

# Nonmonotonic behavior of the nematic tilt angle in a temperature-induced surface transition

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We report on a nonmonotonic temperature behavior of the pretilt in cells containing polymers as alignment layers. The latter are very promising since they enable control of the anchoring of the liquid crystal. We show that such a behavior cannot be interpreted by the standard Landau or mean-field theory. We propose a generalization of the mean-field model, including the temperature dependence of the anchoring due to the polymer layer that enables a description of the nonlinear behavior. The agreement between the predictions of the model and the experimental data is good.

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## I. INTRODUCTION

Nematic liquid crystals are formed by strongly anisometric molecules. In the bulk the intermolecular interaction tends to orient the molecular axis parallel to an average direction, termed the nematic director and indicated by the unit vector  $\mathbf{n}$ . In the absence of external fields, all directions of  $\mathbf{n}$  in the bulk are equivalent. Close to a surface limiting the nematic material, the nematic symmetry is broken. In this case, in the absence of bulk torques acting on the nematic molecules, the nematic director is aligned along a given direction, called the easy direction  $\mathbf{n}_0$ . The easy direction is the one which minimizes the anisotropic part of the surface energy characterizing the interface nematic-substrate,  $f_s$ . As discussed by several authors,  $f_s$  is partially connected with the reduced symmetry of the nematic liquid crystal at the limiting surface and partially due to the direct interaction between the nematic molecules and the molecules of the substrate [1]. Long ago, Bouchiat and Langevin-Cruchon reported on the temperature dependence of the surface tilt angle at the free surface [2]. Since then, several other researchers observed a temperature dependence of the surface tilt angle [3–12]. The phenomenon was termed the *temperature surface transition* (TST). To our knowledge, all the reported temperature surface transitions indicate a monotonic dependence of the tilt angle on the temperature. The first interpretation of this phenomenon was given by Sluckin and Poniewierski [13] by means of a Landau-like expansion of the surface energy and extended by other authors to more general cases [14–16]. According to this model, the anisotropic part of the surface energy characterizing the interface nematic-substrate is expanded in power series of the nematic scalar order parameter [17]. However, since the nematic order parameter is not a small quantity, such a model is expected to work well only very close to the nematic-isotropic transition [18]. A different model, based on a generalization of the mean-field theory, where the molecular surface interaction is used as small parameter in the perturbational expansion of the surface energy, was proposed a few years ago

[19,20]. In the models of temperature-induced surface transitions based on the Landau-like expansion or on the mean-field theory, thermal effects arise only from the temperature dependence of the degree of alignment of the nematic molecules, because the physical properties of the substrate are supposed to be temperature independent in the range where the temperature surface transition appears. The models quoted above only in this case correctly describe the behavior of nematic liquid crystals in contact with a solid substrate [21]. However, deviations from the predictions of the models are expected for nematic samples oriented by means of surfactants, for instance, because their thermal behavior could be similar to that of the liquid crystal materials.

Here, we report on a different type of temperature surface transition, where the nematic tilt angle is changing in a nonmonotonic manner with the temperature. We have experimentally investigated nematic cells containing alignment layers made from side-chain polymers. The side groups of the polymers (**P1**) and (**P2**) are alkyl chains and mesogenic groups in two different proportions. The aligning layers have been unidirectionally rubbed in order to obtain a preferred direction of alignment and assembled in antiparallel position in such a manner that the easy axes on the two surfaces are parallel. With these arrangements of the limiting surfaces, the nematic orientation across the cell is position independent, and there is not elastic distortion induced by the surfaces. The experimental cells have been filled with the nematic liquid crystal MJ05963 (Merck) and oriented by two polymers deposited on the surfaces, indicated by P1 and P2, described above. We have observed a nonmonotonic dependence of the nematic tilt angle on the temperature (see Fig. 1). The nonmonotonic behavior is more pronounced for the cell oriented by the polymer P2 containing more mesogenic side groups. The measurements have been done using a capacitive technique, detecting the temperature dependence of the capacitance of the cell and comparing it with the one of the sample perfectly oriented in planar or homeotropic geometry. The cells in the high-temperature region exhibit an alignment close to the homeotropic alignment.

In Sec. II we show that the models discussed above are unable to predict the observed nonmonotonic trend of the tilt angle with temperature. In Sec. III we propose a generalization of the mean-field model where the temperature dependence of the substrate is taken into account by means of a surface field and show that the experimentally observed non-

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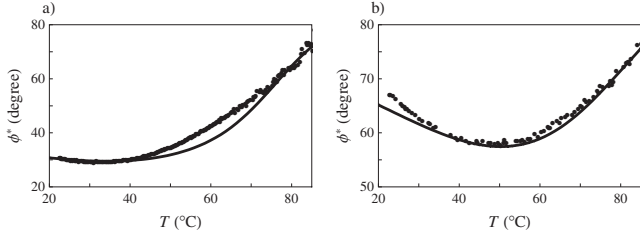


FIG. 1. Temperature dependence of the tilt angle  $\phi^*$  in a nematic cell oriented by a rubbed polymer. The nonmonotonic trend of  $\phi^*$  vs  $T$  is connected with the presence of an orienting effect of the polymer on the liquid crystal depending on the degree of order of the polymer itself. The term in the surface energy related to this effect has been chosen proportional to the scalar formed with the tensor order parameters of the two ordered media in contact. (a) Liquid crystal MJ05963 in contact with the polymer P1. (b) Liquid crystal MJ05963 in contact with the polymer P2 with more mesogenic side groups.

monotonic behavior of the nematic tilt angle can be interpreted in terms of this model. Section IV is devoted to the conclusions.

## II. PREVIOUS MODELS FOR THE TST

Let us first show that the models based on the Landau-like expansion or on the mean-field theory cannot predict a non-monotonic behavior of the nematic tilt angle in the temperature-induced surface transitions. In the analysis reported in the following it is assumed that the liquid crystal has uniform properties across the cell, without any compositional changes near the surfaces, and that the easy axes of the two surfaces are parallel, in such a manner that there is not elastic deformation in the cell. In this situation, the bulk orientation of the liquid crystal is the one minimizing the anisotropic part of the surface energy.

Nematic liquid crystals are characterized, from the symmetry point of view, by the tensorial order parameter  $Q_{ij} = \frac{3}{2}S[n_i n_j - \frac{1}{3}\delta_{ij}]$ , where  $S$  is the scalar order parameter,  $n_i$  are the Cartesian components of the director, and  $\delta_{ij}$  are the elements of the identity tensor of third order [17]. Let us consider a flat surface, with geometrical normal  $\mathbf{k}$ , separating the nematic liquid crystal by an isotropic substrate. According to Landau-like theory [13], the surface energy is decomposed into terms of  $Q_{ij}$  and  $k_i$  as follows:  $f_s = \beta_0 Q_{ij} Q_{ji} + \beta_1 k_i Q_{ij} k_j + \beta_2 k_i Q_{ij} Q_{ji} k_l + \beta_3 (k_i Q_{ij} k_j)^2$ , where the first term depends just on the nematic properties, whereas the remaining terms depend on the relative orientation of the nematic with respect to the geometrical normal. The coefficients  $\beta_i$  are temperature independent, and  $\beta_1$ ,  $\beta_2$ , and  $\beta_3$  depend on the substrate as well as on the liquid crystal. In the following we limit our analysis to the case in which  $\mathbf{n}$ , the nematic director, remains in a plane, which we choose as the  $(x, z)$  plane, where the  $z$  axis is parallel to  $\mathbf{k}$ . We indicate by  $\phi$  the angle formed by  $\mathbf{n}$  with the  $x$  axis in such a manner that  $\mathbf{n} = \mathbf{x} \cos \phi + \mathbf{k} \sin \phi$ , where  $\mathbf{x}$  is the unit vector along the  $x$  axis. By substituting the expression for  $Q_{ij}$  into  $f_s$  and expressing  $f_s$  in terms of the tilt angle  $\phi$ , we obtain

$$f_s = f_0 + \frac{1}{2}A_L \sin^2 \phi + \frac{1}{4}B_L \sin^4 \phi, \quad (1)$$

where the coefficients  $A_L$  and  $B_L$  depend on the temperature via the scalar order parameter as follows:  $A_L = 3[\beta_1 S + \frac{1}{2}(\beta_2 - 2\beta_3)S^2]$  and  $B_L = 9\beta_3 S^2$ . In Eq. (1) the subscript  $L$  indicates that the analysis is performed by means of a Landau-like model. In the frame of the mean-field model presented in [20], the surface energy has to be expanded in power series of the molecular surface potential. In this case we obtain an expression for  $f_s$  of the same kind as the one reported in Eq. (1), where the coefficients are given by  $A_{MF} = aS - bS^{10/3}$  and  $B_{MF} = \frac{7}{3}bS^{10/3}$ , where now the subscript  $MF$  means ‘‘mean field.’’ We point out that in the expressions for  $A_L$  and  $B_L$  are present three phenomenological parameters  $\beta_1$ ,  $\beta_2$ , and  $\beta_3$ , whereas in the ones for  $A_{MF}$  and  $B_{MF}$  only two,  $a$  and  $b$ . At the lowest order in  $S$  the two approaches predict a linear dependence of  $f_s$  on the scalar order parameter. However, at the second order in  $S$ , the Landau model predicts a correction proportional to  $S^2$ , whereas the mean-field model a correction proportional to  $S^{10/3}$ . As underlined in [20] the mean-field model is expected to work well in the nematic phase, where  $S \sim 1$ , whereas the Landau-like model works only close to the nematic-isotropic transition, where  $S$  is small. In both cases the anisotropic part of the surface energy is given by an expression of the type of Eq. (1), with coefficients  $A$  and  $B$  that differ for the two models. In general, the stable surface orientation is the one minimizing  $f_s$ . By imposing  $df_s/d\phi = 0$  we obtain for the easy tilt angle  $\phi = 0$ ,  $\phi = \pi/2$ , and  $\sin^2 \phi^* = -A/B$ . The third solution exists only if  $0 \leq (-A/B) \leq 1$ , as we assume from now on, since we are interested in the temperature surface transitions where  $\phi = \phi(T)$ . Taking into consideration that  $(d^2 f_s / d\phi^2)_0 = A$ ,  $(d^2 f_s / d\phi^2)_{\pi/2} = -(A+B)$ , and  $(d^2 f_s / d\phi^2)_{\phi^*} = -2A[1 + (A/B)]$ , it follows that if  $A < 0$ ,  $B > 0$ , and  $|A/B| < 1$ , the stable state is the tilted one,  $\phi^*$ . From the expression defining  $\phi^*$  we get for the temperature dependence of the nematic tilt angle the expression

$$\frac{d\phi^*}{dT} = -\frac{1}{\sin(2\phi^*)} \frac{d}{dT} \left( \frac{A}{B} \right). \quad (2)$$

By using for  $A$  and  $B$  the expressions predicted by the Landau-like model and taking into account that the temperature dependence of the coefficients is through the scalar order parameter  $S$ , from Eq. (2) we get

$$\left( \frac{d\phi^*}{dT} \right)_L = \frac{1}{\sin(2\phi^*)} \frac{\beta_1}{3\beta_3} S^{-2} \frac{dS}{dT}, \quad (3)$$

whereas using the expressions for  $A$  and  $B$  predicted by the mean-field theory we have

$$\left( \frac{d\phi^*}{dT} \right)_{MF} = \frac{1}{\sin(2\phi^*)} \frac{a}{b} S^{-10/3} \frac{dS}{dT}. \quad (4)$$

Since  $0 \leq \phi^* \leq \pi/2$ , it follows that  $\sin(2\phi^*) > 0$ . Furthermore,  $S > 0$ ,  $dS/dT < 0$ , and the coefficients  $\beta_1$  and  $\beta_3$ , as well as  $a$  and  $b$ , are temperature independent. Consequently, we conclude that both models predict a monotonic depen-

dence of the tilt angle, in agreement with some experimental observations.

### III. OUR MODEL FOR THE TST

To interpret our data shown in Fig. 1, we propose a modified version of the mean-field model discussed above. In our analysis we suppose that the alignment effect of the polymer on the nematic liquid crystal is a combination of physicochemical and steric interactions. These interactions are related to the isotropic- and nematiclike properties of the polymers, respectively. We assume that the physicochemical interactions are responsible for an easy-direction temperature-independent  $\phi_1$ , which in the following will be assumed close to the planar one. The relevant anchoring strength  $w_1$  is supposed to be temperature dependent, in agreement with the predictions of the mean-field model [20]. We assume furthermore that the polymer side chain has a nematiclike order described by a scalar order parameter  $S_p$ , giving information on the fluctuation of the polymer side groups with respect to an average direction, we indicate by  $\mathbf{m}$ . The relevant tensorial order parameter is  $Q_{ij}^p = \frac{3}{2} S_p [m_i m_j - \frac{1}{3} \delta_{ij}]$ , in analogy with the equivalent quantity defined for the nematic liquid crystal. The steric part of the surface energy, connected with the degree of the order of the polymer side groups, is responsible for a surface energy proportional to  $Q_{ij} Q_{ij}^p \propto S S_p [(\mathbf{n} \cdot \mathbf{m})^2 - \frac{1}{3}]$ . Written in terms of the tilt angle we have for the anisotropic part of the surface energy of the nematic in contact with the polymer, ignoring an inessential constant,

$$f_s = \frac{1}{2} w_1 \sin^2(\phi - \phi_1) + \frac{1}{2} w_2 \sin^2(\phi - \phi_2), \quad (5)$$

where  $\phi_2$  and  $w_2$  are the easy axis and anchoring strength connected to the polymer side groups, respectively. By operating as before, we obtain that the easy axis  $\phi^*$  is defined by  $df_s/d\phi=0$ , from which we get

$$\tan(2\phi^*) = \frac{w_1 \sin(2\phi_1) + w_2 \sin(2\phi_2)}{w_1 \cos(2\phi_1) + w_2 \cos(2\phi_2)}. \quad (6)$$

Note that for  $w_1 \rightarrow \infty$ ,  $\phi^* \rightarrow \phi_1$ , and for  $w_2 \rightarrow \infty$ ,  $\phi^* \rightarrow \phi_2$ , as expected. Inverting Eq. (6) we have

$$\phi^* = \arccos \left\{ \frac{w_1 \cos(2\phi_1) + w_e + w_2 \cos(2\phi_2)}{2w_e} \right\}^{1/2}, \quad (7)$$

where  $w_e = \sqrt{w_1^2 + 2w_1 w_2 \cos[2(\phi_1 - \phi_2)] + w_2^2}$  is the effective anchoring energy connected to the effective easy axis  $\phi^*$ . From Eq. (7), considering that  $w_1 = w_1(T)$  as well as  $w_2 = w_2(T)$ , via the scalar order parameters  $S$  and  $S_p$ , we obtain

$$\frac{d\phi^*}{dT} = \frac{1}{2} \left( w_1 \frac{dw_2}{dT} - w_2 \frac{dw_1}{dT} \right) \frac{\sin[2(\phi_2 - \phi_1)]}{w_e^2}. \quad (8)$$

From Eq. (8) it is clear that if there exists a temperature  $T_0$  such that  $w_1 dw_2/dT = w_2 dw_1/dT$ ;  $\phi^*(T)$  can have an extremum, for  $T = T_0$ , and then the temperature dependence of the tilt angle will be not monotonic. By assuming that the easy direction induced by the isotropic rubbed polymer is close to

the planar one and the relevant anchoring energy strength  $w_1 = \alpha S + \beta S^{10/3}$ , in agreement with the mean-field model [20,22], and that  $w_2 = q S S_p$ , where  $\alpha$ ,  $\beta$ , and  $q$  are phenomenological temperature-independent constants, we can predict the nonmonotonic temperature dependence of the tilt angle. Using the definition of  $w_e$  and taking into account that, at  $T = T_0$ ,  $w_1 dw_2/dT = w_2 dw_1/dT$ , we obtain  $(dw_e/dT) = (w_e/w_1)(dw_1/dT)$ , from which we derive that at  $T_0$  the effective anchoring energy  $w_e$  does not vanish and its temperature derivative is finite.

In the analysis presented above we have assumed that  $\phi_1 \neq 0$  and  $\phi_2 \neq \pi/2$  in such a manner that the anchoring transition is continuous. In the case  $\phi_1 = 0$  and  $\phi_2 = \pi/2$  the surface energy  $f_s$ , beside a term independent of the tilt angle, is  $f_s = \frac{1}{2} w(T) \sin^2 \phi$ , where  $w(T) = w_1(T) - w_2(T)$ . In this frame work the easy axis is  $\phi^* = 0$  if  $w_1 > w_2$  or  $\phi^* = \pi/2$  if  $w_1 < w_2$ . The transition from planar to homeotropic orientation is abrupt (discontinuous), and it takes place at the temperature  $T^*$  defined by  $w_1 = w_2$ , which according to the analysis reported above is equivalent to  $\alpha + \beta S^{7/3} = q S_p$ . We stress that for  $T < T^*$  the alignment of the nematic imposed by the surface layer is planar and independent of  $T$ , whereas for  $T > T^*$  it is homeotropic. For  $T < T^*$  and  $T > T^*$  the effective anchoring energy  $w$  is, on the contrary, temperature dependent according to the relation  $w(T) = q S_p S - (\alpha S + \beta S^{10/3})$ . This means that the presence of the surface field due to the polymer is equivalent, in the mean-field formalism, to a phenomenological parameter  $\alpha' = \alpha - q S_p$ , which is *temperature dependent* via  $S_p$ .

For the numerical calculations we assume for the temperature dependences of the scalar order parameters  $S_p$  and  $S$  the expressions

$$S_p(T) = S_p(T_{PC}) \sqrt{\frac{T_P - T}{T_P - T_{PC}}},$$

$$S(T) = S(T_{NC}) \sqrt{\frac{T_N - T}{T_N - T_{NC}}}, \quad (9)$$

where  $T_{PC}$  and  $T_{NC}$  are the transition temperatures for the polymer and the liquid crystal, respectively.  $S_p(T_{PC})$  and  $S(T_{NC})$  the scalar orders at the transitions, assumed first order, and  $T_P$  and  $T_N$  two temperatures close to  $T_{PC}$  and  $T_{NC}$  [23]. In Fig. 1(a) we show the experimental data relevant to the liquid crystal MJ05963, oriented with polymer layers containing side groups 90% alkyl chains and 10% mesogenic groups (P1) and Fig. 1(b) the experimental data relevant to the same liquid crystal oriented with polymer layers containing side groups 75% alkyl chains and 25% mesogenic groups (P2). The best fit for Fig. 1(a) is obtained with the parameters  $T_N = 86$  °C,  $T_{NC} = 85$  °C,  $S(T_{NC}) = 0.1$ ,  $T_P = 130$  °C,  $T_{PC} = 129$  °C,  $S(T_{PC}) = 0.07$ ,  $\beta/\alpha = 0.66$ ,  $q/\alpha = 1.975$ ,  $\phi_1 = 0.03$ , and  $\phi_2 = \pi/2$ . The best fit for Fig. 1(b) is obtained with the same parameters  $T_N$ ,  $T_{NC}$ ,  $S(T_{NC})$ ,  $T_P$ ,  $T_{PC}$ , and  $S(T_{PC})$ , of Fig. 1(a), and  $\beta/\alpha = 0.79$ ,  $q/\alpha = 1.93$ ,  $\phi_1 = 0.03$ , and  $\phi_2 = \pi/2$ . Note that  $\alpha > 0$  and  $\beta > 0$  in such a manner that the physicochemical interactions between the polymer layer and the nematic result in a homeotropic alignment, and  $q > 0$  indicates that the polymer layer tends to induce alignment

along its *director*  $\mathbf{m}$ . The fits are reasonably good, considering that we have approximated the scalar order parameters by Eqs. (9) over the full temperature range [24].

In the analysis reported above we have assumed, for simplicity, that the physicochemical interactions of the liquid crystal with the polymer layer are promoting orientation close to the planar one so that the problem can be solved in a simple manner. If we remove this simplifying hypothesis, the easy axis, related to the physicochemical interactions, is tilted and can change with the temperature, as discussed in Sec. II. In this case, the surface energy that should be considered is

$$f_s = f_0 + \frac{1}{2}A \sin^2 \phi + \frac{1}{4}B \sin^4 \phi + \frac{1}{2}w_2 \sin^2(\phi - \phi_2). \quad (10)$$

In this framework, the surface tilt angle is given by the equation

$$(A + B \sin^2 \phi^*) \sin(2\phi^*) + w_2 \sin[2(\phi^* - \phi_2)] = 0, \quad (11)$$

which cannot be solved, easily, with respect to  $\phi^*$ . The solution has to be obtained numerically, but the main conclusions on the temperature dependence of  $\phi^*$  agree with the one reported above.

#### IV. CONCLUSIONS

We have reported on capacitive measurements of temperature dependences of the tilt angle of a commercial nematic liquid crystal on two types of treated surfaces. The aligning surfaces are coated with polymers, attached with a mixture of alkyl chains and mesogenic side group, which can induce homeotropic alignment on the considered nematic liquid crystal. According to our experimental data, if most of the side groups are mesogenic, the surface treatment induces a very prominent nonmonotonic trend of the nematic tilt angle as a function of the temperature. On the other hand, if the side groups are mainly alkyl chains, the surface treatment is responsible for a less prominent nonmonotonic trend. We have shown that the models proposed so far to interpret the temperature-induced surface transitions in nematic liquid crystals, which are based on the Landau theory on the mean-field model, cannot describe the nonmonotonic behavior of the nematic tilt angle on the temperature. We propose a generalization of the mean-field model, where the orienting polymer is responsible for a new term in the surface energy, which depends on the order parameter of the nematic and of the polymer. The proposed model predicts, at certain conditions, a nonmonotonic dependence of the nematic tilt angle on the temperature. The theoretical predictions compare reasonably well with our experimental observation.

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