatty acids as a function of the length of the fatty acid alkyl chain reported in [11] with the theoretical model described in the text, based on the elastic deformation of the orienting molecules.

In the analysis presented above we have assumed that the orientation of the molecules of the nematic liquid crystal in contact with the structured substrate coincides with the one of the orienting groups. In other words, that the coupling between the nematic molecules and aligning molecules is strong. In the opposite case, when the interaction energy between the molecules of the nematic and the orienting groups is comparable with the other energies entering in the problem, our analysis has to be generalized. A simple way to do this is to assume that the interaction energy between the nematic and orienting groups is proportional to $\cos^2(\phi_n-\phi_p)$, where ϕ_n and ϕ_p are the tilt angles formed by the nematic and aligning molecules with the substrate, respectively. This more general problem is under study, and it will be published elsewhere.

VII. CONCLUSIONS

The anchoring of the liquid crystals on the confining solid substrates is of vital importance for the performance of the liquid crystal displays (LCD) since such important LCD characteristics as the threshold voltage for Freedericksz transition U_{th} and both rise τ_r and fall τ_f time depend on the anchoring strength [18]. For instance, weak anchoring gives low U_{th} and short τ_r, but long τ_f. On the contrary, strong anchoring gives high U_{th} and long τ_r, but short τ_f. It is obvious that it is impossible to achieve at the same time low U_{th} and short both τ_r and τ_f just by fixing the anchoring strength by means of the known so far methods. As it has been pointed out in this work, by a proper selection of the length of the aliphatic chains and the length of the spacers of the mesogenic side groups forming the structured surface, the anchoring condition for a nematic on such a surface could be tuned to be weak, thus resulting in low U_{th} and short τ_r. On the other hand, the nonzero torque, due to the elastic deformation and the compression taking place in the alignment film under an applied electric field, will reinforce the relaxation process to the initial field-free nondeformed state of the liquid crystal resulting in shortening of τ_f. In fact, as it has been discussed at the end of Sec. V, the effective anchoring energy due to the structured surface presents a minimum for the homeotropic orientation of the nematic liquid crystal. For small deviations from this equilibrium orientation, the effective anchoring energy is of the type proposed by Rapini and Papoular [1]. This means that the elastic torque due to the surface energy corresponding to the homeotropic orientation vanishes. On the other hand, the planar nematic orientation does not correspond to a maximum for the surface anchoring energy, as it follows from Fig. 3. From this observation it follows that if the initial homeotropic orientation is modified in a planar orientation by means of an external field, and after that the distorting field is removed, the initial torque acting on the nematic director is not zero, and the elastic relaxation begins under the effect of this torque.

The model presented in this paper is phenomenological, and based on the hypothesis that the structured surface can be described in an elastic manner. It is based on the assumption that the coupling energy between the nematic liquid crystal and the mesogenic side groups attached to the aliphatic chains is larger than the elastic energy involved in the chain deformation. A generalization of the model to the case where the two energies are of the same order of magnitude does not present any difficulties. However, in this case also the dissipation between the structured surface and the nematic liquid crystal has to be taken into account, as discussed in [10]. This aspect of the problem presents a fundamental interest related to the surface viscosity [19].

The proposed here model of the anchoring of a nematic on a structured surface gives a general information about the important parameters that enable the tuning of the anchoring in a desirable way giving thus a guideline for the design of appropriate alignment materials possessing advanced performance.

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