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Temperature-induced surface transition in nematic liquid crystals oriented by evaporated SiO$_x$

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Temperature induced surface transitions observed in nematic liquid crystals oriented by obliquely evaporated SiO$_x$ are analyzed. It is shown that the experimental data can be interpreted with a theory for the thermal renormalization of the anisotropic part of the surface energy based on the mean field approximation. By assuming that the nematic scalar order parameter is given by the Maier-Saupe theory, the fit is obtained with only one free parameter. The temperature behaviors of the polar and azimuthal angles are in agreement with the proposed model over the whole temperature range.

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I. INTRODUCTION

Nematic liquid crystals in contact with an anisotropic solid substrate are oriented in a well defined manner [1]. In the absence of bulk distortion, the direction imposed by the surface is called "easy axis." It is defined as the surface nematic orientation minimizing the anisotropic part of the surface energy, f_s, which describes the nematic-substrate interaction. To theoretically analyze the temperature dependence of the easy axis, f_s is usually expanded in terms of the elements of symmetry characterizing the solid substrate and the nematic liquid crystal [2]. The solid substrate is characterized by its surface normal and its crystallographic axes, whereas the nematic liquid crystal is characterized by the tensor order parameter **Q** [3]. The elements of this tensor are $Q_{ij}=(3/2)SN_{ij}$, where S is the nematic scalar order parameter, $N_{ij}=n_in_j-(1/3)\delta_{ij}$ (n_k being the k Cartesian component of the nematic director), and δ_{ij} the elements of the three-dimensional identity tensor. By operating in this way, f_s is written as

$$f_s=\sum_{m=0}^{\infty}\mathcal{R}_m, \tag{1}$$

where $\mathcal{R}_0$ is $\mathbf{n}$ independent; $\mathcal{R}_2=M_{ij}^{(2)}N_{ij}$, $\mathcal{R}_4=M_{ijkl}^{(4)}N_{ij}N_{kl}$, and so on, and $M^{(2i)}$ are tensors of $2i$ order characterizing the substrate. Expression (1) allows one to write f_s in terms of the symmetry of the problem. It is rigorous and always possible. However, the use of Eq. (1) is possible only if it reduces to a polynomial, or if we have an idea about the convergence of the series. This implies that it should be possible to identify a small parameter ϵ in the problem, and to consider Eq. (1) as a power expansion in ϵ. In the past, the nematic scalar order parameter S was used as a small parameter [4–7]. However, since the nematic-isotropic phase transition is of first order, with a jump of order parameter $\Delta S\sim 0.3$ at the nematic-isotropic temperature, S is never very small [8]. Consequently, an expansion of the type (1) in power of S up to the second order may be questionable [4–7].

In a recent paper we proposed a mean field analysis of the anisotropic part of the surface energy. According to our model [9], valid in the weak anchoring case, tensors $M^{(2i)}$ scale with the temperature according to the law $M^{(2i)}(T)\propto S_{2i}(T)$, where $S_{2i}(T)$ is the $2i$th nematic scalar order parameter [10]. In Ref. [9] we analyzed experimental data obtained by other groups, and found a good agreement with our theory. The data analyzed were relevant to planar-homeotropic temperature surface transitions [11–13]. In this case there is only one curve to be fitted, with two free parameters. Consequently a good agreement between theory and experiment is not too surprising. For this reason, in this paper, we analyze the temperature surface transitions observed in nematic samples aligned by SiO$_x$-evaporated surfaces [14,15]. In this case, changing the temperature, both the polar and the azimuthal angles, characterizing the nematic director, change. Hence it is necessary to fit, with the same parameters, two angles vs temperature. We will show that this is actually possible with only one free parameter. The model presented here will also be compared to a previously published model for the same phenomenon [7].

Our paper is organized as follows. In Sec. II the anisotropic part of the surface energy relevant to a nematic liquid crystal in contact with a SiO$_x$-evaporated surface is analyzed, and the possible temperature induced surface transitions discussed. In Sec. III we compare our prediction with the experimental data, and show that a reasonably good agreement between theory and experiment is achieved, although only one free parameter appears in the model. The main limits of our model are discussed in Sec. IV.

II. SURFACE ENERGY

Let us consider a nematic liquid crystal in contact with a flat solid substrate, over which SiO$_x$ has been evaporated at an angle α with respect to the geometrical normal of the substrate. The Cartesian reference frame used has the z axis parallel to the geometrical normal, the y axis in the evaporation plane, which coincides with the (y,z) plane. It follows that the x axis is parallel to the grooves produced by the evaporation [16]. The anisotropic part of the surface energy of the system is, at the fourth order in **n**, and in analogy with Eq. (1),

$$f_s=\tfrac{1}{4}L_{ijkl}n_in_jn_kn_l+\tfrac{1}{2}H_{ij}n_in_j\,. \tag{2}$$

From the symmetry of the problem, we have

$$f_s(n_x,n_y,n_z)=f_s(-n_x,n_y,n_z), \tag{3}$$

which restricts the number of elements in expression (2). By putting $\mathcal{L}=L_{ijkl}n_in_jn_kn_l$, and $\mathcal{H}=H_{ij}n_in_j$, expression (2) can be written as $f_s=(1/4)\mathcal{L}+(1/2)\mathcal{H}$. Using condition (3), $\mathcal{L}$ and $\mathcal{H}$ reduce to

$$\mathcal{L}=A_1n_x^4+A_2n_y^4+A_3n_z^4+B_1n_x^2n_y^2+B_2n_x^2n_z^2+B_3n_x^2n_yn_z \\ +C_1n_y^3n_z+C_2n_y^2n_z^2+C_3n_yn_z^3 \tag{4}$$

and

$$\mathcal{H}=a_1n_x^2+a_2n_y^2+a_3n_z^2+bn_yn_z\,. \tag{5}$$

Expressions (4) and (5) are valid for all problems having the symmetry of Eq. (3). In this case, taking into account that $|\mathbf{n}|=1$, and hence $n_x^2+n_y^2+n_z^2=1$, it is possible to rewrite expressions (4) and (5) as

$$\mathcal{L}=(A_1+A_2-B_1)n_y^4+(A_1+A_3-B_2)n_z^4 \\ +(2A_1-B_1-B_2+C_2)n_y^2n_z^2+(B_3+C_3)n_yn_z^3+C_1n_y^3n_z \\ +(B_1-2A_1)n_y^2+(B_2-2A_1)n_z^2+A_1 \tag{6}$$

and

$$\mathcal{H}=(a_2-a_1)n_y^2+(a_3-a_1)n_z^2+bn_yn_z+a_1\,. \tag{7}$$

From expressions (6) and (7) we conclude that, in general, if condition (3) holds, f_s contains ten phenomenological parameters. The actual nematic orientation, in the absence of bulk distortion, is obtained by minimizing $f_s=f_s(n_y,n_z)$ with respect to n_y and n_z.

In our case the situation is simpler. According to the experimental data (also see Ref. [14]), **n** moves on the plane (x',y'), shown in Fig. 1, forming the angle $(\pi/2)-\alpha$ with the (x,y) plane, which coincides with the substrate. The existence of this plane was discussed long ago by Monkade *et al.* [17] and Jerome *et al.* [18]. An analysis of the anchoring energy of a nematic liquid crystal over a grazing SiO$_x$ evaporated amorphous substrate, based on the symmetry, was developed by Nobili and Durand [19].

The reason why surface reorientation takes place on a plane, when the evaporation angle is in a well defined range, can be understood using mechanical arguments. As discussed by Goodman *et al.* [20], in special conditions of evaporation, there is the formation of SiO$_x$ structures giving rise to the grooves. In the evaporation plane, the shape of these structures is columnarlike. The columns are nearly parallel to the evaporation direction. Let us assume that the SiO$_x$ material imposes a planar alignment of the liquid crystal in contact with it, and that the nematic molecules can rotate on the SiO$_x$ substrate. In this framework, only if the nematic director is moving on the plane defined by the column and the grooves there is no elastic deformation. Since the easy direction has to minimize the anisotropic part of the surface energy, we conclude that the temperature surface transition has to take place on this plane.

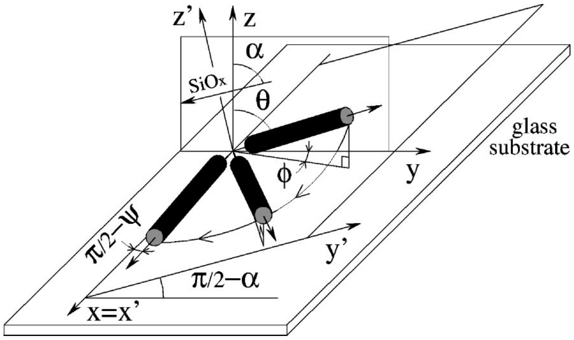

FIG. 1. Schematic representation of the temperature induced anchoring transition of a nematic liquid crystal on a SiO$_x$ surface (the arrows indicate the direction of motion upon increasing the temperature). The z axis is parallel to the geometrical normal of the substrate, whereas the evaporation plane coincides with the (y,z) plane. The angle α is the evaporation angle. During the temperature-induced anchoring transition, **n** remain in the plane (x',y'). Note that the director orientation is in principle symmetric with respect to the evaporation plane; see Ref. [14].

In the reference frame (O,xyz), **n** is defined by $\mathbf{n}=(\sin\theta\sin\phi,\sin\theta\cos\phi,\cos\theta)$, whereas in the reference frame $(O,x'y'z')$ is defined by $\mathbf{n}=(\sin\psi,\cos\psi,0)$. Since **n** is moving on the plane (x',y') we have $n_y=n_z\tan\alpha$, as follows from Fig. 1. In the reference frame, where $n_{z'}=0$, f_s given by Eq. (2), taking into account Eqs. (6) and (7), becomes

$$f_s=-\tfrac{1}{4}An_{y'}^4-\tfrac{1}{2}(B-C)n_{y'}^2+D, \tag{8}$$

where we have put $A=B_1-(A_1+A_2)$, $B=2A_1-B_1$, $C=a_2-a_1$, and $D=A_1+a_1$. As follows from Eq. (8), in the particular case under investigation, the expression for the anisotropic part of the surface energy contains only two phenomenological parameters, A and $B-C$, whereas D can be included in the isotropic surface tension characterizing the interface nematic-solid substrate. The actual value of $n_{y'}$ is the one minimizing f_s, under the hypothesis that the sample is characterized by uniform nematic orientation; hence there is no bulk elastic deformation.

In terms of ψ, f_s, given by Eq. (8) reads

$$f_s=-\tfrac{1}{4}A\cos^4\psi-\tfrac{1}{2}(B-C)\cos^2\psi+D. \tag{9}$$

The stable states are obtained by putting $df_s/d\psi=0$, whose solutions are

$$\psi=0,\quad \psi=\pi/2\quad\text{and}\quad \cos^2\psi^*=(C-B)/A. \tag{10}$$

The solutions are stable if $d^2f_s/d\psi^2>0$, i.e.,

$$\left(\frac{d^2 f_s}{d\psi^2}\right)_0 = A+B-C>0,$$

$$\left(\frac{d^2 f_s}{d\psi^2}\right)_{\pi/2} = C-B>0, \tag{11}$$

$$\left(\frac{d^2 f_s}{d\psi^2}\right)_{\psi*} = \frac{[C-(A+B)](C-B)}{A}>0.$$

According to our model concerning the thermal renormalization of the surface energy [9],

$$A=mS^{10/3}, \quad B=nS^{10/3}, \quad C=qS, \tag{12}$$

where m, n, and q are temperature independent coefficients. Expressions (12) hold in the Akulov-Zener limit, where $\langle P_4\rangle \sim S^{10/3}$, as discussed in Ref. [9]. In this approximation the stable tilted solution of Eq. (10) can be written as

$$\cos^2\psi = \frac{qS-nS^{10/3}}{mS^{10/3}}, \tag{13}$$

where we have removed the asterisk. Equation (13) allows one to analyze the temperature dependence of the surface director if the nematic scalar order parameter $S=S(T)$ is known.

III. COMPARISON WITH EXPERIMENTAL DATA

To compare our theoretical predictions with the experimental data, let us assume that there are two temperatures T_1 and T_2 such that (a) for $T \geqslant T_1$ the stable orientation is $\psi = \pi/2$, and (b) for $T \leqslant T_2$ the stable orientation is $\psi=0$. The temperature T_1 has been experimentally detected ($T_1 \sim 51\,°\mathrm{C}$), whereas T_2 has not been observed experimentally; however to have a good agreement between the model and the experimental data, we assume $T_2 \sim 20\,°\mathrm{C}$, which is within a realistic range. The temperature T_2 is, in our theoretical analysis, a kind of virtual critical temperature connected with a surface transition toward the uniform tilted alignment (**n** perpendicular to the grooves). From the definition of T_1 and T_2 it follows that

$$q=nS_1^{7/3} \quad \text{and} \quad m=n[(S_1/S_2)^{7/3}-1], \tag{14}$$

where $S_1=S(T_1)$ and $S_2=S(T_2)$. Consequently, Eq. (13) can be rewritten as

$$\cos\psi = \sqrt{\frac{1-(S_1/S)^{7/3}}{1-(S_1/S_2)^{7/3}}} = \sqrt{\tau}, \tag{15}$$

which gives real solutions only if $S_1 \leqslant S \leqslant S_2$. Conditions (11) relevant to the stability of the different orientations, using Eqs. (12) and (14), read

$$\left(\frac{d^2 f_s}{d\psi^2}\right)_0 = nS^{10/3}[(S_1/S_2)^{7/3}-(S_1/S)^{7/3}]>0,$$

$$\left(\frac{d^2 f_s}{d\psi^2}\right)_{\pi/2} = nS^{10/3}[(S_1/S)^{7/3}-1]>0, \tag{16}$$

$$\left(\frac{d^2 f_s}{d\psi^2}\right)_{\psi*} = n\frac{[(S_1/S)^{7/3}-(S_1/S_2)^{7/3}][(S_1/S)^{7/3}-1]}{[(S_1/S_2)^{7/3}-1]}>0,$$

which imply $S>S_2$, $S<S_1$, and $S_1<S<S_2$, respectively. Note that in Eq. (15) only T_2 is a free parameter, because T_1 has been detected experimentally.

When $\psi=\psi(T)$ is known, it is possible to determine the angles characterizing **n** in the laboratory frame (O,xyz), θ and ϕ. From Fig. 1 it follows that $\cos\theta = \cos\alpha\cos\psi$, and $\tan\phi = \tan\psi/\sin\alpha$. Using expression (15) for $\cos\psi(T)$, we obtain, finally,

$$\cos\theta = \cos\alpha\sqrt{\tau} \tag{17}$$

and

$$\tan\phi = \frac{1}{\sin\alpha}\sqrt{\frac{1-\tau}{\tau}}. \tag{18}$$

In Eqs. (17) and (18) there is only one free parameter S_2, since S_1, connected with the high temperature surface transition, and α, the evaporation angle, are experimentally detected.

To fit the experimental data, we assume that S is given by the Maier-Saupe mean field theory. In this framework the nematic scalar order parameter S is given by the self-consistent equation [8]

$$S = \frac{\int_0^1 P_2(\cos\xi)\exp[\beta v S P_2(\cos\xi)]d(\cos\xi)}{\int_0^1 \exp[\beta v S P_2(\cos\xi)]d(\cos\xi)}, \tag{19}$$

where $P_2(\cos\xi)=(3/2)(\cos^2\xi - 1/3)$ is the second order Legendre polynomial, $\beta = 1/k_B T$, and v a material parameter determined by the nematic-isotropic phase transition temperature T_{NI} by means of the equation $k_B T_{NI}/v = 0.22019$.

The temperature induced transitions start at a position somewhere on the plane (x',y') (see Fig. 1), where the starting position depends on the evaporation angle [14]. Then, as the temperature is increased, the molecules reorient toward an orientation parallel to the x' axis. A representative set of measurements of the temperature induced transition described above is shown in Fig. 2, together with the best fit of Eqs. (17) and (18) (solid lines), obtained for $T_2 = 20\,°\mathrm{C}$. This value of T_2 is consistent with the experimental data. Also shown is the fit of a previously published model [7] using *four* free parameters (dashed lines). The agreement between the model and the experimental data, as well as the previously published model, is reasonably good for both the polar

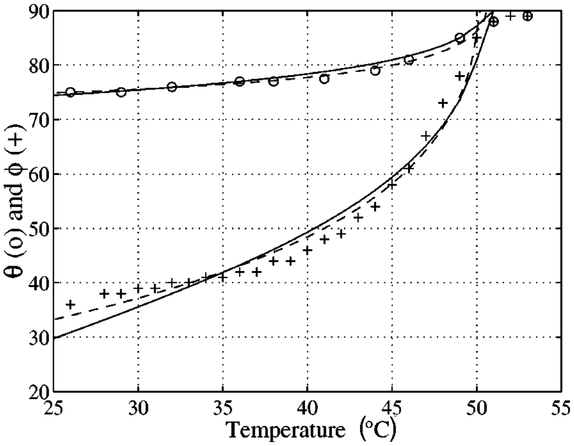

FIG. 2. Experimental values of the polar $\theta(o)$ and azimuthal $\phi(+)$ angles characterizing the nematic surface director vs the temperature *T*. The solid lines are the theoretical best fits obtained by means of Eqs. (17) and (18), derived from the model for the thermal renormalization of the anisotropic part of the surface energy, with $T_2 = 20\,°\mathrm{C}$. The dashed lines represent the model presented in Ref. [7].

and azimuthal angle over the whole temperature range. This is especially apparent when considering that *both* the solid curves shown in Fig. 2 were obtained by only using one and the same free parameter for the two curves. It is true that the dashed lines are slightly closer to the data points, but that should be expected for a model with four free parameters. The model is also sounder in that it avoids using the assumption that the order parameter should be small (which is not really the case). The experimental data shown was taken on a sample with 200 Å thick (measured perpendicular to the glass substrate) SiO_x evaporated at $\alpha = 73°$, cf. Fig. 1. The two substrates of the cell were aligned antiparallel and with a separation of $6\,\mu$m, and this gap was filled with the nematic liquid crystal E7 (Merck Ltd). The details of the cell preparation, experimental setup, and more experimental results can be found in Ref. [14]. The experimental data presented in Fig. 2 were measured upon heating, neglecting a small hysteresis found in the original data [14]. This simplification was introduced since the theoretical model is limited to hysteresis-free phenomena.

To practically obtain the fits (solid lines) shown in Fig. 2, we first solved Eq. (19) for *S* over the temperature interval in question. Then expression (15) was used, together with Eqs. (17) and (18), which only leaves $S_2 = S(T_2)$ (or rather T_2) as a free parameter, since S_1 is fixed by T_1 (see the beginning of this paragraph). The best fit of the experimental measurements is obtained for $T_2 = 20°$, which is, as underlined above, within a realistic range.

To ensure that the Akulov-Zener limit, where $\langle P_4 \rangle \sim S^{10/3}$, is valid, we also calculated θ and ϕ using the full expression for $\langle P_4 \rangle$. In this case, Eq. (19) has to be completed with a corresponding equation for S_4, using the fourth order Legendre polynomial, giving S_4 as a function of temperature. Also, Eqs. (17) and (18) will have a more complicated form without using the approximation above, but the calculations are straightforward. Once again, the fits can be obtained using T_2 as a free parameter [here affecting both $S(T_2)$ and $S_4(T_2)$], and it turns out that the fits are very close to the ones shown in Fig. 2. In particular the best fits are obatined for the same value of $T_2 = 20\,°\mathrm{C}$. Therefore, we draw the conclusion that the Akulov-Zener limit is indeed valid for our case.

IV. CONCLUSIONS

We have analyzed a temperature surface transitions observed in nematic samples oriented by obliquely evaporated SiO_x. We have shown that this phenomenon can be interpreted in the framework of a model for the thermal renormalization of the anchoring energy of nematic liquid crystals recently proposed. The agreement between the experimental data and the theoretical best fit is reasonably good, even if the nematic scalar order parameter is evaluated in the Maier-Saupe approximation. Of course, the agreement could be improved if the nematic is described by means of a generalized Maier-Saupe model, where the number of free parameters is larger. Nevertheless, the good agreement between our theory and the experiment data represents a confirmation of our model of the thermal renormalization of the anchoring energy. We have also shown how our new model represents a major theoretical improvement from a previously published model.

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