Modulated structures in nematic monolayers formed by symmetric molecules

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(Received 31 August 2004; revised manuscript received 4 November 2004; published 24 February 2005)

An analysis based on symmetry yields a general form for the deformation elastic energy of a nematic monolayer, formed by achiral symmetric molecules, deposited on a solid substrate. Lifshitz-invariant-like terms in the energy, which originate from the substrate field, can induce a modulated-tilt state if the anchoring energy is sufficiently low. A way to enhance the symmetry breaking is to apply a destabilizing magnetic or electric field that serves to lower the anchoring energy. In the case of an initial state with homeotropic alignment, the phase diagram displays a cusp-shaped tilt-modulated state intervening between two uniform tilt states.

DOI: 10.1103/PhysRevE.71.022701 PACS number(s): 61.30.Gd, 68.47.Pe, 83.10.Bb, 83.60.Np

I. INTRODUCTION

Langmuir monolayers of liquid crystals have been extensively studied in the past [1–3]. A challenging issue is the prediction and observation of structural transitions giving rise to tilt-modulated phases in the absence of molecular chirality [4–7]. Modulated states in achiral centrosymmetric materials have been of intense interest both for the underlying physics and for applications. In thin layers and nanostructures, modulated states may arise from surface-field-inducing Lifshitz-invariant-like terms.

Up to now all published studies have been based on particular forms for the elastic energy density of the membrane, able to explain the special experimental results obtained for particular systems. Further the effect of external fields on monolayers has attracted less attention.

In the present paper, we construct a general form of the deformation elastic energy of a single nematic layer formed by symmetric molecules on a solid substrate and we examine the effect of an electric field on the monolayer. We show that a linear term in the deformation tensor can give rise to a spontaneous periodic tilt deformation of the director if the corresponding elastic constant λ is stiffer than a threshold value λ_{th}. In the opposite case, when $\lambda < \lambda_{th}$, the application of a destabilizing electric or magnetic field can induce the uniform-tilt $\leftrightarrow$ modulated-tilt transition at a first threshold field. A second structural transition takes place at a second threshold field, and the modulated tilt state disappears, giving rise to another uniform tilt state. When the geometrical normal to the substrate coincides with its easy direction and in the limit where λ goes to zero, we show that the phase diagram presents a cusp where three different structures meet.

II. ELASTIC ENERGY DENSITY

We consider a monolayer formed by rodlike molecules deposited on a flat surface with unit normal **k**. The molecules are supposed achiral and apolar. The average molecular orientation in the layer is given by the nematic director **n** [8] with $|\mathbf{n}|=1$. The energy density of the deformed film can be expanded in a power series of the director spatial derivatives $n_{i,j}=\partial n_i/\partial x_j$ [9]. Limiting the expansion up to the second order in the deformation tensor $n_{i,j}$, we obtain

$$f(n_{i,j}) = \gamma_0 + \lambda_{ij} n_{i,j} + \frac{1}{2} H_{ijkl} n_{i,j} n_{k,l}, \tag{1}$$

where γ_0 is the energy density of the uniform state. We assume that the director **n** possesses the inversion symmetry—i.e., that the two ends of a molecule forming the film are equivalent. Strictly speaking, our analysis is valid for a monomolecular film formed by symmetric molecules deposited on a solid substrate or for a free-standing monomolecular films formed by symmetric molecules. However, the presented analysis can be easily extended to Langmuir monolayer, where the head and the tail of a molecule are essentially different.

By decomposing the elastic tensors λ and H in terms of the elements of the layer symmetry—i.e., **n**,**k** and of the identity tensor—we obtain for the elastic deformation energy density of the monolayer the expression

$$\begin{aligned} f = \gamma_0 + \nu \nabla \cdot \mathbf{n} - \lambda \mathbf{k} \cdot [\mathbf{n} \times \nabla \times \mathbf{n}] + \frac{1}{2}\{K_1 (\nabla \cdot \mathbf{n})^2 \\ + K_2 [\mathbf{n} \cdot \nabla \times \mathbf{n}]^2 + K_3 [\mathbf{n} \times \nabla \times \mathbf{n}]^2\} + \frac{1}{2}\{K_4 [\nabla (\mathbf{k} \cdot \mathbf{n})]^2 \\ + K_5 [(\mathbf{k} \cdot \nabla)(\mathbf{k} \cdot \mathbf{n})]^2 + K_6 [\mathbf{k} \cdot (\mathbf{n} \times \nabla \times \mathbf{n})]^2 \\ + K_7 (\nabla \cdot \mathbf{n})(\mathbf{k} \cdot \nabla)(\mathbf{k} \cdot \mathbf{n})\}. \end{aligned} \tag{2}$$

Expression (2) is not an expansion in terms of a small angle, but an expansion in terms of small deformations $n_{i,j}$ on the range of the molecular forces responsible for the monomolecular film under investigation. The calculations relevant to the linear terms in $n_{i,j}$ are discussed in detail in [10]. The elastic constant ν and λ are connected to the so-called Lifshitz invariants. In our framework, where **n** is equivalent to $-\mathbf{n}$, $\nu=0$. The connection of λ with the intermolecular potential responsible for the ordered phase under consideration has been discussed in [10]. There it has been shown that if the intermolecular potential is such as to give a splay-bend elas-

tic constant K_{13} [9], also the elastic constant λ is different from zero. The quantities K_1, K_2, and K_3 are the equivalent of the usual Frank's elastic constants, and K_4, K_5, K_6, and K_7 are typical elastic constants of the lamellar structure [11]. The elastic constants K_i have the dimensions of a bulk elastic constant, $k_{ii} \sim 10^{-11}$J/m [8], times a molecular length $\ell \sim 10^{-9}$m. Their order of magnitude is then $K_i \sim 10^{-20}$. We note that all the terms appearing in Eq. (2) are true scalar and hence invariant for all changes of the reference frame (true rotations or mirror reflections) [12].

We restrict our present study to one-dimensional deformations in the presence of an external destabilizing electric field and the director $\mathbf{n}$ is contained in the (x,z) plane. In this framework $\mathbf{n}=\sin\theta(x)\mathbf{i}+\cos\theta(x)\,\mathbf{k}$, where θ is the tilt angle in respect to the geometrical normal of the substrate. Of course, more general analyses are possible, where $\mathbf{n}=\mathbf{n}(x,y)$, and it is not restricted to a plane. The work is in progress and will be published elsewhere.

The uniform-tilt state energy density in Eq. (2) coincides with the anisotropic part of the surface tension and is assumed to be of the Rapini-Papoular form [13]

$$\gamma_0(\theta) = -\frac{1}{2} w_0 \cos^2(\theta - \theta_0), \tag{3}$$

with $\theta_0=\cos^{-1}(\mathbf{k}\cdot\mathbf{n}_0)$ denoting the tilt angle preferred by the substrate. $\mathbf{n}_0$ is the substrate easy axes, and $w_0>0$ is the anchoring energy strength.

The presence of an electric field $\mathbf{E}$ in the plane of the layer [17] adds a new term to f of the type

$$f_d(\theta) = -\frac{1}{2}\epsilon_a\epsilon_0\,\ell\,(\mathbf{E}\cdot\mathbf{n})^2, \tag{4}$$

where ϵ_0 is the absolute dielectric permittivity of free space and ϵ_a the dielectric anisotropy of the nematogenic material. Therefore, the energy density of the uniform state is renormalized by the electric field and is rewritten as

$$\gamma(\theta) = \gamma_0(\theta) + f_d(\theta) = -\frac{1}{2} w_0[\cos^2(\theta - \theta_0) + \mu \sin^2\theta], \tag{5}$$

where $\mu=\epsilon_a\epsilon_0\ell E^2/w_0$ is a measure of the relative strength of the external electric field with respect to the orienting field responsible for the anisotropic part of the surface energy. Equation (5) shows that in the presence of an electric field the Rapini-Papoular approximation does not work any longer. In this case the easy tilt angle θ_e is given by

$$\tan(2\theta_e) = \frac{\sin(2\theta_0)}{\cos(2\theta_0) - \mu}. \tag{6}$$

For $\mu>0$—i.e., $\epsilon_a>0$—the electric field tends to orient the director along it; it follows that $\theta_0 \leqslant \theta_e \leqslant \pi/2$. On the contrary, if $\mu<0$—i.e., $\epsilon_a<0$—the electric field tends to orient $\mathbf{n}$ perpendicular to it, and hence $0 \leqslant \theta_e \leqslant \theta_0$.

Finally, the total free energy density of the monolayer as function of the tilt angle is

$$f = -\lambda \sin^2\theta\frac{d\theta}{dx} + \frac{1}{2}\kappa h(\theta)\left(\frac{d\theta}{dx}\right)^2 + \gamma(\theta). \tag{7}$$

Here, $h(\theta)=(1+a\sin^2\theta+b\sin^4\theta)$, $\kappa=K_1$, $a=[(K_3+K_4)/K_1]-1$, and $b=K_6/K_1$. Thermodynamic stability of the above free energy density requires $h(\theta)>0$. Since b is positive, the latter inequality holds always for $a \geqslant 0$, as we suppose throughout this paper. A detailed analysis will be given elsewhere.

III. PERIODIC DEFORMATIONS IN NEMATIC MONOLAYERS

Minimization of the elastic energy per unit length in the y direction,

$$\mathcal{F}[\theta(x)] = \int f\left(\theta, \frac{d\theta}{dx}\right)dx, \tag{8}$$

leads to the first integral

$$\frac{1}{2}\kappa h(\theta)\left(\frac{d\theta}{dx}\right)^2 - \gamma(\theta) = \frac{1}{2\mathcal{R}^2}, \tag{9}$$

where $\mathcal{R}$ is an integration constant. Here, it is more convenient to work with reduced quantities. Henceforth, lengths are measured in $\sqrt{\kappa/w_0}$ units and surface energy in w_0 units.

A modulated structure should have the reduced period

$$\Lambda_r = \eta\int_0^{2\pi} \sqrt{\frac{h(\theta)}{1-\eta^2[\cos^2(\theta-\theta_0)+\mu\sin^2\theta]}}\,\mathrm{d}\theta. \tag{10}$$

The subscript r stands for reduced units. The integration constant $\eta=\mathcal{R}\sqrt{w_0}$ is found by minimization of the average energy per period ρ_M with respect to η. The latter minimization yields the equation

$$\lambda_r = \frac{1}{\pi\eta}\int_0^{2\pi} \sqrt{h(\theta)\{1-\eta^2[\cos^2(\theta-\theta_0)+\mu\sin^2\theta]\}}\,\mathrm{d}\theta. \tag{11}$$

Then, the energy of the modulated structure is calculated using Eq. (11). From the stability condition $\rho_M<\rho_H$, where $\rho_H=\mathcal{F}(\theta_0)/\Lambda=\gamma(\theta_0)$ is the energy of the homogeneous state, we deduce that the tilt modulation is a stable state with respect to the uniform-tilt state when the elastic constant λ_r is stiffer than a threshold value λ_{th}. The value λ_{th} corresponds to $\Lambda_r \to \infty$ and is obtained when $\eta \to \eta_{\max}$ given by

$$\eta_{\max} = \sqrt{2/\{1+\mu+\sqrt{1+\mu^2-2\mu\cos(2\theta_0)}\}}. \tag{12}$$

Then, the value λ_{th}, above which tilt modulation appears, is

$$\lambda_{th} = \frac{1}{\pi\eta_{\max}}\int_0^{2\pi} \sqrt{h(\theta)\{1-\eta_{\max}^2(\cos^2[\theta-\theta_0]+\mu\sin^2\theta)\}}\,\mathrm{d}\theta. \tag{13}$$

Up to now, we have shown that the phase diagram of this model exhibits a disordered (unmodulated) phase with a uniform-tilt angle θ_0 and a modulated-tilt phase where θ is a function of position: $\theta=\theta(x)$. The modulated structure is

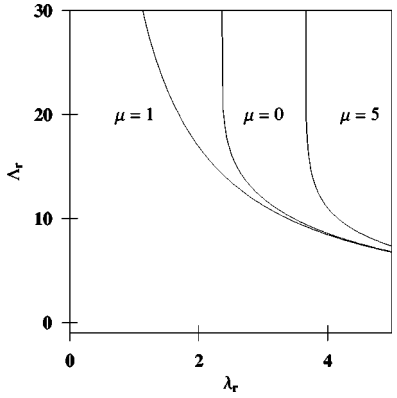

FIG. 1. Plot of Λ_r vs λ_r under a destabilizing electric field: (i) left curve for $\mu=1$, (ii) middle curve for $\mu=0$, and (iii) right curve for $\mu=5$. The coefficients are $a=3$, $b=1$, and $\theta_0=0$.

driven by the λ term, which is linear in the gradient operator and therefore favors inhomogeneous ordering. This latter term competes with the $h(\theta)$ elastic term which favors uniform ordering. A case of special interest is a monolayer with homeotropic anchoring in the absence of an external field.

For a monolayer with $\theta_0=0$, Eq. (12) gives $\eta_{max}=1$, if $\mu<1$, and $\eta_{\max}=1/\sqrt{\mu}$, if $\mu>1$. In this case, Eq. (13) yields

$$\lambda_{th}=\frac{\sqrt{1-\mu}}{\pi}\int_0^{2\pi}\sqrt{h(\theta)\sin^2\theta}\,\mathrm{d}\theta, \tag{14}$$

if $\mu\leqslant 1$, and

$$\lambda_{th}=\frac{\sqrt{\mu-1}}{\pi}\int_0^{2\pi}\sqrt{h(\theta)\cos^2\theta}\,\mathrm{d}\theta, \tag{15}$$

if $\mu\geqslant 1$. Since $\lambda_{th}\sim|\mu-1|^{1/2}$, the function $\lambda_{th}=\lambda_{th}(\mu)$ presents a cusp at $\mu=1$. The slope of $\lambda_{th}(\mu)$, at $\mu=1$, becomes infinite. $\lambda_{th}(\mu)$ has a minimum equal to zero at $\mu=1$; i.e., tilt modulation appears as soon as $\lambda_r\neq 0$. The wavelength of the modulation is given by the expression

$$\Lambda_r=\frac{1}{\lambda_r}\left\{\frac{1}{\sqrt{\pi}}\int_0^{2\pi}\sqrt{h(\theta)}\,\mathrm{d}\theta\right\}^2, \tag{16}$$

and for $\lambda_r\neq 0$, Λ_r is a finite quantity.

For a monolayer with $\theta_0\neq 0$ the cusp disappears and $\lambda_{th}(\mu)$ becomes differentiable for all μ.

In the case of a nematogenic material with positive dielectric anisotropy, Fig. 1 represents the reduced period Λ_r as function of λ_r for three electric field values: (i) the curve in the middle, in absence of the electric field, (ii) the lower curve for $\mu=1$, and (iii) the upper curve for $\mu=5$. The other parameters are kept constant at the values: $a=3$, $b=1$, and $\theta_0=0$. Note that the wavelength of the instability diverges when approaching the threshold value λ_{th}. The instability threshold, which is at $\lambda_{th}=2.35$ for zero field ($\mu=0$), reduces to zero for $\mu=1$, while for $\mu=5$ it seems to become 3.66, larger than its zero-field value. For weak fields $\mu<1$, the instability threshold decreases with respect with the zero-field value, but stronger fields seems to drive the instability threshold to higher values. In order to understand this seeming nonmonotonic behavior of the instability threshold with the field we construct the phase diagram in the (μ, λ_r) plane.

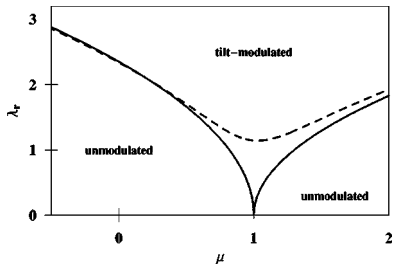

FIG. 2. The (μ,λ_r) phase diagram for an homeotropic monolayer (solid line) and for a tilted monolayer (dashed line). $\mu\leqslant 0$, corresponds to nematogenic materials with negative dielectric anisotropy.

Figure 2 shows the phase diagram in presence of an electric field for $\theta_0=0$ (solid line). The value of λ_{th} in the absence of field first reduces with the amplitude of the destabilizing field and becomes zero for $\mu=1$, where a cusp appears. For higher fields ($\mu>1$), another transition takes place, this time from the modulated-tilt state to a uniform-tilt state, and the threshold increases monotonically. For a stabilizing field, molecules with negative dielectric anisotropy, the threshold increases with the field as expected. When $\theta_0\neq 0$, the minimum of λ_{th} is different from zero (dashed line) and the derivative discontinuity disappears. When the easy axis is in the layer plane, the minimum goes to $\mu=-1$, and the instability may arise only for a material with negative dielectric anisotropy. Note that at the cusp (where $\theta_0=0$ and $\mu=1$), the total surface tension is θ independent; i.e., the anisotropic part of the surface tension vanishes. In particular, from Eq. (5) it follows that for $\theta_0=0$ the effective easy tilt angle is homeotropic ($\theta_e=0$) for $\mu<1$ and planar ($\theta_e=\pi/2$) for $\mu>1$; i.e., at the cusp three different structures merge: homeotropic, planar, and tilt modulated. Around the cusp, the width of the tilt-modulated region in μ varies as λ_r^2. At the cusp point two second-order transition lines merge to a second-order transition point. The cusp point is a Lifshitz point [14,15] in the (μ,λ) plane and a triple point in the plane of anchoring coefficients. In this latter plane, adding higher-order terms in the anchoring energy results in anchoring transitions between homeotropic, planar, and tilted structures [16].

The action of an electric field in the plane of the monolayer can induce uniform tilt and/or modulated tilt [17]. Consider a case where the substrate induces uniform homeotropic alignment—i.e., $\lambda_r<\lambda_{th}$—in the absence of the electric field. According to the phase diagram of Fig. 2, increasing the electric field should induce a transition towards a tilt-modulated state. The modulation should persist up to a second threshold field above which another uniform-tilt state appears. If $\lambda_r>\lambda_{th}$ in the absence of an electric field, the initial phase is a tilt-modulated one. Applying a strong enough field the tilt modulation disappears above a threshold field and the stable structure is a uniform-tilt state.

A rough estimation of the electric field amplitude to induce a tilt modulation is done by taking $\epsilon_a\sim 10$, and $w\sim 10^{-3}\,\mathrm{J/m^2}$. At the cusp, $\mu=1$, and hence $E_{cr}\sim 50\,\mathrm{V}/\mu\mathrm{m}$.

The latter field is rather high but experimentally attainable [18]. In order to reduce the critical field at a few volts per micrometer one has to use a substrate with anchoring energy $w \lesssim 10^{-6}$ J/m^2. Such substrates are now available [19,20].

IV. CONCLUSIONS

In summary, we constructed the general form of the deformation elastic energy of a nematic monolayer by considering the symmetry of an achiral nematogenic material and that of a flat substrate. The phase diagram has a ground uniform-tilt state and a one-dimensional modulated-tilt state. The periodic tilt deformation is induced by a Lifshitz invariant term linked to the substrate symmetry. In the presence of a destabilizing electric field, the instability threshold λ_{th} decreases towards zero with the field amplitude. Increasing sufficiently the field amplitude results in a second threshold above which the field destroys tilt modulation in favor of a new uniform-tilt state. When the substrate normal is the easy direction, the phase diagram presents cusp-shaped tilt-modulated state intervening between two uniform-tilt states. At the cusp point, homeotropic, planar, and tilt-modulated states merge. In our analysis we have assumed that the anisotropic part of the surface energy relevant to the interaction of the film with the substrate is of the Rapini-Papoular form. In this case at the cusp the surface and field contributions compensate each other. For more general forms of the surface energy this exact compensation could be impossible. In this case the cusp disappears.

ACKNOWLEDGMENT

This work has been partially supported by INFM.

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