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Statistical theory of the compensating effect when anchoring with two orthogonal photoaligned polymers

Andrei Th. Ionescu and Emil S. Barna
Facultatea de Fizica, Universitatea din Bucuresti, POB MG-11, R-76900 Bucharest, Romania

Giovanni Barbero
Dipartimento di Fisica, Politecnico di Torino and INFM, Unita de Ricerca di Torino, Corso Duca degli Abruzzi 24, I-10129 Torino, Italy

Anca-Luiza Alexe-Ionescu
Departamentul de Fizica, Universitatea "Politehnica" din Bucuresti Splaiul Independentei 313, R-77206, Bucharest, Romania

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In this paper we extend a statistical microscopic analysis to the anchoring properties of polymer films obtained by two concomitant or subsequent polymerization processes along two different directions. We can thus explain the recently observed compensating effect of two orthogonal polymerization processes. An expression for the anchoring energy has been evaluated from the extra Helmholtz free energy within an interface layer where the interactions shift from polymer-nematic interactions to nematic-nematic interactions, as in bulk. The result includes the angular dependence on the two photoaligning directions. A procedure of getting controlled anchoring strength *in situ* is suggested.

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I. INTRODUCTION

Liquid-crystal (LC) electro-optical devices need a substrate with anisotropic surface anchoring properties. Well known methods to achieve this property have been, for instance, obliquely evaporated SiO_x layers, buffed polymer films, etc. All these methods have at least two main disadvantages: physical damage and nonuniformities, generation of dust particles and/or electrostatic charges in the first place, and the fact that once the cell was assembled the anchoring properties can no longer be altered. In the 1990s a new technique emerged, called photoalignment, which allows one to align and realign the director $\hat{\mathbf{n}}$ on the substrate of the filled cell. It was first 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. The aligning effect of *polyimide* or of *para-fluorocinnamoyl cellulose* films exposed to LPUV has also been reported [1–5].

An important parameter of photoalignment is the exposure time to UV because both experiment and theoretical arguments lead to a well defined irradiation time that gives the maximum anisotropy of the polymer layer [2,5–7]. In the following we will consider that the photopolymer orienting layer generates a microscopic surface field decaying toward the bulk [7]. This model of a surface field responsible for the liquid-crystal orientation, *diluted* in space over a thin anchoring layer, had been already used in Ref. [8] and discussed recently in Refs. [9–11].

In our previous paper [7] a statistical approach for the nematic order, also taking into account the surface anisotropy, has been made in the frame of mean field theory. It 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 layer 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, ξ is the typical length over which the interaction forces between the polymer and the liquid crystal take place in the sense of diluted surface potential mentioned above [8–11].

Beyond ξ the pure liquid-crystal Boltzmann-type distribution function and, consequently, the order parameter do not depend on any particular direction, i.e., there is degeneracy of the nematic director in "practically" infinite bulk. Yet, the direction that is imposed by the oriented polymer through the polymer-nematic interaction will give the common orientation of the director in the bulk in order to minimize the elastic energy. In fact, it is this condition of minimum free energy that propagates to the bulk the direction decided within the interface thickness ξ. The same statistical approach used here has been followed to find a microscopic expression of the nematic elastic coefficients (K_{22} in particular), which depends directly on the order parameter in the bulk. From the microscopic point of view, this approach provides a logical transition from the anchoring energy within the interface to the elastic energy in the bulk [12].

In this paper we extend our previous model to the case of two photopolymerization directions. The subject is of large interest and recently both theoretical and experimental work on it has been reported [5]. In particular, our statistical approach can explain on microscopic grounds the compensating effect of two orthogonal irradiations [5].

From a fundamental point of view, the polymer-nematic interface is completely described by all the molecular correlation functions that, in practice, cannot be determined. However, by using the idea of mean field theory of Maier and Saupe [13] one can write the macroscopic free energy as a functional of the orientational distribution $f(\Omega)$ taking into account all the molecular interactions. By molecular interactions we shall consider both nematic molecule–nematic molecule anisotropic interaction and nematic molecule–polymer fragment anisotropic interaction. The function $f(\Omega)$ is obtained by means of a self-consistent calculation, in order to minimize the free energy in the equilibrium state [14–16]. Starting with a true *N*-body distribution function, one can eventually use only a one-particle distribution function that separates the radial distribution from the orientational one [6,7,17]. It is convenient to express it as a density distribution function

$$\frac{N}{V}R(r)f(\theta), \tag{1}$$

where r is the distance between the centers of mass of the two molecules (or a molecule and a polymer fragment) and θ is the angle between the long axes of the molecules (or polymer fragments) and a certain fixed direction. $R(r)$ would only be different from a constant if the distance were very small, i.e., of the order of molecular dimensions. Also, one has to use the normalizing conditions

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

$$\int f(\theta)d\Omega = 1. \tag{2}$$

In Ref. [6], we have analyzed the orientational effect of cross-linked polymerized photopolymers on the nematic liquid crystals. This effect was discussed in terms of the distribution function of polymer fragments that will depend on the time of photopolymerization. Considering the fact that both an increase of polymer cross links on one direction and the decrease of polymer fragments on an orthogonal direction contribute to the anisotropic anchoring of LC, the distribution function of polymers or, better say, the distribution function of fragments responsible for anisotropy is

$$g(\phi) = \frac{1}{\pi}\left(1 + e^{-A(t)\sin^2\phi} - e^{-A(t)\cos^2\phi}\right), \tag{3}$$

where the positive function $A(t)$, starting from 0 for $t=0$, tends to a certain limit for very large t, preventing the polymer distribution to become isotropic again. ϕ being the on-surface projected angle between one pair of unpolarized monomers and the direction of UV light polarization, the term in $\sin^2\phi$ in Eq. (3) gives the increase of polymer fragments along $\phi=0$, whereas the term in $\cos^2\phi$ gives the decrease of polymer fragments along $\phi=\pi/2$, both contributing thus to the total anisotropy. This polymer distribution function can be characterized rather well by an order parameter S_1, smaller than the order parameter S of LC in the bulk, and which goes to zero within the distance ξ.

In the frame of mean field theory, including also the surface anisotropy expressed by the distribution function $g(\phi)$, one can obtain the Boltzmann-type distribution function $f(\theta)$, which in the interface layer depends on both nematic-nematic and nematic-polymer energies. The easy axis is given by the angle $\phi=0$ for which the polymer distribution function has a maximum [7].

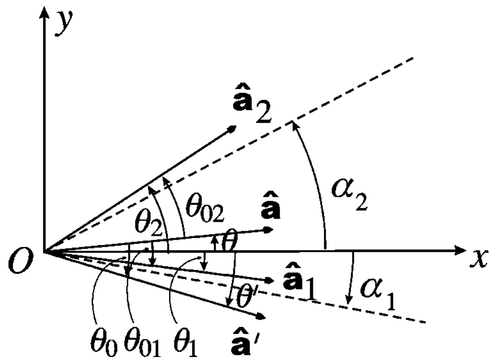

FIG. 1. An in-plane view of the relevant directions and angles. $\hat{\mathbf{a}}$ and $\hat{\mathbf{a}}'$ stand for the LC molecule long axis directions and $\hat{\mathbf{a}}_1$ and $\hat{\mathbf{a}}_2$ for the polymer directions. The angles θ, θ', θ_1, and θ_2 are measured off the *Ox* axis whereas θ_0, θ_{01}, and θ_{02} give the angular distance between $\hat{\mathbf{a}}$ and the other three versors. In this picture the azimuthal angles φ's have not been presented.

In this paper we shall consider two processes of LPUV, either concomitantly or subsequently, each one being characterized by two distribution functions $g_1(\theta_1-\alpha_1)$ and $g_2(\theta_2-\alpha_2)$, which would define, if considered alone, an easy axis along α_1 or α_2, respectively. Following the general ideas of Ref. [7], we shall estimate the anchoring energy coefficient and shall consider the interesting case $\alpha_1-\alpha_2=\pi/2$. A comparison with the experimental data and the theoretical considerations reported in Ref. [5] will show the agreement between our microscopic approach and the tensor phenomenological description used in paper [5], giving thus the later better grounds.

II. THEORETICAL MODEL

Let us consider a representative LC molecule described by its long axis direction $\hat{\mathbf{a}}$, which interacts with other LC molecules ($\hat{\mathbf{a}}'$) and polymer fragments ($\hat{\mathbf{a}}_1$ and $\hat{\mathbf{a}}_2$) oriented about two directions α_1 and α_2, respectively. In Fig. 1 we present a simplified situation where all the four versors lie in the same basal plane ($z=0$). The versor $\hat{\mathbf{a}}$ is characterized by a polar angle θ with respect to the in-plane *Ox* axis and an azimuthal angle φ measured on the *Oyz* plane. The distribution of this molecule in a certain small solid angle $d\Omega$ will be $f(\theta)d\Omega$. In the same way the other three versors will be characterized by the coordinates (θ',φ'), (θ_1,φ_1), (θ_2,φ_2). The distribution of $\hat{\mathbf{a}}'$ will be, of course, the same function $f(\theta')$, and the distributions of $\hat{\mathbf{a}}_1$ and $\hat{\mathbf{a}}_2$ are $g_1(\theta_1-\alpha_1)$ and $g_2(\theta_2-\alpha_2)$. g_1 and g_2 could be different functions, depending on the time and intensity of photopolymerization [6]. As a matter of fact, each distribution function should depend on the appropriate angle φ. Yet, this fact can be disregarded for two reasons: (a) because of the general planar orientation of both LC molecules and polymer fragments the angles φ's have values either very close to zero or very close to π; (b) the distribution of angles φ is symmetric with respect to the *Oxz* plane. Because of the fact that for LC (and for polymer fragments, too) $\hat{\mathbf{a}}$ is equivalent to $-\hat{\mathbf{a}}$ any possible orientation can be characterized by $\theta\in[0,\pi/2]$ and $\varphi\in[0,2\pi]$. For this reason, the limits to integrals should be 0 and $\pi/2$ instead of π. Only that all the functions we will consider are even in $\cos\theta$ or $\sin\theta$ and

$$\int_0^{\pi}F(\cos\theta)d\Omega=2\int_0^{\pi/2}F(\cos\theta)d\Omega,$$

where $F(\cos\theta)$ is even in $\cos\theta$ (or $\sin\theta$). Because of the degree of freedom given by the normalizing condition we shall still use the standard integration limits 0; π for θ and 0; 2π for φ.

The pair interaction potential is considered to depend only on the angle between the long axes of molecules, i.e., $\theta_0=\angle(\hat{\mathbf{a}},\hat{\mathbf{a}}')$, $\theta_{01}=\angle(\hat{\mathbf{a}},\hat{\mathbf{a}}_1)$, $\theta_{02}=\angle(\hat{\mathbf{a}},\hat{\mathbf{a}}_2)$. (The interaction between $\hat{\mathbf{a}}_1$ and $\hat{\mathbf{a}}_2$ is not at all relevant to our system, it only contributes a constant to the internal energy.)

The internal energy is given by all the interactions

$$\begin{aligned}\mathcal{E}=&\frac{1}{2}\int_V d^3r'd\Omega'\frac{N}{V}R(r')f(\theta')\int_V d^3r\,d\Omega\,\frac{N}{V}R(r)f(\theta)\mathcal{V}(r,\theta_0)\\&+\int_V d^3r\,d\Omega\,\frac{N}{V}R(r)f(\theta)\int_V d^3r_1d\Omega_1\frac{N_1}{V}R_1(r_1)g_1(\theta_1-\alpha_1)\mathcal{V}_1(r,\theta_{01})\\&+\int_V d^3r\,d\Omega\,\frac{N}{V}R(r)f(\theta)\int_V d^3r_2d\Omega_2\frac{N_2}{V}R_2(r_2)g_2(\theta_2-\alpha_2)\mathcal{V}_2(r,\theta_{02}).\end{aligned}\tag{4}$$

The factor $\frac{1}{2}$ in the first term in Eq. (4) comes from the fact that we must not count the pairs LC-LC twice. $\mathcal{V}$ is the angle and distance dependent pair potential.

The polymer distribution being considered as fixed, the entropic contribution to the Helmholtz free energy will arise only from the orientation of LC molecules and, using a well known formula [18], one has

$$\begin{aligned}\mathcal{S}=&-k\int_V d^3r\,d\Omega\,\frac{N}{V}R(r)f(\theta)\ln\left[\frac{N}{V}R(r)f(\theta)\right]\\=&-kN\int d\Omega\,f(\theta)\ln[f(\theta)]\\&+\text{constant with respect to } f(\theta).\end{aligned}\tag{5}$$

The condition of minimum free energy at equilibrium implies that

$$\delta\left(\mathcal{F}+\lambda\int f(\theta)d\Omega\right)=0,\tag{6}$$

where $\mathcal{F}=\mathcal{E}-T\mathcal{S}$ stands for Helmholtz free energy and λ is a Legendre multiplier that takes into account the normalizing condition of Eq. (2). As in Refs. [6] and [7] we shall use the following notations:

$$\begin{aligned}nU(\theta_0)&=\frac{N}{V}\int_V d^3r\,\mathcal{V}(r,\theta_0)R(r),\\n_1U_1(\theta_{01})&=\frac{N_1}{V}\int_V d^3r\,\mathcal{V}_1(r,\theta_{01})R_1(r),\end{aligned}\tag{7}$$

$$n_2U_2(\theta_{02})=\frac{N_2}{V}\int_V d^3r\,\mathcal{V}_2(r,\theta_{02})R_2(r),$$

where $n=N/V$ and $n_i=N_i/V$, $i=1$, 2 are the densities of molecules and of polymer fragments of one or the other kind with respect to the *total volume of the sample V*. Then

$$\begin{aligned}M(\theta)&=n\int d\Omega'f(\theta')U(\theta_0),\\M_1(\theta,\alpha_1)&=n_1\int d\Omega_1g_1(\theta_1-\alpha_1)U_1(\theta_{01}),\\M_2(\theta,\alpha_2)&=n_2\int d\Omega_2g_2(\theta_2-\alpha_2)U_2(\theta_{02}).\end{aligned}\tag{8}$$

Because the free energy $\mathcal{F}$ does not contain explicitly the derivative of the function $f(\theta)$, the Euler-Lagrange equation associated to the condition (6) is simply

$$\frac{\partial}{\partial f}\left(\mathcal{F}+\lambda\int f(\theta)d\Omega\right)=0.\tag{9}$$

Eventually [7], one gets

$$f(\theta,\alpha_1,\alpha_2)=\frac{1}{Z}\exp\left[-\frac{M(\theta)+M_1(\theta,\alpha_1)+M_2(\theta,\alpha_2)}{kT}\right],\tag{10}$$

where

$$Z=\int \exp\left[-\frac{M(\theta)+M_1(\theta,\alpha_1)+M_2(\theta,\alpha_2)}{kT}\right]d\Omega. \tag{11}$$

The radial dependence of the pair potentials $\mathcal{V}$ is not known, except for the fact that they have the general behavior of a Lennard-Jones potential. Nor is the dependence on θ of the average potentials U known exactly. In fact, Lennard-Jones and Morse potentials parametrize successfully van der Waals forces for pointlike or spherically shaped bodies. It was not until late 1970s and early 1980s, when Berne and Pechukas, and Gay and Berne suggested the first orientation dependent van der Waals potential to describe (uniaxial) ellipsoids of revolution. Much later Berardi, Fava, and Zannoni suggested a biaxial Gay-Berne potential used also by Ginzburg, Glaser, and Clark (see Refs. [19–21], and references therein). Yet, these potentials lead to complicated calculations and, as far as our paper is concerned, may be avoided. So, we can take into account only the fact that interactions must be even in θ_0 or θ_{0i} and have a minimum when these angles are zero. This comes from the fact that the van der Waals dispersion energy is minimum when the molecules are parallel (that is, $\sim\cos^2\theta$) and the repulsive steric energy must be maximum when the two molecules are at right angle (that is, $\sim\sin^2\theta$). 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's up to the second order in $\cos\theta_0$ or $\cos\theta_{0i}$, namely,

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

$$U_1(\theta_{01})=-u_1P_2(\cos\theta_{01}), \tag{12}$$

$$U_2(\theta_{02})=-u_2P_2(\cos\theta_{02}),$$

where $P_2(\cos\theta)$ is the Legendre polynomial of the second order. We have to emphasize that u and u_i's do not have dimensions of energy, but energy×volume, as it turns out from Eq. (7). 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. $M(\theta)$ can be evaluated as in Ref. [7],

$$M(\theta)=-unSP_2(\cos\theta), \tag{13}$$

where

$$S=2\pi\int_0^{\pi}f(\theta')P_2(\cos\theta')\sin\theta'\,d\theta' \tag{14}$$

is the scalar order parameter of the nematic.

In the same manner

$$M_1(\theta,\alpha_1)=-u_1n_1S_1(\alpha_1)P_2(\cos\theta),$$

$$M_2(\theta,\alpha_2)=-u_2n_2S_2(\alpha_2)P_2(\cos\theta), \tag{15}$$

where we have introduced

$$S_1(\alpha_1)=2\pi\int_0^{\pi}g_1(\theta_1-\alpha_1)P_2(\cos\theta_1)\sin\theta_1 d\theta_1,$$

$$S_2(\alpha_2)=2\pi\int_0^{\pi}g_2(\theta_2-\alpha_2)P_2(\cos\theta_2)\sin\theta_2 d\theta_2. \tag{16}$$

$S_1(\alpha_1)$ and $S_2(\alpha_2)$ can be considered the order parameters of the distribution of polymer fragments along the directions given by α_1 and α_2, respectively [6]. Let us define the adimensional new quantities

$$\varepsilon=\frac{un}{kT},\quad \varepsilon_1=\frac{u_1n_1}{kT},\quad \varepsilon_2=\frac{u_2n_2}{kT}, \tag{17}$$

which represent the interaction energy of one LC molecule with all the other molecules in the covolume (for ε) or with the polymer fragments along α_1 or α_2, in kT units.

One can easily rewrite now Eqs. (10) and (11)

$$Z=\int \exp\{[\varepsilon S+\varepsilon_1S_1(\alpha_1)+\varepsilon_2S_2(\alpha_2)]P_2(\cos\theta)\}d\Omega \tag{18}$$

and

$$f(\theta,\alpha_1,\alpha_2)=\frac{1}{Z}\exp\{[\varepsilon S+\varepsilon_1S_1(\alpha_1)+\varepsilon_2S_2(\alpha_2)]P_2(\cos\theta)\}. \tag{19}$$

It is worth mentioning that $f(\theta,\alpha_1,\alpha_2)$ is not a *true* Boltzmann function because the parameters S, $S_1(\alpha_1)$ and $S_2(\alpha_2)$ have been defined in Eqs. (14) and (17) with the use of $f(\theta,\alpha_1,\alpha_2)$ itself. We encounter here a typical self-consistent problem that can be solved numerically to get the best value of S for given $S_1(\alpha_1)$ and $S_2(\alpha_2)$ (see also Ref. [7]). An immediate consequence of the fact that $f(\theta,\alpha_1,\alpha_2)$ is only a Boltzmann-like distribution function is that the quantity Z itself is *not* a true partition function, and we should not expect that the well known formula $\mathcal{F}=-NkT\ln Z$ holds true. Indeed, coming back to Eqs. (4) and (5), one can see that [7]

$$\mathcal{F}=NkT(\tfrac{1}{2}\varepsilon S^2-\ln Z). \tag{20}$$

Introducing the free energy density in kT units, one has

$$F=\frac{\mathcal{F}}{VkT}=-n\ln Z+\frac{n\varepsilon S^2}{2}. \tag{21}$$

Following a procedure presented in Ref. [7], up to a constant

$$n\ln Z=n\varepsilon S^2, \tag{22}$$

so, eventually, we have the free energy density

$$F=-\frac{n}{2}\ln Z=-\frac{n}{2}\varepsilon S^2. \tag{23}$$

A first glance at Eq. (23) would tell us that the free energy density does not depend on the interaction of LC molecules with the anchoring polymers. Yet, this interaction exists because, as has been mentioned before, the self-consistent determination of S depends on the values $S_1(\alpha_1)$ and $S_2(\alpha_2)$. Of course, this only happens in the interface region of thickness ξ. Another consequence of Eq. (23) is that F has a minimum for a nonzero value of S, a well known result in the liquid-crystal field.

III. PHOTOALIGNMENT ON TWO ORTHOGONAL DIRECTIONS

So far, we have not considered the polymer distribution functions, apart from mentioning a result obtained by us in Ref. [6], i.e., Eq. (3). More generally we may consider that the distribution function of polymer fragments is, apart from a normation factor, given by

$$g(\phi)=1+h(\sin^2\phi)-h(\cos^2\phi), \tag{24}$$

where h is an even function in $\sin^2\phi$ (or $\cos^2\phi$). As mentioned before, a very interesting case is that in which one performs two irradiations with UV light polarized along orthogonal directions. We shall also consider that the irradiation time and all other experimental conditions are the same. In this case the function h would be the same. In fact, let us consider $\alpha_2=\alpha_1+\pi/2$, then

$$g(\theta-\alpha_1)=1+h[\sin^2(\theta-\alpha_1)]-h[\cos^2(\theta-\alpha_1)],$$

and

$$\begin{aligned} g\left(\theta-\alpha_1-\frac{\pi}{2}\right)&=1+h[\cos^2(\theta-\alpha_1)]-h[\sin^2(\theta-\alpha_1)]\\ &=2-g(\theta-\alpha_1). \end{aligned}$$

If we come back to definitions (16)

$$\begin{aligned} S_2\left(\alpha_1+\frac{\pi}{2}\right)&=2\pi\int_0^\pi g\left(\theta_2-\alpha_1-\frac{\pi}{2}\right)P_2(\cos\theta_2)\sin\theta_2 d\theta_2\\ &=2\pi\times2\int_0^\pi P_2(\cos\theta_2)\sin\theta_2 d\theta_2\\ &\quad-2\pi\int_0^\pi g(\theta_2-\alpha_1)P_2(\cos\theta_2)\sin\theta_2 d\theta_2\\ &=0-S_1(\alpha_1). \end{aligned} \tag{25}$$

Of course, this result is submitted to the condition that $S_1(\alpha_1)<\frac{1}{2}$, because an order parameter cannot be smaller than $-\frac{1}{2}$. Normally, the order parameter of a polymer distribution is much smaller than $\frac{1}{2}$ (see Ref. [6]).

The direction of $\hat{\mathbf{n}}$ in a bulk liquid crystal is degenerate; when there is a slightest anisotropy the liquid crystal aligns along it. As a consequence we can always consider $\alpha_1=0$, that is, the Ox direction is along one of the photopolymerization directions, the other direction thus making an angle α to it (in particular, $\alpha=\pi/2$).

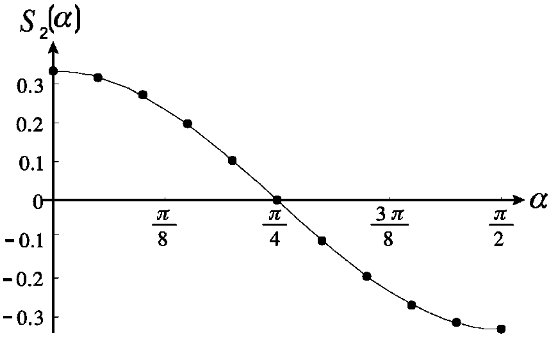

FIG. 2. Computed values of S_2 for 11 values of α (dots). The full line represents the function $S_1\cos 2\alpha$.

When $\alpha\neq\pi/2$ Eq. (25) no longer holds true, nevertheless the closer is α to $\pi/2$ the closer will be S_2 to $-S_1$. In Fig. 2 we have represented by dots the numerical calculations of $S_2(\alpha)$ for several values of α ($\alpha=n\pi/20$, $n=0,1,\ldots,10$) using the function $g(\phi)=(1/\pi)(1+e^{-\sin^2\phi}-e^{-\cos^2\phi})$. The line represents the function $S_1\times\cos 2\alpha$. One can see the very good agreement between this function and the calculated values of $S_2(\alpha)$. In Appendix A we have proved that the function $S_1\times\cos 2\alpha$ is a very good approximation of $S_2(\alpha)$, not only for the distribution $g(\phi)$ written above, but also for a larger class of distributions. In our case, that is, when $A(t)\equiv1$, S_1 is 0.3337. If, for different values of t, $A(t)$ is different from 1, the actual values of S_1 will change. Playing with the irradiation time, we can cancel the effect of the first polymer orientation even if the second polymerization is not along $\alpha=\pi/2$, but in the region $\pi/4<\alpha\leqslant\pi/2$.

In Fig. 3 we have plotted the LC distribution function $f(\theta)$ for different values of S, S_1, and S_2. When $\varepsilon S+\varepsilon_1S_1+\varepsilon_2S_2$ becomes zero, the distribution function is the straight line $f(\theta)=1/\pi$, i.e., the surface does not force any anisotropy. When the previous sum becomes negative, an anisotropic distribution starts to grow along $\alpha=\pi/2$.

In general, ε_1, ε_2, S_1, and S_2 cannot be computed, nor can their contribution be separated, that is, we can rather introduce two parameters m_1 and m_2

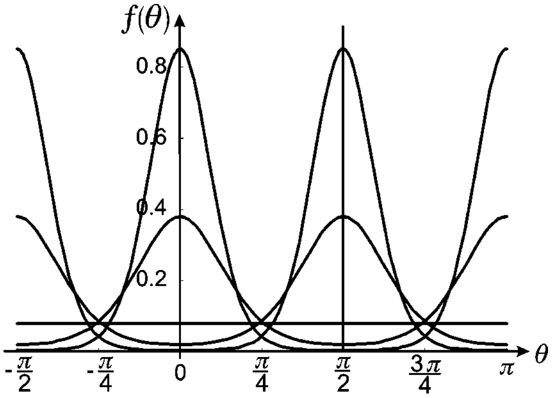

FIG. 3. LC distribution function $f(\theta)$ for various values of m. The greater is m, the narrower and higher is the distribution function. To $m=0$ there correspond the constant distribution $f(\theta)=1/\pi$, i.e., isotropy. For $m<0$ the distribution peaks about $\pi/2$ instead of 0.

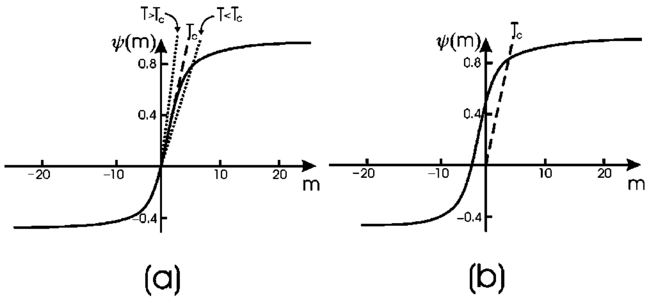

FIG. 4. The function $\psi(m)$ (full curve) and $S=m/\varepsilon$ (broken lines) when $m_1+m_2=0$, case (a) and when $m_1+m_2\neq 0$, case (b). In case (b) one expects a nematic order at any temperature but only in a very narrow layer of thickness ξ.

$$m_i=\varepsilon_i S_i(\alpha_i), \quad i=1,2. \tag{26}$$

In the same way we introduce

$$m=\varepsilon S, \tag{27}$$

which may be written as

$$\begin{aligned}\frac{m}{\varepsilon}=S&=\int d\Omega\, f(\theta,\alpha_1,\alpha_2)P_2(\cos\theta)\\&=\frac{\int_0^\pi P_2(\cos\theta)\exp[(m+m_1+m_2)P_2(\cos\theta)]\sin\theta\, d\theta}{\int_0^\pi \exp[(m+m_1+m_2)P_2(\cos\theta)]\sin\theta\, d\theta}\\&=\psi(m).\end{aligned} \tag{28}$$

Representing graphically the function $\psi(m)$ and intercepting it with the line m/ε, one can get the order parameter for a certain value of ε, which corresponds to a certain temperature $T=nu/k\varepsilon$. Figure 4(a) represents the case when either $m_1=m_2=0$, or $m_1+m_2=0$. The first case corresponds to an infinite volume filled with LC's, the broken line giving the isotropic-nematic transition temperature T_c. The second case corresponds to the interesting situation when there were two similar UV polymerization processes along orthogonal directions. Figure 4(b) represents the case where there is a shift of the curve to the left due to the existence of a well defined easy axis. In this case, $m_1+m_2\neq 0$, there is an intercept at finite S for any slope of m/ε line, that is, for any temperature. This result might seem strange but we must not forget that either m_1 or m_2 are proportional to the polymer fragment densities n_1 or n_2, which decrease to zero within the distance ξ. As a matter of fact the result is only valid in the layer of thickness ξ where one should expect a certain order of the liquid crystal even beyond the clearing temperature. It has been mentioned that S_1 or S_2 can be varied by changing the irradiation time t. Acting in this way we can first start with a state of no easy axis, seen in crossed-polarized microscopy as a mosaic of planar domains randomly oriented. Then we initiate the polymerization process along one direction only. The immediate results will consist in increasing the size of favored domains (where the director $\hat{\mathbf{n}}$ is almost parallel to the easy axis) and the decreasing of the other. The cell behaves macroscopically anisotropic. If then we stop this process and start a similar process of UV polymerization along an orthogonal direction, the parameter m_2 tends toward $-m_1$ and the cell becomes isotropic again. Shiyanovskii *et al.* have done this type of experiment, the results of which (see Figs. 2, 3, and 4 of Ref. [5]) are in excellent agreement with the discussion above. It is worth mentioning that the compensating effect of the two orthogonal irradiations works well even close to saturation. In fact, there is no limitation of that kind in our procedure except, of course, the case when the saturation is already reached, that is, there are no "free" monomers to undergo the photopolymerization even along an orthogonal direction. Considering that the interaction of LC molecules to polymer fragments should not depend on their orientation with respect to the laboratory frame, the values ε_1 and ε_2 should be equal. In this case the condition $m_1+m_2=0$ implies $S_2=-S_1$, which, remembering also Eqs. (3), (24), (25), or (A13), is achieved, for orthogonal directions, only if the irradiation times are equal. Figure 4 in paper [5] shows quite clearly this symmetry with respect to time.

Of course, all these facts can be expressed in terms of a macroscopic anchoring energy. In our paper [7] we have linked the anchoring energy coefficient to the order parameter of the polymer fragments distribution. For only one direction of photopolymerization the result was [Eq. (50) in Ref. [7]]

$$w_a=\frac{n\xi}{12}kT\frac{\varepsilon_1 S_1}{m+m_1}Q(m+m_1), \tag{29}$$

where

$$Q(\mu)=\frac{2\exp\left(\frac{3\mu}{2}\right)\sqrt{\frac{6\mu}{\pi}}}{\operatorname{erf} i\left(\sqrt{\frac{3\mu}{2}}\right)}-2-3\mu. \tag{30}$$

[The function $\operatorname{erf} i(x)\equiv i(-ix)=\int_0^x e^{t^2}\,dt$ is strictly real although it contains the imaginary number $i=\sqrt{-1}$.]

Mutatis mutandis, in the case of two photopolymerizations along different directions, Eq. (29) becomes [see Eq. (B14) of Appendix B]

$$w_a=\frac{n\xi}{12}kT\frac{\varepsilon_1 S_1+\varepsilon_2 S_2}{m+m_1+m_2}Q(m+m_1+m_2). \tag{31}$$

If the two directions are orthogonal, by adjusting also the irradiation times, one can reach even the situation when $\varepsilon_1 S_1+\varepsilon_2 S_2=0$, leading to $w_a=0$, that is, the cell will be macroscopically isotropic, concording to experimental results and phenomenological arguments of Shiyanovskii *et al.* [5].

IV. CONCLUSIONS

We have analyzed from a microscopic point of view the anchoring properties induced by two concomitant or subsequent photopolymerization processes along orthogonal directions. We have seen that, all the other conditions being preserved, the polymer distribution order parameter S_2 associated to the second process of photopolymerization may be expressed as a simple function of the first one, namely,

$$S_2=S_1\cos 2\alpha. \tag{32}$$

Introducing this result in Eq. (31) we get

$$w_a=\frac{n\xi}{12}kT\,\frac{\varepsilon_1 S_1(1+\cos 2\alpha)}{\varepsilon S+\varepsilon_1 S_1(1+\cos 2\alpha)}\,Q(\varepsilon S+\varepsilon_1 S_1\times(1+\cos 2\alpha)). \tag{33}$$

So, the angle α enters the expression of the anchoring energy coefficient. If the experimental conditions are not identical in the two processes, we have to write

$$1+\frac{\varepsilon_2}{\varepsilon_1}\cos 2\alpha$$

instead of $1+\cos 2\alpha$. But $\varepsilon_2/\varepsilon_1$ should not differ much from 1, yet being time dependent. In any case, for $\alpha>\pi/4$, one may find a certain value of time and/or irradiation intensity to drive the value of w_a to zero. Because all this can be done with the cell already assembled, this might be a good procedure to have controlled anchoring strength *in situ.*

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APPENDIX A

Let

$$g(\phi)=c[1+h(\sin^2\phi)-h(\cos^2\phi)],$$

where c is a normation constant in order to have [6]

$$\int_0^{\pi}g(\phi)d\phi=1. \tag{A1}$$

We have to get a certain relation between

$$S_1=2\pi\int_0^{\pi}g(\theta)P_2(\cos\theta)\sin\theta\,d\theta \tag{A2}$$

and

$$S_2(\alpha)=2\pi\int_0^{\pi}g(\theta+\alpha)P_2(\cos\theta)\sin\theta\,d\theta, \tag{A3}$$

taking into account the special properties of the function $h(\sin^2\phi)$, namely, it is an even function $[h(\phi)=h(-\phi)]$ and symmetric with respect to $(\pi/2)[h(\phi+\pi/2)=h(-\phi+\pi/2)]$. Also, the following property:

$$\int_0^{2\pi}h(\sin^2\phi)\cos(2n\phi)d\phi=-\int_0^{2\pi}h(\cos^2\phi)\cos(2n\phi)d\phi$$

holds true if n is odd integer.

Let us expand $g(\phi)$ in a Fourier series

$$g(\phi)=\frac{a_0}{2}+\sum_{n=1}^{\infty}[a_n\cos(n\phi)+b_n\sin(n\phi)]. \tag{A4}$$

It is not very difficult to see that the properties of the function h imply that the only nonzero coefficients of the expansion are

$$a_0\quad\text{and}\quad a_{2(2k+1)},\qquad k=0,1,2,\ldots.$$

We have thus the series

$$g(\phi)=\frac{a_0}{2}+a_2\cos(2\phi)+a_6\cos(6\phi)+a_{10}\cos(10\phi)+\cdots, \tag{A5}$$

where

$$a_0=\frac{1}{\pi}\int_0^{2\pi}g(\phi)d\phi=\frac{2}{\pi}, \tag{A6}$$

$$a_{2(2k+1)}=\frac{1}{\pi}\int_0^{2\pi}g(\phi)\cos[2(2k+1)\phi]d\phi. \tag{A7}$$

Thus, the order parameter S_1 can be approximated by a series

$$S_1=s_2+s_6+s_{10}+\cdots, \tag{A8}$$

$$s_{2(2k+1)}=a_{2(2k+1)}\int_0^{\pi}P_2(\cos\theta)\cos[2(2k+1)\theta]\sin\theta\,d\theta, \tag{A9}$$

and S_2 (α) will be given by the series

$$S_2(\alpha)=s_2\cos(2\alpha)+s_6\cos(6\alpha)+s_{10}\cos(10\alpha)+\cdots, \tag{A10}$$

which can be seen quite easily analyzing the integrals (see Ref. [22])

$$a_{2(2k+1)}\int_0^{\pi}P_2(\cos\theta)\cos[2(2k+1)(\theta+\alpha)]\sin\theta\,d\theta=\cos[2(2k+1)\alpha]s_{2(2k+1)}. \tag{A11}$$

In fact, we can drop out the terms proportional to $\cos(6\alpha)$, $\cos(10\alpha)$,..., as the coefficients s_6 and s_{10} are very small compared to s_2. For instance, if $h(\sin^2\phi)=e^{-\sin^2\phi}$ and $c=1/\pi$,

$$S_1=0.3337-4.889\times10^{-4}-4.429\times10^{-7}+\cdots. \tag{A12}$$

So, within the experimental errors, we can use the rule

$$S_2(\alpha)=S_1\cos(2\alpha). \tag{A13}$$

Even more, $S_2(\pi/2)=-S_1$ and $S_2(\pi/4)=0$ are true in any approximation.

APPENDIX B

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 functions 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. Of course, the liquid-crystal–polymer interaction shall exist only in a small layer of thickness ξ, much smaller than the cell thickness. The value of the torsion angle, i.e., $\alpha(\xi)\equiv\varphi$, will depend on the interaction with the polymer and also on the order parameter of the latter. In the case of polymers photopolymerized along two orthogonal directions, the angle φ will depend on the balance between ε_1 and ε_2, but in the general case, when both the directions and the time intervals of photopolymerization are different, the angle φ will depend on the sum $\varepsilon_1S_1+\varepsilon_2S_2$. Note that when the angle between the two directions is large (approaching $\pi/2$) one of the order parameters, for instance S_2, becomes negative.

In a recent paper [7] we considered that, if $\varepsilon>\varepsilon_1$ and $\varepsilon>\varepsilon_2$, the value of S does not vary too much within the surface layer of thickness ξ, and for each “sublayer” the distribution function can be written as

$$f(\theta+\alpha)=\frac{1}{Z_1}\exp\{\varepsilon SP_2(\cos\theta)+(\varepsilon_1S_1+\varepsilon_2S_2)\times P_2[\cos(\theta+\alpha)]\}, \tag{B1}$$

where α varies linearly with z,

$$\alpha(z)=\varphi\frac{z}{\xi}. \tag{B2}$$

Note that in the equation above we have considered separately $\varepsilon SP_2(\cos\theta)$ and $(\varepsilon_1S_1+\varepsilon_2S_2)P_2[\cos(\theta+\alpha)]$ because the nematic-nematic interaction must be invariant to a rotation of an angle α, whereas the nematic-polymer interaction would certainly depend on α. It is only the nematic-polymer interaction that gives an increase in the free energy, due to the fact that $f(\theta+\alpha)$ no longer minimizes the free energy density. Of course,

$$Z_1=\int\exp\{\varepsilon SP_2(\cos\theta)+(\varepsilon_1S_1+\varepsilon_2S_2)\times P_2[\cos(\theta+\alpha)]\}d\Omega \tag{B3}$$

as well as

$$F_1=-\frac{n}{2}\ln Z_1 \tag{B4}$$

will be functions of z. The extra free density as a function of z will be

$$\Delta F(z)=-\frac{n}{2}\ln\frac{Z_1}{Z} \tag{B5}$$

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

$$\Delta\mathcal{F}=kT\int_0^{\xi}\Delta F(z)dz. \tag{B6}$$

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,

$$w_\alpha\equiv\frac{1}{2}\frac{\partial^2\Delta\mathcal{F}}{\partial\varphi^2}\bigg|_{\varphi=0} \tag{B7}$$

is the coefficient of the azimuthal anchoring. The definition tells us that the azimuthal distortion needs to be very small, so we can use a series development of $P_2[\cos(\theta+\alpha)]$ with respect to α, up to $O(\alpha^3)$,

$$P_2[\cos(\theta+\alpha)]=P_2(\cos\theta)+\Delta P, \tag{B8}$$

where ΔP is very small.

The partition function will be

$$\begin{aligned}Z_1&=\int\exp\{\varepsilon SP_2(\cos\theta)+(\varepsilon_1S_1+\varepsilon_2S_2)P_2[\cos(\theta+\alpha)]\}d\Omega\\&=\int\exp\{\varepsilon SP_2(\cos\theta)+(\varepsilon_1S_1+\varepsilon_2S_2)P_2(\cos\theta)\}\exp[(\varepsilon_1S_1+\varepsilon_2S_2)\Delta P]d\Omega\\&\approx\int\exp[\varepsilon SP_2(\cos\theta)+(\varepsilon_1S_1+\varepsilon_2S_2)P_2(\cos\theta)][1+(\varepsilon_1S_1+\varepsilon_2S_2)\Delta P]d\Omega\end{aligned}$$

$$=Z\left\{1+\frac{1}{Z}\int \exp[(\varepsilon S+\varepsilon_1 S_1+\varepsilon_2 S_2)P_2(\cos\theta)][(\varepsilon_1 S_1+\varepsilon_2 S_2)\Delta P]d\Omega\right\}$$

$$=Z\left\{1+\int f(\theta)[(\varepsilon_1 S_1+\varepsilon_2 S_2)\Delta P]d\Omega\right\}, \tag{B9}$$

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

$$\Delta F=-\frac{n}{2}\ln\frac{Z_1}{Z}$$

$$=-\frac{n}{2}\ln\left\{1+\int f(\theta)[(\varepsilon_1 S_1+\varepsilon_2 S_2)\Delta P]d\Omega\right\}$$

$$\simeq-\frac{n}{2}\int f(\theta)[(\varepsilon_1 S_1+\varepsilon_2 S_2)\Delta P]d\Omega, \tag{B10}$$

where ΔP is

$$\Delta P=3\alpha\cos\theta\sin\theta+\tfrac{3}{2}\alpha^2(1-2\cos^2\theta)+O(\alpha^3), \tag{B11}$$

and hence results the extra free energy density

$$\Delta F(z)=\frac{n\alpha^2(\varepsilon_1 S_1+\varepsilon_2 S_2)}{4(\varepsilon S+\varepsilon_1 S_1+\varepsilon_2 S_2)}\times\left\{\frac{2\exp[\tfrac{3}{2}(\varepsilon S+\varepsilon_1 S_1+\varepsilon_2 S_2)]\sqrt{\dfrac{6}{\pi}(\varepsilon S+\varepsilon_1 S_1+\varepsilon_2 S_2)}}{\operatorname{erf} i\left[\sqrt{\dfrac{3(\varepsilon S+\varepsilon_1 S_1+\varepsilon_2 S_3)}{2}}\right]}-2-3(\varepsilon S+\varepsilon_1 S_1+\varepsilon_2 S_2)\right\}, \tag{B12}$$

where erf i (x) has been already defined.

The extra free energy per unit surface will be

$$\Delta\mathcal{F}=kT\int_0^{\xi}\Delta F\left(\frac{z\varphi}{\xi}\right)dz=kT\frac{\xi}{\varphi}\int_0^{\varphi}\Delta F(\alpha)d\alpha=\frac{n\xi}{12}\varphi^2 kT\frac{\varepsilon_1 S_1+\varepsilon_2 S_2}{\varepsilon S+\varepsilon_1 S_1+\varepsilon_2 S_2}Q(\varepsilon S+\varepsilon_1 S_1+\varepsilon_2 S_2), \tag{B13}$$

the function Q being defined by Eq. (30). Eventually, we get

$$w_\alpha=\frac{1}{2}\frac{\partial^2\Delta\mathcal{F}}{\partial\varphi^2}\bigg|_{\varphi=0}=\frac{n\xi}{12}kT\frac{\varepsilon_1 S_1+\varepsilon_2 S_2}{\varepsilon S+\varepsilon_1 S_1+\varepsilon_2 S_2}Q(\varepsilon S+\varepsilon_1 S_1+\varepsilon_2 S_2). \tag{B14}$$

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