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Statistical approach to the orienting photopolymer–nematic-liquid-crystal anchoring energy

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A statistical approach for the nematic order on an orienting photopolymer, also taking into account the surface anisotropy, has been formulated in the framework of mean field theory. This approach gives a Boltzmann-type orientational distribution function depending on both nematic-nematic and nematic-polymer interaction energies. The azimuthal anchoring energy coefficient has been evaluated from the extra Helmholtz free energy within an interface of thickness ξ that may be interpreted as the length over which the density changes from pure polymer to pure liquid crystal or, generally speaking, as the typical length over which the interaction between polymer and liquid crystal takes place. In the case of surface anisotropy given by linearly polarized UV photopolymerization, the anchoring energy coefficient depends on the exposure time and on ξ.

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I. INTRODUCTION

A central problem for constructing liquid crystal electro-optical devices is obtaining a substrate with anisotropic surface anchoring properties. Well known methods to achieve this condition are, for instance, to use obliquely evaporated SiO$_x$ layers, Langmuir-Blodgett films, or rubbed polymer films. The most common surface treatment, i.e., the mechanical rubbing of polyimide layers, has some disadvantages like physical damage and nonuniformities and generation of dust particles and/or electrostatic particles. A nonrubbing alignment process for polymer layers would not have the disadvantages listed above. The recently studied photoalignment process is an alternative polymer treatment for the surface anchoring of liquid crystals. First, it has been demonstrated that poly(vinyl)4-methoxycinnamate and poly(vinyl)cinnamate films, when exposed to linearly polarized ultraviolet light (LPUV) can be effective as alignment layers [1]. The aligning effect of polyimide films exposed to LPUV light has also been reported [2].

One of the main physical parameters of photoalignment is the exposure time because both the experiment and theoretical arguments lead to a well defined UV irradiation time which gives the maximum anisotropy of the polymer layer [1,3]. We may consider that the photopolymer orienting layer generates a microscopic surface field decaying toward the bulk. The anisotropy of the surface is given by an order parameter eventually depending on the exposure time [3]. Of course, the anchoring properties of the substrate must also be linked to the properties of the liquid crystal.

To study the order induced in a nematic material by a photopolymer layer, a rigorous statistical mechanical analysis is quite complicated. In the case of phase separation between the nematic and the polymer, the transition from the surface to the bulk can be described by the variation of both the density of polymer molecules and the density of liquid crystal molecules in an interface of thickness ξ. More generally, ξ represents the typical length over which the long-range interaction forces between polymer and liquid crystal occur. Even in the case of a well defined border between polymer and liquid crystal, the density variation approach can be used to mimic the presence of these surface forces.

From a fundamental point of view, the polymer-nematic interface is completely described by all the molecular correlation functions, which, in practice, cannot be determined. However, by using the mean field theory of Maier and Saupe [4] one can write the macroscopic Helmholtz free energy as a functional of the orientational distribution $f(\Omega)$ taking into account all the molecular interactions. The function $f(\Omega)$ is obtained by means of a self-consistent calculation, in order to minimize the free energy in the equilibrium state [5–7].

Starting with a pairwise-additive potential energy

$$\mathcal{U}=\sum_{(i,j)} \mathcal{V}(r_{ij},\Omega_i,\Omega_j),$$

one constructs the free energy

$$\mathcal{F}=\mathcal{E}-T\mathcal{S}=\int dr^N\int d\Omega^N\left[\sum_{(i,j)} \mathcal{V}(r_{ij},\Omega_i,\Omega_j)\right]P^{(N)}$$
$$+kT\int dr^N\int d\Omega^N P^{(N)}\ln P^{(N)},$$

where the first integral stands for the internal energy and the second one takes into account the entropy. The N-particle distribution function $P^{(N)}$ is

$$P^{(N)}(r_1,\ldots,r_N,\Omega_1,\ldots,\Omega_N)\equiv\frac{\exp[-\beta\mathcal{U}(r^N,\Omega^N)]}{\int dr^N\int d\Omega^N\exp[-\beta\mathcal{U}]},$$

$$\beta=\frac{1}{kT}.$$

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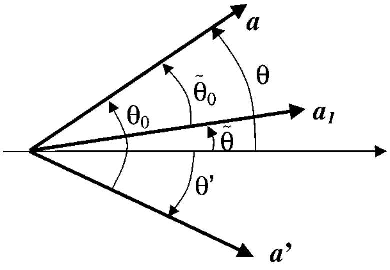

FIG. 1. Schematic drawing of two liquid crystal molecules *a* and a' and a polymer molecule a_1. Not all the angles are in the same plane.

Of course, the full *N*-body distribution function cannot be used as it is. The mean field approximation simplifies this distribution function. Eventually, we can use only a one-particle distribution function, which separates the radial distribution from the orientational one [8]:

$$R(r)\frac{N}{V}f(\theta). \tag{1.1}$$

$R(r)$ is different from a constant only if the distance is very small, i.e., of the order of several molecular dimensions. Also, one has to use the normalizing conditions

$$\int_V R(r)\frac{N}{V}r^2 dr = N, \tag{1.2}$$

$$\int f(\theta)d\Omega = 1.$$

In a recent paper [3], we analyzed the orientational effect of cross-linked polymerized photopolymers on nematic liquid crystals. We discussed this effect in terms of a time dependent distribution function of the polymers, $g(\theta_1)$.

In this paper we start with a theoretical model for the nematic order including surface anisotropy in the framework of mean field theory. It gives us a Boltzmann-type distribution function depending on both nematic-nematic and nematic-polymer interaction energies. Then, assuming a small twist occurs, we will evaluate the anchoring energy from the extra Helmholtz free energy. Concluding remarks end the paper.

II. THEORETICAL MODEL

Let us consider one liquid crystal molecule *a* interacting via θ_0 and $\tilde{\theta}_0$ with a liquid crystal molecule a' and a polymer molecule a_1 (Fig. 1). To evaluate the internal energy of the system one has to take into account the interactions between liquid crystal molecules and also the interactions of polymer sidechains with nematic molecules. Hence the internal energy will be given by

$$\begin{aligned}\mathcal{E} = {} & \frac{1}{2}\int_V d^3r'\, d\Omega' \frac{N}{V}R(r')f(\theta') \\ & \times \int_V d^3r\, d\Omega\, \frac{N}{V}R(r)f(\theta)\mathcal{V}(r,\theta_0) \\ & + \int_V d^3r\, d\Omega\, \frac{N}{V}R(r)f(\theta) \\ & \times \int_V d^3r_1 d\Omega_1 \frac{N_1}{V}R_1(r_1)g(\tilde{\theta})\mathcal{V}_1(r,\tilde{\theta}_0),\end{aligned} \tag{2.1}$$

where the subscript 1 and the tilde are associated with the polymer long axis.

Introducing the average potentials

$$nU(\theta_0) = \frac{N}{V}\int d^3r\, \mathcal{V}(r,\theta_0)R(r),$$

$$n_1U_1(\tilde{\theta}_0) = \frac{N_1}{V}\int d^3r\, \mathcal{V}_1(r,\tilde{\theta}_0)R_1(r), \tag{2.2}$$

where n and n_1 are the concentrations of nematic molecules and polymer molecules, respectively, in the interface of thickness ξ,

$$n = \frac{N}{V} \quad \text{and} \quad n_1 = \frac{N_1}{V} \tag{2.3}$$

Equation (2.3) can be written as

$$\begin{aligned}\mathcal{E} = {} & \frac{Nn}{2}\int d\Omega' f(\theta')\int d\Omega\, f(\theta)U(\theta_0) \\ & + Nn_1\int d\Omega_1 g(\tilde{\theta})\int d\Omega\, f(\theta)U_1(\tilde{\theta}_0).\end{aligned} \tag{2.4}$$

By considering the contribution of the orientational degrees of freedom of the liquid crystal molecules to the entropy of the system, one has

$$\begin{aligned}\mathcal{S} &= -k\int d^3r\, d\Omega\, \frac{N}{V}R(r)f(\theta)\ln\left[\frac{N}{V}R(r)f(\theta)\right] \\ &= -kN\int d\Omega\, f(\theta)\ln[f(\theta)] + \text{const.}\end{aligned} \tag{2.5}$$

To obtain the best orientational distribution function $f(\theta)$ we have to minimize the Helmholtz free energy $\mathcal{F} = \mathcal{E} - T\mathcal{S}$, with the constraint $\int f(\theta)d\Omega = 1$. So $\delta(\mathcal{F} + \lambda\int f(\theta)d\Omega) = 0$ implies that

$$\frac{\delta}{\delta f}\left(\mathcal{F} + \lambda\int f(\theta)d\Omega\right) = \frac{\partial}{\partial f}\left(\mathcal{F} + \lambda\int f(\theta)d\Omega\right) = 0, \tag{2.6}$$

because the free energy $\mathcal{F}$ does not contain explicitly the derivative of the function $f(\theta)$.

Introducing

$$n\int d\Omega' f(\theta')U(\theta_0)=M(\theta),$$

$$n_1\int d\Omega_1 g(\tilde{\theta})U_1(\tilde{\theta}_0)=M_1(\theta), \tag{2.7}$$

one gets

$$f(\theta)=\frac{1}{Z}\exp\left[-\frac{M(\theta)+M_1(\theta)}{kT}\right] \tag{2.8}$$

with the standard notation for the partition function,

$$Z(T)=\int \exp\left[-\frac{M(\theta)+M_1(\theta)}{kT}\right]d\Omega. \tag{2.9}$$

The average interaction potentials U and U_1 cannot be known exactly and we can take into account only the fact that the interactions must be even in θ_0 and $\tilde{\theta}_0$, and have a minimum for $\theta_0=0$ and for $\tilde{\theta}_0=0$. This comes from the fact that the van der Waals dispersion energy is minimum when the molecules are parallel (that is, it is proportional to $\cos^2\theta$) and the repulsive steric energy must be maximum when the two molecules are at right angle (that is, proportional to $\sin^2\theta$). But $\sin^2\theta=1-\cos^2\theta$ and, apart from a constant, both interactions lead to a minimum proportional to $\cos^2\theta$. We can develop U up to the second order in $\cos\theta_0$ and $\cos\tilde{\theta}_0$, namely,

$$U(\theta_0)=-uP_2(\cos\theta_0),$$

$$U_1(\tilde{\theta}_0)=-u_1P_2(\cos\tilde{\theta}_0), \tag{2.10}$$

where $P_2(\cos\theta)$ is the Legendre polynomial of second order. We have to emphasize that u and u_1 do not have dimensions of energy, but energy times volume, as is shown by Eq. (2.4). They should represent approximately the depth of the potential well times the covolume, i.e., a region including the first molecule inside which the second's center can never be found because of the molecular impenetrability.

Let us evaluate $M(\theta)$:

$$\begin{aligned}M(\theta)&=-un\int d\Omega' f(\theta')P_2(\cos\theta_0)=-un\int_0^\pi f(\theta')\\&\quad\times\left[\int_0^{2\pi}P_2(\cos\theta_0)d\varphi'\right]\sin\theta' d\theta'\\&=-unP_2(\cos\theta)2\pi\int_0^\pi f(\theta')P_2(\cos\theta')\sin\theta' d\theta'\\&=-unSP_2(\cos\theta)\end{aligned} \tag{2.11}$$

where $S=2\pi\int_0^\pi f(\theta')P_2(\cos\theta')\sin\theta' d\theta'$ is the scalar order parameter of the nematic, and for this calculation we used the equations

$$\begin{aligned}\int_0^{2\pi}&P_2(\cos\theta_0)d\varphi'\\&=2\pi P_2(\cos\theta)P_2(\cos\theta')\\&\quad+\frac{1}{3}\int_0^{2\pi}P_{21}(\cos\theta)P_{21}(\cos\theta')\cos(\varphi-\varphi')d\varphi'\\&\quad+\frac{1}{12}\int_0^{2\pi}P_{22}(\cos\theta)P_{22}(\cos\theta')\\&\quad\times\cos 2(\varphi-\varphi')d\varphi',\end{aligned} \tag{2.12}$$

and similar relations for the nematic-polymer interaction:

$$\begin{aligned}\int_0^{2\pi}P_2(\cos\tilde{\theta}_0)d\varphi'&=2\pi P_2(\cos\theta)P_2(\cos\tilde{\theta})\\&\quad+\frac{1}{3}\int_0^{2\pi}P_{21}(\cos\theta)P_{21}(\cos\tilde{\theta})\\&\quad\times\cos(\varphi-\varphi')d\varphi'\\&\quad+\frac{1}{12}\int_0^{2\pi}P_{22}(\cos\theta)P_{22}(\cos\tilde{\theta})\\&\quad\times\cos 2(\varphi-\varphi')d\varphi'.\end{aligned} \tag{2.13}$$

P_{21} and P_{22} have the standard significance of associated Legendre functions.

The last two terms vanish because the integrals from 0 to 2π of $\cos(\varphi-\varphi_i)$ or $\cos 2(\varphi-\varphi_i)$ also vanish. Then

$$\begin{aligned}M_1(\theta)&=-u_1n_1\int d\Omega_1 g(\tilde{\theta})P_2(\cos\tilde{\theta}_0)\\&=-u_1n_1\int_0^{2\pi}d\varphi_1\int_0^\pi g(\tilde{\theta})P_2(\cos\tilde{\theta}_0)\sin\tilde{\theta}\,d\tilde{\theta}\\&=-u_1n_1P_2(\cos\theta)2\pi\int_0^\pi g(\tilde{\theta})P_2(\cos\tilde{\theta})\sin\tilde{\theta}\,d\tilde{\theta}\\&=-u_1n_1S_1P_2(\cos\theta),\end{aligned} \tag{2.14}$$

where

$$S_1=2\pi\int_0^\pi g(\tilde{\theta})P_2(\cos\tilde{\theta})\sin\tilde{\theta}\,d\tilde{\theta}. \tag{2.15}$$

Eventually, we get

$$f(\theta)=\frac{1}{Z}\exp[(unS+u_1n_1S_1)P_2(\cos\theta)/kT]. \tag{2.16}$$

For the sake of simplicity we introduce the nondimensional parameters $\varepsilon=un/kT$ and $\varepsilon_1=u_1n_1/kT$ representing the magnitudes of nematic-nematic and nematic-polymer interactions in kT units. Hence, the partition function becomes

$$Z=\int \exp[(\varepsilon S+\varepsilon_1S_1)P_2(\cos\theta)]d\Omega, \tag{2.17}$$

and the orientational distribution function has the expression

$$f(\theta)=\frac{1}{Z}\exp[(\varepsilon S+\varepsilon_1 S_1)P_2(\cos\theta)]. \tag{2.18}$$

Now, let us evaluate the internal energy of the system

$$\begin{aligned}\mathcal{E}&=\frac{Nn}{2}\int d\Omega' f(\theta')\int d\Omega\, f(\theta)U(\theta_0)\\&\quad+Nn_1\int d\Omega_1 g(\tilde{\theta})\int d\Omega\, f(\theta)U_1(\tilde{\theta}_0)\\&=N\left(\frac{1}{2}\int f(\theta)M(\theta)d\Omega+\int f(\theta)M_1(\theta)d\Omega\right).\end{aligned}\tag{2.19}$$

To obtain the internal energy in terms of the scalar order parameters S and S_1 we have to calculate

$$\begin{aligned}\int f(\theta)M(\theta)d\Omega&=-\int_0^{\pi}\int_0^{2\pi}unSf(\theta)P_2(\theta)\sin\theta\, d\theta\, d\varphi\\&=-unS^2=-kT\varepsilon S^2\end{aligned}\tag{2.20}$$

and

$$\begin{aligned}\int f(\theta)M_1(\theta)d\Omega&=-u_1n_1S_1\int_0^{\pi}\int_0^{2\pi}f(\theta)P_2(\theta)\sin\theta\, d\theta\, d\varphi\\&=-u_1n_1SS_1=-kT\varepsilon_1SS_1\end{aligned}\tag{2.21}$$

and the result is

$$\mathcal{E}=-NSkT(\tfrac{1}{2}\varepsilon S+\varepsilon_1S_1). \tag{2.22}$$

Similar calculations allow us to obtain the nematic orientational entropy $\mathcal{S}$:

$$\begin{aligned}\mathcal{S}&=-Nk\int d\Omega\, f(\theta)\ln[f(\theta)]\\&=-Nk\int d\Omega\,\frac{\exp[(\varepsilon S+\varepsilon_1S_1)P_2(\cos\theta)]}{Z}\\&\quad\times\ln\left\{\frac{\exp[(\varepsilon S+\varepsilon_1S_1)P_2(\cos\theta)]}{Z}\right\}\\&=-Nk\int d\Omega\,\frac{\exp[(\varepsilon S+\varepsilon_1S_1)P_2(\cos\theta)]}{Z}\\&\quad\times\{(\varepsilon S+\varepsilon_1S_1)P_2(\cos\theta)-\ln Z\}.\end{aligned}\tag{2.23}$$

Then,

$$\begin{aligned}-T\mathcal{S}&=NkT\int d\Omega\, f(\theta)[\varepsilon S+\varepsilon_1S_1]P_2(\cos\theta)\\&\quad+NkT\int d\Omega\, f(\theta)[-\ln Z]\\&=NkT[\varepsilon S^2+\varepsilon_1SS_1-\ln Z].\end{aligned}\tag{2.24}$$

By taking into account Eqs. (2.23) and (2.24), the free energy is obtained as

$$\begin{aligned}\mathcal{F}&=\mathcal{E}-T\mathcal{S}=NkT[-\tfrac{1}{2}\varepsilon S^2-\varepsilon_1SS_1+\varepsilon S^2+\varepsilon_1SS_1-\ln Z]\\&=NkT(\tfrac{1}{2}\varepsilon S^2-\ln Z).\end{aligned}\tag{2.25}$$

Let us introduce the free energy density in kT units:

$$F=\frac{\mathcal{F}}{VkT}=-n\ln Z+\frac{\varepsilon nS^2}{2}. \tag{2.26}$$

The free energy density, depends on the liquid crystal order parameter S and on the partition function Z. In turn, the partition function Z depends on S and S_1 as well as on n and n_1. The last two parameters are calculated with respect to the same value V so, considering the same order of magnitude for liquid crystal and polymer densities,

$$\frac{n_1}{n}\sim\frac{\xi}{d}, \tag{2.27}$$

where ξ is the thickness of the interface region and d is the thickness of the sample, which is much larger than ξ. When one is discussing bulk properties, n_1 may be neglected with respect to n, and ε_1 may be neglected with respect to ε.

We may simplify further the expression of the free energy density. Let us express $f(\theta)$ as a function of $x=\cos\theta$. Then

$$\begin{aligned}f(\theta)&=\frac{1}{Z}\exp[(\varepsilon S+\varepsilon_1S_1)P_2(x)],\\Z&=2\pi\int_{-1}^{1}\exp[(\varepsilon S+\varepsilon_1S_1)P_2(x)]dx.\end{aligned}\tag{2.28}$$

One gets

$$\begin{aligned}\frac{dZ}{d\varepsilon}&=2\pi\int_{-1}^{1}\frac{\partial}{\partial\varepsilon}\exp[(\varepsilon S+\varepsilon_1S_1)P_2(x)]dx\\&=2\pi\int_{-1}^{1}P_2(x)S\exp[(\varepsilon S+\varepsilon_1S_1)P_2(x)]dx=ZS^2\end{aligned}\tag{2.29}$$

and

$$\frac{1}{Z}\frac{dZ}{d\varepsilon}=\frac{d}{d\varepsilon}\ln Z=S^2. \tag{2.30}$$

Integrating with respect to ε, apart from a constant, we obtain

$$\ln Z=\varepsilon S^2 \tag{2.31}$$

or

$$\frac{\varepsilon nS^2}{2}=\frac{n}{2}\ln Z. \tag{2.32}$$

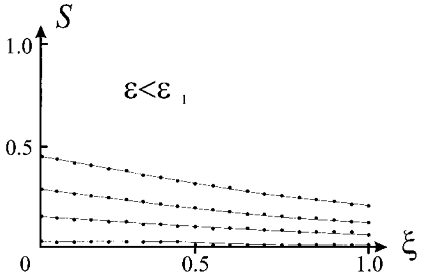

FIG. 2. Self-consistent calculation of the order parameter for a nematic-nematic interaction ε much smaller than the nematic-polymer interaction ε_1. The nematic-polymer interaction decreases from top to bottom. In bulk the nematic phase disappears because ε is smaller than a critical value ($\approx$4.5). Lines are guides to the eye.

We now have two alternative expressions for the free energy density:

$$F=-n\ln Z+\frac{n}{2}\ln Z=-\frac{n}{2}\ln Z=-\frac{n}{2}\varepsilon S^2. \qquad (2.33)$$

III. EVALUATION OF ANCHORING COEFFICIENT

The nematic liquid crystal properties in the interface of thickness ξ are investigated by considering the effect of the surface field induced by the photopolymer layer. In the absence of a surface interaction, the director orientation will become degenerate. It is the surface interaction that imposes the orientation of the director.

Let us consider a very thin layer of liquid crystal in contact with a polymer having the order parameter S_1, lower than the normal value of the order parameter S of the nematic phase. To explain the transition from the surface to the bulk in terms of the variation of both nematic density and also polymer density, we assumed the simplest dependence on z of the form $n_1(z)=ne^{-z/\xi}$ and $n(z)=n(1-e^{-z/\xi})$. For the sake of simplicity we have considered that the densities of the polymer and the liquid crystal are equal, and also that in the interface $[z\in(0,\xi)]$ the sum of $n_1(z)$ and $n(z)$ is equal to n.

If we divide the interface into small sublayers of thickness dz at a certain z, we will have in each of them a distribution function centered on $\theta=0$, but having different widths, i.e., different order parameters.

In Figs. 2 and 3 we have plotted the z dependence of S for some values of ε, ε_1, and S_1 solving the self-consistent equation for S, namely,

$$S=\frac{\int_{-1}^{1}\exp[(\varepsilon S+\varepsilon_1 S_1)P_2(x)]P_2(x)dx}{\int_{-1}^{1}\exp[(\varepsilon S+\varepsilon_1 S_1)P_2(x)]dx}, \qquad (3.1)$$

where $x=\cos\theta$. In Fig. 2 we have used a value of ε that normally would not allow the formation of the nematic phase. If ε_1 is larger enough than ε the nematic phase exists only in a region of the order of ξ, decaying in the bulk to an isotropic liquid. In Fig. 3 ε has the normal value of a liquid crystal ($\approx$4.5) and even if $\varepsilon_1 S_1$ is small the value of the liquid crystal order parameter S increases with increasing z and approaches a certain limit for $z=\xi$.

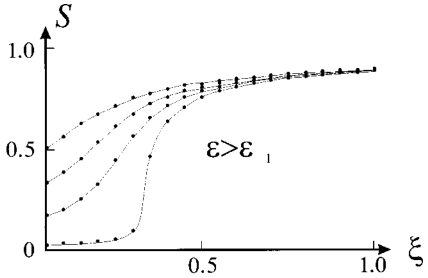

FIG. 3. Self-consistent calculation of the order parameter for a nematic-nematic interaction greater than the nematic-polymer interaction. The nematic-polymer interaction decreases from top to bottom. ε is now larger than the critical value. Lines are guides to the eye.

As previously discussed, the lifting of director degeneracy is due to the liquid-crystal–polymer interaction. If an external agent (a magnetic field, for instance) tends to rotate the director in the surface plane, the distribution function in the sublayers of thickness dz will have maxima not for the value $\theta=0$ but for certain angles $\alpha\neq 0$, where α will vary with z.

Considering that, for $\varepsilon/\varepsilon_1$ large, the value of S does not vary too much even in the interface, the distribution function $f(\theta+\alpha)$ is of the same kind for each sublayer:

$$f(\theta+\alpha)=\frac{1}{Z_1}\exp[\varepsilon SP_2(\cos\theta)+\varepsilon_1 S_1 P_2(\cos(\theta+\alpha))] \qquad (3.2)$$

where α, for the sake of simplicity, varies linearly with z,

$$\alpha(z)=\varphi\frac{z}{\xi}. \qquad (3.3)$$

Note that in Eq. (3.2) we have considered $\varepsilon SP_2(\cos\theta)$ and $\varepsilon_1 S_1 P_2(\cos(\theta+\alpha))$ separately because the nematic-nematic interaction must be invariant to a rotation of angle α, whereas the nematic-polymer interaction will certainly depend on α. It is only the nematic-polymer interaction that gives an increase in the free energy. Of course,

$$Z_1=\int \exp[\varepsilon SP_2(\cos\theta)+\varepsilon_1 S_1 P_2(\cos(\theta+\alpha))]d\Omega \qquad (3.4)$$

will be a function of z.

Together with Z_1, $F_1=-(n/2)\ln Z_1$ will also be a function of z. The extra free energy density, as a function of z, will be

$$\Delta F(z)=-\frac{n}{2}\ln\frac{Z_1}{Z}. \qquad (3.5)$$

Thus, the extra energy per unit surface due to a torsion of the director will be

$$\Delta\mathcal{F}=kT\int_0^{\xi}\Delta F(z)dz. \tag{3.6}$$

We have to consider the fact that beyond the value ξ, i.e., in the bulk, the liquid crystal is undistorted, so the extra free energy density is zero.

The result of the integration depends on the torsion angle φ. By definition

$$\frac{1}{2}\left.\frac{d^2\Delta\mathcal{F}}{d\varphi^2}\right|_{\varphi=0}=w_a \tag{3.7}$$

is the coefficient of the azimuthal anchoring. To calculate the anchoring coefficient w_a we must not forget that the azimuthal distortion needs to be very small, so we can make a series development of $P_2(\cos(\theta+\alpha))$ with respect to α, up to $O(\alpha^3)$:

$$P_2(\cos(\theta+\alpha))=P_2(\cos\theta)+\Delta P, \tag{3.8}$$

where ΔP is very small.

The partition function will be of the kind

$$\begin{aligned}Z_1&=\int\exp[\varepsilon SP_2(\cos\theta)+\varepsilon_1S_1P_2(\cos(\theta+\alpha))]d\Omega\\&=\int\exp[(\varepsilon S+\varepsilon_1S_1)P_2(\cos\theta)]\exp(\varepsilon_1S_1\Delta P)d\Omega\\&\approx\int\exp[(\varepsilon S+\varepsilon_1S_1)P_2(\cos\theta)][1+\varepsilon_1S_1\Delta P]d\Omega\\&=Z\left\{1+\frac{1}{Z}\int\exp[(\varepsilon S+\varepsilon_1S_1)P_2(\cos\theta)](\varepsilon_1S_1\Delta P)d\Omega\right\}\\&=Z\left\{1+\int f(\theta)(\varepsilon_1S_1\Delta P)d\Omega\right\},\end{aligned} \tag{3.9}$$

where, if a is small, we use the approximation $e^a\simeq1+a$. With the same approximation written in the form $\ln(1+a)\simeq a$, one gets

$$\begin{aligned}\Delta F(z)&=-\frac{n}{2}\ln\frac{Z_1}{Z}=-\frac{n}{2}\ln\left\{1+\int f(\theta)(\varepsilon_1S_1\Delta P)d\Omega\right\}\\&\simeq-\frac{n}{2}\int f(\theta)(\varepsilon_1S_1\Delta P)d\Omega,\end{aligned} \tag{3.10}$$

where ΔP is

$$\Delta P=3\alpha\cos\theta\sin\theta+\tfrac{3}{2}\alpha^2(1-2\cos^2\theta)+O(\alpha^3). \tag{3.11}$$

Hence the extra free energy density is

$$\Delta F(z)=\frac{n\alpha^2\varepsilon_1S_1}{4(\varepsilon S+\varepsilon_1S_1)}\times\left[\frac{2\exp\left[\frac{3}{2}(\varepsilon S+\varepsilon_1S_1)\right]\sqrt{(6/\pi)(\varepsilon S+\varepsilon_1S_1)}}{\operatorname{erf}i[\sqrt{3(\varepsilon S+\varepsilon_1S_1)/2}]}-2-3(\varepsilon S+\varepsilon_1S_1)\right], \tag{3.12}$$

the function $\operatorname{erf}i(x)\equiv i\operatorname{erf}(-ix)=\int_0^x\exp(t^2)dt$ being strictly real although it contains the imaginary number $i=\sqrt{-1}$.

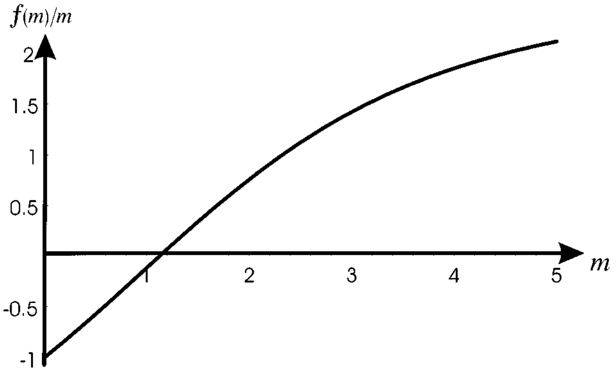

FIG. 4. $f(m)/m$ as a function of m, where $m=\varepsilon S+\varepsilon_1S_1$ and $f(m)$ is defined in Eq. (3.13).

In Fig. 4 we represent a plot of $f(m)/m$ as a function of $m\equiv\varepsilon S+\varepsilon_1S_1$, where

$$f(m)=\frac{2e^{3m/2}\sqrt{6m/\pi}}{\operatorname{erf}i(\sqrt{3m/2})}-2-3m. \tag{3.13}$$

$f(m)/m$ is positive only for $m>1.128$, which is just the value for which the isotropic to nematic transition appears in bulk. It corresponds to a value of ε around 4.5.

The extra free energy per unit surface will be

$$\begin{aligned}\Delta\mathcal{F}&=kT\int_0^{\xi}\Delta F\left(\frac{z\varphi}{\xi}\right)dz=kT\frac{\xi}{\varphi}\int_0^{\varphi}\Delta F(\alpha)d\alpha\\&=\frac{n\xi}{12}\varphi^2\frac{\varepsilon_1S_1}{m}f(m)kT,\end{aligned} \tag{3.14}$$

and

$$w_a=\frac{1}{2}\left.\frac{d^2\Delta\mathcal{F}}{d\varphi^2}\right|_{\varphi=0}=\frac{n\xi}{12}kT\frac{\varepsilon_1S_1}{m}f(m). \tag{3.15}$$

Considering that S also varies in the interface together with $n(z)$ and $n_1(z)$, it is possible to make a self-consistent numerical computation. The result for the constant w_a as a tridimensional plot with respect to εS and ε_1S_1 is presented in Fig. 5.

One may consider typical values for liquid crystals as follows: molecular mass $M=0.5$ kg/mol, average density (in

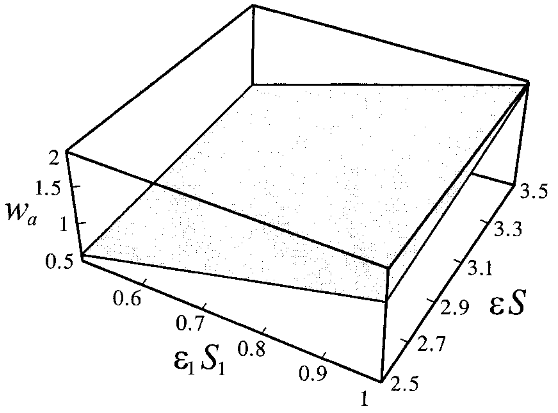

FIG. 5. Three-dimensional plot of the anchoring coefficient w_a as a function of S_1 and S. The height is in mJ/m^2.

the region up to ξ) $\rho=5\times10^2$ kg/m^3, interface thickness $\xi=5$ nm, $T=300$ K. With these values

$$\frac{n\xi kT}{12}\approx 1\,\frac{\mathrm{mJ}}{\mathrm{m}^2},$$

and the function

$$\frac{f(m)}{m}=\frac{1}{m}\left\{\frac{2e^{3m/2}\sqrt{6m/\pi}}{\mathrm{erf}\,i(\sqrt{3m/2})}-2-3m\right\}$$

is 2 for $m=4$, corresponding to nematic scalar order parameters around 0.7 (see also Fig. 3). For $\varepsilon\approx4.5$, $\varepsilon_1\approx3$, $S_1\approx0.3$, the anchoring coefficient is

$$w_a\approx 1.8\,\frac{\mathrm{mJ}}{\mathrm{m}^2}.$$

The numerical computation presented in Fig. 5, which also implies a self-consistent calculus for S, agrees well with this value, giving for w_a numerical values between 1 and 2 mJ/m^2. This order of magnitude corresponds to a strong anchoring.

IV. CONCLUDING REMARKS

Using a mean field approximation we have obtained a self-consistent Boltzmann-type orientational distribution function which depends both on the nematic-nematic interaction energy ε and on the nematic-polymer energy ε_1, and also on the polymer order parameter S_1. In the interface region of thickness ξ, S depends on z by means of $n(z)$ and $n_1(z)$. Assuming that the twist angle α, induced, for instance, by an external field, is small, we have estimated the excess free energy density, which depends quadratically on α. This gives a finite azimuthal anchoring energy coefficient w_a which depends on the interface thickness ξ, the nematic-polymer interaction ε_1, the polymer order parameter S_1, and a certain function $f(m)$. The last two are the most important because through the dependence on S_1 one gets a dependence on the exposure time to the UV light [1,3]. Actually, for values of εS of physical interest, i.e., εS up to 3 and $\varepsilon_1 S_1$ up to 1, the function $(\varepsilon_1 S_1/m)f(m)$ may be expanded in series and one gets

$$\frac{\varepsilon_1 S_1}{m}f(m)=-0.08+1.68\varepsilon_1 S_1+0.25(\varepsilon_1 S_1)^2$$

which is an almost linear dependence on $\varepsilon_1 S_1$ if the latter is not larger than 1, i.e., we have a mainly linear dependence of w_a on S_1. It was shown in Figs. 3 and 4 that S depends on the values of S_1 only in the transition region of order ξ, not in the bulk. So the contribution of S_1 to the bulk state of a nematic liquid crystal is just to give the direction of **n**. On the other hand, as far as the anchoring energy is concerned, the value of S_1 is essential because the anchoring coefficient w_a does depend on S_1 both directly and also by means of S, which depends, in turn, on S_1 within the transition region.

One may also see that, although w_a depends linearly on the transition width ξ, one has little (if any) control of ξ. The only parameter that may be controlled, for example, by changing the exposure time [3], is S_1.

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