PHYSICAL REVIEW E VOLUME 49, NUMBER 6 JUNE 1994

Stochastic contribution to the anchoring energy: Deviation from the Rapini-Papoular expression

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(Received 10 June 1993; revised manuscript received 14 February 1994)

The effect of a stochastic contribution to the surface energy, coming from the direct interaction between an orienting film and a solid substrate, is considered. It is shown that in the hypothesis in which the nematic liquid crystal orientation coincides with the film orientation, the well known Rapini-Papoular expression for the anisotropic part of the surface energy is modified. More precisely the anchoring strength, connected with the square of the sine of the deformation angle, is renormalized. Furthermore, there appears an additional contribution, proportional to the fourth power of the same quantity, whose coefficient is equal in modulus and opposite in sign. The physical origin of the considered effect is connected with the elastic contribution to the surface energy of the film.

PACS number(s): 61.30.−v

I. INTRODUCTION

Nematic liquid crystals are anisotropic fluids [1]. They are formed by strongly asymmetric molecules, which in a first approximation can be considered of cylindrical shape. The ratio length over diameter is usually larger than 2–3. Due to the existence of intermolecular forces such as the Van der Waals one, the major axes **a** of the molecules forming the nematic phase tend to be parallel. The average orientation, in a statistical sense, of the molecular axis is called the director and is usually indicated by **n**. In the absence of external interactions, **n** is indeterminate. The **n** orientation in the bulk can be fixed by means of an external field, e.g., an electric or magnetic one. In a real sample, of finite thickness, the **n** orientation depends on the surface treatment. It is experimentally known that a nematic liquid crystal in contact with a solid surface tends to be oriented in a well defined manner, dependent on the surface considered [2]. In the absence of bulk constraints, this direction is called the easy direction. From a phenomenological point of view, it is useful to introduce the idea of the anisotropic surface potential $f(\mathbf{n}_s)$, where $\mathbf{n}_s$ is the surface director. By means of $f(\mathbf{n}_s)$ the easy direction $\boldsymbol{\pi}$ is defined by

$$\partial f/\partial n_{si}=0\ , \tag{1}$$

in the absence of bulk constraints. In the event that a bulk deformation is imposed, for instance, by means of an external field, the surface orientation of the nematic liquid crystal may change or not. In the first case the anchoring is called weak, in the second case strong. The most important case, from the application point of view, is the weak anchoring case, because the threshold fields necessary to induce a deformation in special geometries are a decreasing function of the anchoring energy [3].

Long ago Rapini and Papoular proposed for the anisotropic surface potential the expression

$$f=-\tfrac{1}{2}W(\mathbf{n}\cdot\boldsymbol{\pi})^2\ , \tag{2}$$

in which W is called the anchoring strength and $\boldsymbol{\pi}$ is the above mentioned easy direction [4]. Possible deviations from expression (2) can be due to different physical origins. For instance, if the flexoelectric properties of the nematic phase are considered, the effective surface potential can contain a fourth power in $(\mathbf{n}_s\cdot\boldsymbol{\pi})$, having electrical origin [5]. Furthermore, if one takes into account that nematic materials are quadrupolar ferroelectric media, to the gradient of order near the surface, it is possible to associate an electric polarization [6]. To this polarization is connected an electrostatic self-energy depending again on $(\mathbf{n}_s\cdot\boldsymbol{\pi})^4$ [5]. All the calculations and models are based on the hypothesis that the surfaces are homogeneous. In this paper, we will show that the random nature of the surface introduces a fourth order term in the equivalent surface energy, even if the flexoelectricity and the ferroelectric quadrupolar nature of the nematic phase are neglected.

For the sake of simplicity, we consider a simple model in which the orienting film [like a Langmuir-Blodgett (LB) film] is monomolecular and formed of rodlike molecules. The mean orientation of the film is due to the interaction between the molecules forming the film itself and between the molecules of the film and the substrate over which the film is deposited. Furthermore we suppose that the nematic liquid crystal orientation follows that of the orienting film. This is equivalent to supposing that the film is not compact. The molecules of the nematic liquid crystal may enter in the holes (free places) present in the structure of the film. In this manner the nematic molecules in "contact" with the film are oriented by steric interaction (with the molecules of the film). Then this first layer of nematic molecules orients the bulk nematic liquid crystal by means of the anisotropic intermolecular interaction characterizing the nematic phase.

This model of the interface LB film–nematic liquid crystal was proposed some years ago by Hiltrop and Stegemeyer [7]. It has been recently reconsidered by Komitov *et al.* and by Alexe-Ionescu *et al.* to analyze the temperature-induced surface transitions in nematic liquid crystals [7].

Our paper is organized as follows. In Sec. II the elastic theory of a monomolecular orienting film is described. In Sec. III the presence of a stochastic surface field is considered. There we will show that the stochastic part of the surface field is equivalent to a fourth order term in $(\mathbf{n}_s\cdot\boldsymbol{\pi})$. In Sec. IV the main conclusions of our paper are stressed.

II. ELASTIC ENERGY DENSITY OF A MONOMOLECULAR FILM

Let us consider a monomolecular film formed by rigid rodlike molecules of length l. Let $\mathbf{m}$ be the direction of the molecular major axis. Due to the interaction of the molecules and the substrate we have a film with two-dimensional (2D) order. One end of each rod is attached to the solid substrate in a quasiregular pattern, whereas the other end is free. In this model, a molecule of the film may bend with an angle ϑ under the action of the direct interaction with the substrate and the interaction connected with the other molecules of the film. We will use a Cartesian reference frame having the x and y axes parallel to the solid surface, and the z axis normal to it. By using a molecular approach we want to evaluate the elastic energy of the monomolecular film. The starting point is the assumption of a two body interaction of the kind

$$g(\mathbf{m},\mathbf{m}',\mathbf{r})d\Sigma\, d\Sigma' \ , \tag{3}$$

between the surface elements $d\Sigma, d\Sigma'$, where $\mathbf{m}$ and $\mathbf{m}'$ are the directions of the molecular major axis at $\mathbf{R}$ and $\mathbf{R}'$, respectively, and $\mathbf{r}=\mathbf{R}'-\mathbf{R}$ [8]. In our analysis we suppose that the order of the film is perfect and hence $\mathbf{m}$ coincides with the statistical average of the molecular major axis of the molecules forming the film. In a continuum description the vector $\mathbf{m}$ (which may be considered of modulus 1) depends on the coordinates $\mathbf{R}$ of the considered point on the solid substrate: $\mathbf{m}=\mathbf{m}(\mathbf{R})$. $g(\mathbf{m},\mathbf{m}',\mathbf{r})$ is the intermolecular interaction energy. It is supposed short range, i.e., $g(\mathbf{m},\mathbf{m}',\mathbf{r})=0$ for $|\mathbf{r}|>\rho$, where $\rho\sim 1/\sqrt{\sigma}$ and σ is the surface density of the molecules of the film. This is equivalent to stating that we neglect long range electrostatic contributions in the interaction energy between the molecules of the film. These long range terms may be analyzed separately, as shown in [7].

In order to express the excess energy associated with a surface distribution of $\mathbf{m}$, let us suppose

$$\mathbf{m}'=\mathbf{m}(\mathbf{R}')=\mathbf{m}(\mathbf{R})+\delta\mathbf{m} \ , \tag{4}$$

where $|\delta\mathbf{m}|\ll 1$. This hypothesis means that in our analysis $\mathbf{m}$ is considered a macroscopic quantity and hence changes over macroscopic distances $d\gg\rho$. Only in this case it is possible to build an elastic theory for the orienting film. In this frame, $g(\mathbf{m},\mathbf{m}',\mathbf{r})$ may be expanded in power series of $\delta\mathbf{m}$. Simple calculations give

$$\begin{aligned} g(\mathbf{m},\mathbf{m}',\mathbf{r}) &= g(\mathbf{m},\mathbf{m}+\delta\mathbf{m},\mathbf{r}) \\ &= g(\mathbf{m},\mathbf{m},\mathbf{r})+\lambda_i\delta m_i+\tfrac{1}{2}\mu_{ij}\delta m_i\delta m_j \ , \end{aligned} \tag{5}$$

where

$$\lambda_i=\left[\frac{\partial g}{\partial m_i'}\right]_{\delta m=0} \ , \text{ and } \mu_{ij}=\left[\frac{\partial^2 g}{\partial m_i'\partial m_j'}\right]_{\delta m=0} \ , \tag{6}$$

and $g(\mathbf{m},\mathbf{m},\mathbf{r})$ is the uniform part of the interaction energy. Equation (5) holds because $g(\mathbf{m},\mathbf{m}',\mathbf{r})$ is supposed an analytical function of the scalar quantities $\mathbf{m}\cdot\mathbf{m}'$, $\mathbf{m}\cdot\mathbf{u}$, and $\mathbf{m}'\cdot\mathbf{u}$, where $\mathbf{u}=\mathbf{r}/|\mathbf{r}|$, of the kind

$$g(\mathbf{m},\mathbf{m}',\mathbf{r})=\sum_{a,b,c}C_{a,b,c}(r)(\mathbf{m}\cdot\mathbf{m}')^a(\mathbf{m}\cdot\mathbf{u})^b(\mathbf{m}'\cdot\mathbf{u})^c \ ,$$

where the expansion coefficients $C_{a,b,c}(r)$ depend only on the modulus of r. By means of this expression for g it is possible to evaluate the tensors λ_i and μ_{ij} given by (6). But this is not important for our analysis and we will not enter into this kind of calculations. They may be useful to connect the elastic constants of the film to the intermolecular interaction characterizing the film itself.

In the hypothesis that the interaction range of the intermolecular forces is small, δm_i may be expanded in power series of $\mathbf{r}$ as

$$\delta m_i=m_{i,\alpha}(\mathbf{R})x_\alpha+\tfrac{1}{2}m_{i,\alpha\beta}(\mathbf{R})x_\alpha x_\beta \ , \tag{7}$$

where $m_{i,j}(\mathbf{R})=(\partial m_i/\partial x_j)_{\mathbf{R}}$, and x_α are the Cartesian components of $\mathbf{r}$. Since we are dealing with a macroscopic theory, $|\delta m_i|$ must be very small for $0<|\mathbf{r}|<\rho$. This implies, as follows from (7), that $|m_{i,\alpha}|\ll 1/\rho$ and $|m_{i,\alpha\beta}|\ll 1/\rho^2$. Consequently, in a continuum description the vector $\mathbf{m}$ has to change smoothly with $\mathbf{R}$. In the opposite case in which $|m_{i,\alpha}|\sim 1/\rho$ and $|m_{i,\alpha\beta}|\sim 1/\rho^2$, the $|\delta m_i|$ are no longer small quantities and the elastic approximation (5) does not work well. However, since we are interested in nonhomogeneities appearing over a scale very large with respect to ρ, the elastic approximation works. Hence in the following we will assume that $m_{i,\alpha}$ and $m_{i,\alpha\beta}$ satisfy the above mentioned inequalities.

By substituting (7) into (5) one obtains

$$\begin{aligned} g(\mathbf{m},\mathbf{m}',\mathbf{r}) &= g(\mathbf{m},\mathbf{m},\mathbf{r})+\lambda_i(\mathbf{r})x_\alpha m_{i,\alpha}(\mathbf{R}) \\ &\quad +\tfrac{1}{2}\{\lambda_i(\mathbf{r})m_{i,\alpha\beta}(\mathbf{R}) \\ &\quad +\mu_{ij}(\mathbf{r})m_{i,\alpha}(\mathbf{R})m_{j,\beta}(\mathbf{R})\}x_\alpha x_\beta \ . \end{aligned} \tag{8}$$

Equation (8) gives the interaction energy between two elements characterized by the orientations $\mathbf{m}=\mathbf{m}(\mathbf{R})$ and $\mathbf{m}'=\mathbf{m}(\mathbf{R}'=\mathbf{R}+\mathbf{r})$, whose relative position is $\mathbf{r}$, in terms of the spatial derivatives of $\mathbf{m}$. It is important to remember that g rapidly decreases with $|\mathbf{r}|$, like λ_i and μ_{ij}. Furthermore, in the elastic limit,

$$|\lambda_i x_\alpha m_{i,\alpha}|\gg|(\lambda_i m_{i,\alpha\beta}+\mu_{ij}m_{i,\alpha}m_{j,\beta})x_\alpha x_\beta| \ ,$$

as follows from the above discussion concerning $|m_{i,\alpha}|$ and $|m_{i,\alpha\beta}|$.

In the mean field approximation, the energy of the film

$f(\mathbf{R})$ at the point $\mathbf{R}$ is obtained by integrating $\frac{1}{2}g$ over $\mathbf{r}\in(x,y)$. By using expression (8) we obtain

$$\begin{aligned} f(\mathbf{R})&=\int_{\Sigma_\infty} g(\mathbf{m},\mathbf{m}',\mathbf{r})d\Sigma' \\ &=f_0(\mathbf{m})+\Lambda_{i\alpha}m_{i,\alpha}(\mathbf{R})+\tfrac{1}{2}N_{i\alpha\beta}m_{i,\alpha\beta}(\mathbf{R}) \\ &\quad+\tfrac{1}{2}M_{ij\alpha\beta}m_{i,\alpha}(\mathbf{R})m_{j,\beta}(\mathbf{R})\ , \end{aligned} \tag{9}$$

where Σ_∞ means that the integration over r is extended over the range of the intermolecular forces giving rise to the film. In (9) we have put

$$f_0(\mathbf{m})=\tfrac{1}{2}\int_{\Sigma_\infty} g(\mathbf{m},\mathbf{m},\mathbf{r})d\Sigma'\ , \tag{10}$$

$$\Lambda_{i\alpha}=\tfrac{1}{2}\int_{\Sigma_\infty} \lambda_i(\mathbf{r})x_\alpha d\Sigma'\ , \tag{11}$$

and, furthermore,

$$N_{i\alpha\beta}=\tfrac{1}{2}\int_{\Sigma_\infty} \lambda_i(\mathbf{r})x_\alpha x_\beta d\Sigma'\ , \tag{12}$$

$$M_{ij\alpha\beta}=\tfrac{1}{2}\int_{\Sigma_\infty} \mu_{ij}(\mathbf{r})x_\alpha x_\beta d\Sigma'\ . \tag{13}$$

From (12) one derives

$$N_{i\alpha\beta}=N_{i\beta\alpha}\ . \tag{14}$$

Furthermore, from (13) and (6), it follows that

$$M_{ij\alpha\beta}=M_{ji\alpha\beta}=M_{ij\beta\alpha}=M_{ji\beta\alpha}\ . \tag{15}$$

The meaning of the different terms introduced before is very simple. $f_0(\mathbf{m})$ is the surface energy density of a uniformly oriented film ($\mathbf{m}$ position independent), whereas Λ, N, and M play the role of elastic constants. Tensors Λ, N, and M have to be decomposed by using the elements of symmetry of the film. In our case in which the film is assumed flat, its elements of symmetry are the geometrical normal $\mathbf{k}$ (parallel to the z axis) and the vector $\mathbf{m}$ [9].

Let us consider first $f_0(\mathbf{m})$. It can be expanded in power series of $\mathbf{m}\cdot\mathbf{k}$, or in terms of Legendre polynomials. In the event of uniform $\mathbf{m}$, the energy of the film alone reduces to $f_0(\mathbf{m})$. Of course the film is not alone, because it is in contact with the solid substrate. Hence we have to take into account also the direct interaction between the molecules of the film and the molecules of the substrate [10]. In the hypothesis of isotropic solid substrate, the surface free energy due to the direct interaction is of the kind $\psi(\mathbf{m}\cdot\mathbf{k})$. This energy depends on the Van der Waals interaction, dielectric interaction, and so on. It depends on the physical properties of the solid substrate. In the ideal case of a homogeneous surface, ψ is position independent. But as is well known real surfaces are never homogeneous. More precisely, on average they have approximately the same properties, but from point to point they change in a more or less stochastic manner. Hence we can write

$$\psi(\mathbf{m}\cdot\mathbf{k},\mathbf{r})=\psi_{\text{av}}(\mathbf{m}\cdot\mathbf{k})+\delta\psi(\mathbf{m}\cdot\mathbf{k},\mathbf{r})\ , \tag{16}$$

where $\delta\psi(\mathbf{m}\cdot\mathbf{k},\mathbf{r})$ takes into account the stochastic part of the direct interaction between the film and the solid substrate (due, for instance, to free ions or local irregularities). The total surface energy (due to the intrinsic part and the direct interaction) is then

$$F_0=f_0(\mathbf{m}\cdot\mathbf{k})+\psi(\mathbf{m}\cdot\mathbf{k},\mathbf{r})=G_0(\mathbf{m}\cdot\mathbf{k})+\delta\psi(\mathbf{m}\cdot\mathbf{k},\mathbf{r})\ , \tag{17}$$

where

$$G_0(\mathbf{m}\cdot\mathbf{k})=f_0(\mathbf{m}\cdot\mathbf{k})+\psi_{\text{av}}(\mathbf{m}\cdot\mathbf{k})$$

is the uniform part of the total surface energy.

Let us imagine that the uniform film on the considered surface tends to be in homeotropic alignment (i.e., $\mathbf{m}\|\mathbf{k}$). In a first approximation we assume for $G_0(\mathbf{m}\cdot\mathbf{k})$ the expression

$$G_0(\mathbf{m}\cdot\mathbf{k})=-\tfrac{1}{2}W(\mathbf{m}\cdot\mathbf{k})^2\ .$$

The total surface energy F_0 is then given by

$$F_0=-\tfrac{1}{2}W(\mathbf{r})(\mathbf{m}\cdot\mathbf{k})^2\ , \tag{18}$$

where

$$W(\mathbf{r})=W+\Delta W(\mathbf{r})\ , \tag{19}$$

in which $\Delta W(\mathbf{r})$ is the stochastic contribution to W.

III. SOLUTION OF THE PROBLEM

Let us suppose that for $\mathbf{m}$ position independent $f(\mathbf{R})$ is a minimum. This implies that the tensor Λ, connected with spontaneous deformations, has to be identically zero. Let us suppose, furthermore, that $\mathbf{m}$ is everywhere parallel to the (x,z) plane. This hypothesis is very restrictive, but, since we want only to analyze the renormalization of the surface energy introduced by the stochastic component of the direct interaction film-substrate, it can be reasonably accepted. By indicating with θ the angle made by $\mathbf{m}$ with $\mathbf{k}$, the total energy of the film is given by

$$\phi=\int_\Sigma \tfrac{1}{2}\{k(\nabla\theta)^2+W(\mathbf{r})\sin^2\theta\}d\Sigma\ , \tag{20}$$

where Σ is the surface of the sample, $W(\mathbf{r})$ is given by Eq. (19), and $\nabla=\mathbf{i}\,\partial/\partial x+\mathbf{j}\,\partial/\partial y$. In (20) k takes into account the elastic properties of the film, coming from the tensor M defined by (13). On the other hand, the tensor N connected with second order derivatives of $\mathbf{m}$ has been neglected, since it can be integrated over Σ, and it reduces to a line contribution. The $\mathbf{m}$ distribution in the film is the one minimizing ϕ given by (20). By minimizing (20) we obtain

$$k\Delta\theta-W(\mathbf{r})\sin\theta\cos\theta=0\ , \tag{21}$$

where $\Delta=\partial^2/\partial x^2+\partial^2/\partial y^2$. By extracting the fluctuating part of $W(\mathbf{r})$, as was done in (19), and putting

$$\theta(\mathbf{r})=\Theta+\delta\theta(\mathbf{r})\ , \tag{22}$$

where Θ is position independent, we can linearize Eq. (21). In this limit Eq. (21), in operational form, is written

$$\hat{L}\delta\theta(\mathbf{r})=\frac{\Delta W(\mathbf{r})}{2k}\sin(2\Theta)\ , \tag{23}$$

where

$$\hat{L}=\Delta-\alpha(\Theta)\ , \tag{24}$$

and

$$\alpha(\Theta)=\frac{W}{k}\cos(2\Theta)\ . \tag{25}$$

$\delta\theta(\mathbf{r})$ may be determined by means of the Green function. Simple calculations give

$$\delta\theta(\mathbf{r})=\int G(\mathbf{r},\mathbf{r}')\frac{\Delta W(\mathbf{r}')}{2k}\sin(2\Theta)d\mathbf{r}'\ , \tag{26}$$

where $G(\mathbf{r},\mathbf{r}')$ is the Green function of Eq. (23). Let us suppose now that

$$\langle\gamma(\mathbf{r})\gamma(\mathbf{r}')\rangle=D_\gamma\exp[-|\mathbf{r}-\mathbf{r}'|/R_\gamma]\ , \tag{27}$$

where $\gamma(r)=\Delta W(r)/k$, D_γ is the dispersion, and R_γ is the correlation length of the random distribution $\gamma(\mathbf{r})$. This kind of correlation function satisfies the fundamental property of stochastic systems, $\lim_{r\to\infty}\langle\gamma(\mathbf{r})\gamma(0)\rangle=0$. By taking into account (27), the effective surface energy defined by

$$\phi_{\text{eff}}=\frac{1}{\Sigma}\int_\Sigma\phi(\mathbf{r})d\mathbf{r} \tag{28}$$

is found to be

$$\phi_{\text{eff}}=\tfrac{1}{2}W\sin^2\Theta+(2\pi)^2D_\gamma R_\gamma^2kI(\alpha R_\gamma^2)\sin^2(2\Theta)\ , \tag{29}$$

where

$$I(\alpha R_\gamma^2)=\frac{1}{1-\alpha R_\gamma^2}+\frac{\ln\alpha R_\gamma^2}{2(1-\alpha R_\gamma^2)^{3/2}}-\frac{\ln(1+\sqrt{1-\alpha R_\gamma^2}\,)}{(1-\alpha R_\gamma^2)^{3/2}}\ . \tag{30}$$

In fact, by taking into account that the Green function of (23) is

$$G(K)=-\frac{1}{K^2+\alpha(\Theta)}\ ,$$

we obtain

$$\langle\gamma(\mathbf{r})\delta\theta(\mathbf{r})\rangle=-2\pi\int_0^\infty r'dr'\int_0^\infty K\,dK\int_0^{2\pi}dX\frac{e^{iKr'\cos X}}{K^2+\alpha(\Theta)}e^{-r'/R_\gamma}\ ,$$

which can be written in the form

$$\langle\gamma(\mathbf{r})\delta\theta(\mathbf{r})\rangle=-(2\pi)^2\int_0^\infty r'dr'\times\int_0^\infty\frac{K\,dK\,J_0(Kr')}{K^2+\alpha(\Theta)}e^{-r'/R_\gamma}\ ,$$

if the Bessel function of zeroth order

$$J_0(Kr)=\frac{1}{2\pi}\int_0^{2\pi}e^{iKr\cos X}dX$$

is introduced. By observing that

$$\int_0^\infty\frac{dK\,K}{K^2+\alpha(\Theta)}J_0(Kr)=K_0(\sqrt{\alpha(\Theta)}r)\ ,$$

where $K_0(\sqrt{\alpha(\Theta)}r)$ is the modified Bessel's function, and substituting this function into the expression of $\langle\gamma(\mathbf{r})\delta\theta(\mathbf{r})\rangle$ and integrating over r, we obtain [11] Eqs. (29) and (30) reported above.

The fluctuation additive term present in (29) arises from the expression

$$\Delta\phi=\frac{k}{2\Sigma}\int_\Sigma\langle\gamma(\mathbf{r})\theta(\mathbf{r}')\rangle\sin(2\Theta)d\Sigma\ . \tag{31}$$

Equation (29) clearly shows that the inclusion of a stochastic spatial variation of the surface field, caused by the direct interaction between the film and the substrate, gives rise to a new functional form of the effective surface energy [12]. More precisely, the usual anchoring strength, in the Rapini-Papoular sense, is renormalized: W is substituted by

$$W_{\text{eff}}=W+\Delta W\ , \tag{32}$$

where

$$\Delta W=(2\pi)^2D_\gamma R_\gamma^2I(\alpha R_\gamma^2)k\ . \tag{33}$$

Furthermore, a new term appears, proportional to $\sin^4\Theta$ and characterized by a coefficient equal to ΔW, but with opposite sign.

Until now we have limited our analysis to the energy of the film. However, as we have already stressed in the Introduction, in the hypothesis that the film is not compact the bulk orientation of the nematic liquid crystal is due to the steric interaction between the first nematic layer and the film. Consequently, the anchoring energy of the nematic liquid crystal coincides with the anchoring energy of the film. Of course the total surface energy of the nematic liquid crystal may contain, besides the steric term discussed above, other contributions due, for instance, to dispersion interactions. However, the steric one is usually the most important in the interface between the nematic liquid crystal and the film. Hence, at least for this kind of interface, our theory is expected to work well.

IV. CONCLUSIONS

The presence of a stochastic term in the direct interaction film–solid-substrate introduces a spatial variation of the vector **m** characterizing the orientation of the film. In the event that the correlation length of the stochastic function under consideration, R_γ, is small enough, the film may be considered uniformly oriented, but its surface energy is no longer given by the Rapini-Papoular expression. The effective surface energy contains the usual term proportional to $\sin^2\Theta$, whose coefficient is renormalized, as shown by Eq. (32). It contains, furthermore, a term proportional to $\sin^4\Theta$, whose coefficient is $-\Delta W$. It follows that the effect of a stochastic contribution to the surface energy is equivalent to the presence of the self-energy connected to the flexoelectric contribution, or to the order electric contribution.

We can estimate the order of magnitude of ΔW given by Eq. (33). The surface elastic constant of the film may be obtained by multiplying the bulk elastic constant of the film $\tilde{K}$ by the thickness of the film l. We assume $\tilde{K}$ of the same order of magnitude of the elastic constant of a nematic liquid crystal: $\tilde{K} \sim 10^{-6}$ dyn [1], and $l \sim 10$ Å. Consequently $k \sim \tilde{K} l \sim 10^{-13}$ erg. The anchoring energy is of the order $W \sim 10^{-2}$ erg/cm^2 [2]. Furthermore, as follows from Eq. (27),

$$D_\gamma = \left[\frac{W}{K} \right]^2 \left\langle \frac{\Delta W(\mathbf{r})}{W} \frac{\Delta W(0)}{W} \right\rangle = \left[\frac{W}{K} \right]^2 \sigma .$$

By assuming $\sigma \sim 10^{-1}$ and $I \sim 1$, a simple calculation gives $\Delta W \sim 10^{-2}$ erg/cm^2, i.e., of the same order as W. This simple estimation shows that the influence of the stochastic part may be very important. In particular, we want to underline that a term proportional to $\sin^4\Theta$ strongly modifies the phase diagram relevant to the surface transitions induced by temperature or by external fields [13,14].

ACKNOWLEDGMENTS

G. Barbero acknowledges financial support from Ministère de l'Education National et du Sport de France. Z. Gabbasova acknowledges financial support from Istituto Nazionale Fisica della Materia (Genova). A. K. Zvezdin thanks the Russian Fund of the Fundamental Research for financial support. A.K.Z. was partially supported by Politecnico di Torino, in the frame of the collaboration Politecnico di Torino–Russian Academy of Sciences.

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