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Phenomenological model for the optically induced easy direction

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We present a phenomenological model to interprete the optically induced easy direction in a nematic cell in the slab approximation. One of the surfaces of the sample is supposed to give strong anchoring, whereas the other, covered with photosensible material, very weak anchoring. We assume that a surface nematic molecule is submitted to a potential connected with its interaction with the surface easy direction, with the surface nematic field, and with the optical induced anisotropy. The case in which the coupling with the nematic order in the bulk is important is considered too. A differential equation for the time evolution of the surface director is proposed, in which the viscous torque is balanced by the torque related to the surface fields. We show that our theoretical predictions are in agreement with experimental data on the optical induced surface orientation. The dependence of the anchoring energy strength on the irradiation time for dye-doped liquid crystals is also investigated.

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I. INTRODUCTION

Light-induced reorientation phenomena in liquid crystals have been widely investigated over the last two decades for both fundamental and technological reasons [1–3]. Within this wide outline, liquid crystal combined cells in which one of the surfaces gives rise to strong planar anchoring and the other is covered with an isotropic layer of photosensitive material, play a special role mainly related to the possibility of photoaligning the liquid crystal director on the isotropic surface. This process is also referred to as light-induced anchoring [1].

Photoalignment effects in liquid crystals were first observed in nematics doped with azo-dyes [4]. The most intriguing aspect of photoalignment is the possibility of generating an easy axis with consequent stable reorientation over an isotropic boundary surface of a liquid crystal cell, upon irradiation with polarized light [5]. This mechanism offers the possibility of regulating the amount of anchoring energy by means of the incident light [6].

The light-induced anchoring processes are, obviously, surface mediated effects. Usually, the photoinduced anisotropy axis arises on the isotropic boundary surface due to the adsorption of polarized light by a photosensitive polymer. This gives rise to photochemical processes which, in turn, are able to realign the molecular director [7]. As mentioned, azo-dyes can also come into play. One possibility is to incorporate them in the polymer layers [8–10], whereas a completely different approach consists in doping the liquid crystal with an azo-dye (usually methyl red) and exploiting its ability to spontaneously adsorb on the isotropic boundary surface during cell filling [11]. Subsequent cell irradiation with polarized light results in this case in the development of surface anisotropy in the dark adsorbed dye layer, with consequent easy axis generation. The final easy axis direction is dictated by the competition between two optically induced processes: desorption of dark molecules and adsorption of dye molecules located close to the illuminated surface. The new orientation can be dynamic or stable depending on the irradiation time and on the incident intensity.

In spite of this large body of experimental work, only a few attempts have been done so far to reach a quantitative theoretical description of the processes involved in the liquid crystal photoalignment. Janossy *et al.* [9] derived, for instance, a qualitative theoretical expression for the induced surface twist angle in the case of a combined cell in which the isotropic surface was covered by a polymer with an azo-dye incorporated. The case of methyl-red doped cells, taking into account the adsorption and desorption phenomena, has been analyzed by Kuksenok and Shiyanoskii [12]. Moreover, a very recent paper furnishes an exhaustive theoretical model of light-induced anchoring in these systems, able to quantitatively describe the wide amount of existing experimental results and to represent the whole evolution of cell orientation with linearly polarized light [13]. However, the proposed model is valid only for irradiation in the isotropic phase, where both effects of liquid crystalline order on the kinetic of surface reorientation and the bulk director reorientation can be neglected.

In this work we propose a phenomenological model for light-induced easy direction in a combined liquid crystal cell, under irradiation in the liquid crystalline nematic phase. Our aim is to propose a set of differential equations characterizing the interaction of the polarized light with the photosensitive substrate, giving rise to the optically induced easy axis. The parameters entering into the equations describing the phenomenon under consideration are related to plausible phenomena. A microscopic theory is necessary to connect them to the fundamental interactions responsible for the macroscopic orientation.

Our paper is organized as follows. In Sec. II the physical system to be investigated is described, and in Sec. III the energy of a nematic molecule at the surface is evaluated. We assume that each surface nematic molecule feels a potential connected via interactions to the surface easy axis, to the nematic field, and to the optically induced anisotropy. The time evolution of the average molecular orientation is described by means of a phenomenological equation. The relaxation time for the reorientation induced by the optical field is determined in the case of finite and negligible anchoring energy. The situation in which the reorientation due to the optical field has a threshold is also considered. The case in which the coupling with the bulk nematic field is important is discussed in Sec. IV. The relaxation of the nematic orientation when the optical field is removed is analyzed in Sec. V, by considering, separately, the case when the photosensitive material is a photopolymer or a photosensitive layer formed by molecules of dyes adsorbed at the surface. Both cases of a pure liquid crystal in contact with a photosensitive substrate and of dye-doped liquid crystal cells are taken into account. The evolution of the surface order parameter induced by the optical field on a photosensitive polymer, and the relevant orientation induced on a nematic liquid crystal, is discussed in Sec. VI, without taking into account the damage of the system in time due to the irradiating light. The intrinsic time for the optically induced easy direction for a system formed by a nematic liquid crystal containing dye molecules, is considered in Sec. VII. There the calculations are performed under the assumption of a complete adsorption of all dye molecules at the surface, without considering the possibility to take into account the angular distribution function of the dye molecules continuously distributed in the bulk. In Sec. VIII the phenomenological equation used to build the formalism is justified by a microscopical point of view. Section IX is devoted to the conclusions.

II. THE PHYSICAL SYSTEM

Let us consider a nematic sample in the shape of a slab of thickness d. The Cartesian reference frame used for the description has the z-axis normal to the limiting surfaces, at $z=0$ and $z=d$. The surface treatment on the surface at $z=0$ is supposed to be planar and strong. The direction of the easy axis is chosen parallel to the x axis. The surface at $z=d$ is assumed to be covered with a photosensitive material, giving weak planar degenerate anchoring. It can be a photopolymer directly in contact with the liquid crystal [4,14] or covered by a surface layer of spontaneously adsorbed dye molecules [11]. The actual nematic orientation on the surface at $z=d$ is such to minimize the total energy of the sample. For the case considered by us, the elastic deformation of the nematic is a pure twist. We indicate by $\phi=\phi(z)$ the twist angle at the coordinate z made by the director with the x axis. The elastic energy density is $f=(k/2)\phi'^2$, where k is the twist elastic constant and $\phi'=d\phi/dz$. The total elastic energy of the sample, per unit surface, is

$$F=\int_0^d \frac{1}{2}k\phi'^2 dz. \tag{1}$$

The director profile is obtained by minimizing F, taking into account that the anchoring energy is strong on the surface at $z=0$ and extremely weak on the surface at $z=d$. A standard calculation [15] shows that $\phi(z)=0$. It follows that the presence of the nematic liquid crystal is such to induce on the surface covered with the photosensitive material an easy direction parallel to the one on the surface characterized by strong anchoring. Let us assume now that the surface at $z=d$, covered with photosensitive material, is irradiated by polarized light, whose polarization direction makes an angle ϕ_e with the x axis. In this situation it is experimentally observed that the sample presents a twist deformation, originated by an easy direction induced by the light on the photosensitive material. The orientation of this easy direction can be orthogonal or parallel to the incident polarization direction and it is strictly dependent on both the incident intensity and the time of irradiation, in the case of isotropic surface covered by an adsorbed layer of dye molecules [13,18]. Our aim is to develop a simple phenomenological model describing this effect. In our analysis we limit the investigation to the case in which the induced orientation increases with the intensity of the light. However, this is not always the case, because light intensity could be responsible for damage of the photosensitive system, as discussed in Refs. [16,17].

III. ENERGY PER SURFACE MOLECULE

We suppose, first, that the easy direction induced by the polarized light is a very rapid phenomenon, and that the easy direction is parallel to the polarization of the incident light. The case in which the formation of the easy axis optically induced takes a time comparable with the nematic orientation will be discussed in a next section. We assume that the interaction due to the presence of the limiting surface is short range. The nematic molecules submitted to the interaction with the substrate will be called surface molecules, and the others bulk molecules. In this framework a surface molecule, whose molecular direction is $\mathbf{a}$, interacts with (1) the easy direction induced by the light $\mathbf{e}$, (2) the easy axis induced by the surface characterized by strong anchoring $\mathbf{v}=\mathbf{x}$, (3) the surface nematic field produced by the other surface molecules, whose direction is $\mathbf{n}=\langle\mathbf{a}\rangle$, (4) the bulk nematic field, due to the bulk nematic molecules.

It follows that the energy per surface molecule is

$$U(\mathbf{a})=U_0-\alpha(\mathbf{a}\cdot\mathbf{v})^2-\beta(\mathbf{a}\cdot\mathbf{n})^2-\gamma(\mathbf{a}\cdot\mathbf{e})^2+U_b, \tag{2}$$

where U_0 is the isotropic part of the surface energy of the molecule, α, β, and γ phenomenological parameters describing the interaction of the considered molecule with the surface field, with the director field and with the anisotropic direction induced optically on the photosensitive material, respectively. The coefficient α is the equivalent of the Rapini-Papoular anchoring strength [19], β is connected with the action of the nematic mean field on a given molecule [20], and γ is proportional to the intensity of the light I, responsible for the optically induced easy axis. Finally, U_b describes the coupling of the surface molecule with the bulk director field. In a first approximation we assume that U_b is negligible with respect to the other contributions. Its importance on the considered phenomenon will be discussed in the next section.

We indicate by ϕ_e, φ, and $\phi=\langle\varphi\rangle$ the angle formed by **e**, **a**, and **n** with the x axis, and rewrite $U(\mathbf{a})=U(\varphi)$ as

$$U(\varphi)=U_0-\alpha\cos^2\varphi-\beta\cos^2(\varphi-\phi)-\gamma\cos^2(\varphi-\phi_e). \tag{3}$$

The time evolution of the surface molecule is given by Newton's law $J(d^2\varphi/dt^2)=\mathcal{T}$, where J is the momentum of inertia of the molecule and $\mathcal{T}$ the total torque acting on it. According to elementary mechanics

$$\mathcal{T}=-\frac{dU(\varphi)}{d\varphi}-\eta\frac{d\varphi}{dt}, \tag{4}$$

where η is the torsional viscosity. In Eq. (4) the first addendum on the right-hand side represents the torque due to the fields acting on the considered molecule, and the second one the viscous torque acting on it. A justification of this term, starting from a stochastic description of the phenomenon, is reported in Sec. VIII. Since the molecular momentum of inertia is negligible, $J\sim 0$, and from $J(d^2\varphi/dt^2)=\mathcal{T}$, taking into account Eqs. (3) and (4) we obtain

$$\eta\frac{d\varphi}{dt}=-\{\alpha\sin(2\varphi)+\beta\sin[2(\varphi-\phi)]+\gamma\sin[2(\varphi-\phi_e)]\}. \tag{5}$$

By taking the statistical average of Eq. (5), we get

$$\eta\frac{d\phi}{dt}=-\{\alpha\sin(2\phi)+\gamma\sin[2(\phi-\phi_e)]\}. \tag{6}$$

Equation (6) is valid in the framework in which the distribution of **a** around **n** is rather narrow. In this situation the action of the nematic field, connected to the coefficient β in Eq. (2) averages to zero [21,22]. The differential Eq. (6) has to be solved with the boundary condition $\phi(0)=0$, stating that before the application of the optical field the sample is, on the surface at $z=d$, in average aligned along the x-axis. Let us consider first the case $\phi_e\neq\pi/2$. In this case from Eq. (6) we get

$$\left(\frac{d\phi}{dt}\right)_0=\frac{\gamma}{\eta}\sin(2\phi_e),\quad\text{and}\quad\tan\phi_f=\frac{\gamma\sin(2\phi_e)}{\alpha+\gamma\cos(2\phi_e)}, \tag{7}$$

where ϕ_f is obtained by putting $d\phi/dt=0$. It follows that $\phi_f=\lim_{t\to\infty}\phi(t)$. In the present case ϕ_f is the actual easy axis in the steady state relevant to the surface at $z=d$. The time evolution of $\phi(t)$ is obtained by Eq. (6). A simple calculation gives

$$\int_0^{\phi(t)}\frac{d\xi}{\alpha\sin(2\xi)+\gamma\sin[2(\xi-\phi_e)]}=-\frac{t}{\eta}. \tag{8}$$

In the case in which the anchoring energy per molecule on the surface at $z=d$, connected to the parameter α in Eq. (2), is negligible with respect to the other contributions appearing in Eq. (3), from Eqs. (7) and (8) we get $\phi_f=\phi_e$ and

$$\phi(t)=\phi_e-\tan^{-1}\left\{\tan\phi_e\exp\left(-2\frac{\gamma}{\eta}t\right)\right\}. \tag{9}$$

From Eq. (9) it follows that the relaxation time for the present surface tilt angle evolution optically induced is $\tau_r=\eta/(2\gamma)$. Since $\gamma\propto I$, it follows that the time evolution of ϕ depends on the dose D, defined by $D=It$. Let us consider now the case $\phi_e=\pi/2$. In this framework (6) becomes

$$\eta\frac{d\phi}{dt}=-(\alpha-\gamma)\sin(2\phi), \tag{10}$$

which always has the solution $\phi=0$. However, if $\gamma>\alpha$, $d\phi/dt>0$, and for $t\to\infty$, $\phi\to\pi/2$. The condition $\gamma=\alpha$ defines the threshold for the optically induced easy axis. The existence of such a threshold has been experimentally observed in Refs. [4] and [7], where it has been shown that if $\phi_e=\pi/2$, the director begins to reorient at a well defined incident energy density.

IV. CASE IN WHICH THE COUPLING WITH THE BULK IS NOT NEGLIGIBLE

In the analysis reported above we have assumed that U_b, describing the interaction of the surface molecule with the nematic field in the bulk, is very small with respect to the other contributions appearing in $U(\mathbf{a})$ given by Eq. (2). We want now to remove this simplifying hypothesis. The statistical average, over the surface molecules, of U_b, will be indicated by $\langle U_b\rangle$. It can be identified with the elastic energy, per surface molecule, due to the coupling of the surface with the bulk. Hence it is approximated by $\langle U_b\rangle=(1/2)k[\phi'(d)]^2(l/\mathcal{N}_n)$, where l is a molecular dimension and $\mathcal{N}_n$ the surface density of nematic molecules. In the considered case, the actual twist angle on the surface at $z=d$ is ϕ. Consequently, according to the elastic theory [15] $\phi'(d)=\phi/d$. It follows that $\langle U_b\rangle$ we are looking for is $\langle U_b\rangle=(1/2)\nu\phi^2$, where $\nu=kl/(\mathcal{N}_nd^2)$, is a new phenomenological parameter that depends on d^{-2}. The torque acting on the surface director due to the coupling with the bulk is then $\mathcal{T}_b=-d\langle U_b\rangle/d\phi=-\nu\phi$. The dynamic equation describing the evolution of $\phi=\phi(t)$ is now

$$\eta\frac{d\phi}{dt}=-\{\nu\phi+\alpha\sin(2\phi)+\gamma\sin[2(\phi-\phi_e)]\}. \tag{11}$$

Let us consider first the case $\phi_e\neq\pi/2$. From Eq. (11) it follows that $(d\phi/dt)_0=(\gamma/\eta)\sin(2\phi_e)$, as in the previous case in which the coupling with the bulk is negligible. In this case $\phi_f=\lim_{t\to\infty}\phi(t)$ is the solution of the transcendental equation

$$\nu\phi_f+[\alpha+\gamma\cos(2\phi_e)]\sin(2\phi_f)=\gamma\cos(2\phi_f)\sin(2\phi_e). \tag{12}$$

The time evolution of $\phi=\phi(t)$ is obtained by Eq. (11). A simple calculation gives

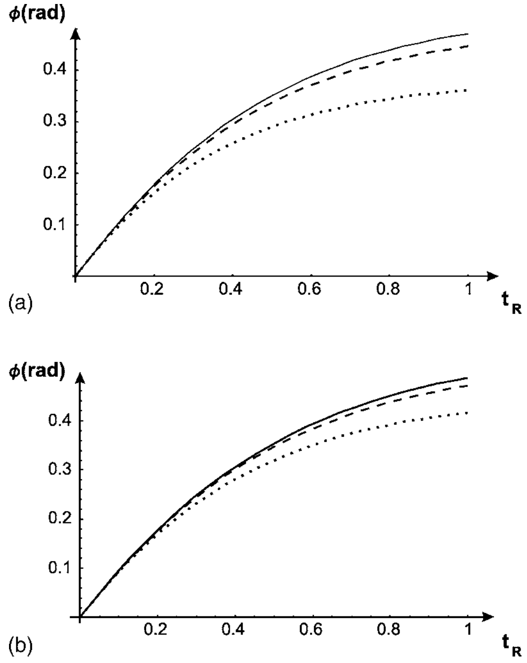

FIG. 1. (a) Time evolution of the surface twist angle ϕ for different values of α/γ. The dimensionless time t_R is defined by $t_R=(\gamma/\eta)t$. Dotted line $\alpha/\gamma=0.5$, dashed line $\alpha/\gamma=0.1$, continuous line $\alpha/\gamma=0$. The latter case corresponds to the situation in which the surface anchoring energy vanishes. $\nu/\gamma=0$, $\phi_e=\pi/4$. (b) Time evolution of the surface twist angle, ϕ, for different values of ν/γ. The dimensionless time t_R is defined by $t_R=(\gamma/\eta)t$. Dotted line $\nu/\gamma=0.5$, dashed line $\nu/\gamma=0.1$, continuous line $\nu/\gamma=1$. The latter case corresponds to the situation in which the interaction of a surface molecule with the bulk is negligible. $\alpha/\gamma=0.5$, $\phi_e=\pi/4$.

$$\int_0^{\phi(t)} \frac{d\xi}{\nu\xi+\alpha\sin(2\xi)+\gamma\sin[2(\xi-\phi_e)]} = -\frac{t}{\eta}. \tag{13}$$

In Fig. 1(a) we show $\phi=\phi(t)$ for three values of α. All curves have the same slope for $t=0$, in agreement with Eq. (7). Increasing the value of α, ϕ_f decreases. In Fig. 1(b) we report $\phi=\phi(t)$ for three values of ν. Even in this case $(d\phi/dt)_0$ is independent of ν. Increasing ν, ϕ_f decreases in monotonic manner. The predicted trends for the surface twist angle reported in Fig. 1 compare well with the ones reported by Janossy *et al.* [8,9]. In Ref. [8] the experimental data relevant to $\phi=\phi(t)$ (see Fig. 1 of Ref. [8]) show that there is no significant thickness dependence, even for short irradiation times, where the twist angle is far from saturation. This indicates that U_b is rather small with respect to the other contributions appearing in Eq. (2).

If $\phi_e=\pi/2$, from Eq. (11) we get

$$\eta\frac{d\phi}{dt} = -[\nu\phi+(\alpha-\gamma)\sin(2\phi)], \tag{14}$$

that always has the solution $\phi=0$. In the limit of small ϕ, from Eq. (14) we deduce that if $\gamma>\alpha+\nu/2$, $d\phi/dt>0$, and the surface tilt angle increases with time. We note that the threshold determined in the case in which the coupling with the bulk is important is higher than the one in which it can be neglected, that is $\gamma>\alpha$, as shown in Sec. III.

V. WHAT HAPPENS WHEN THE OPTICAL FIELD IS REMOVED?

We consider in this section the evolution of the nematic orientation after the removal of the optical field responsible for the new easy direction on the surface at $z=d$. We have to distinguish between two possible situations.

If the photosensitive material is a photopolymer, such that in the presence of the polarized light it gives rise to a photopolymerization along a given direction, coinciding with the optical field or normal to it, the easy axis optically induced is permanent. In this case, removing the optical field, after a long time of irradiation the nematic orientation does not change any longer. What long time means will be discussed in the next section.

If the photosensitive material is formed by molecules of dyes adsorbed at the surface the situation is different. In this case, in the absence of the optical field, the dye molecules are in the ground state aligned along the easy axis imposed by the surface with strong anchoring. In the presence of the optical field, part of the dye molecules are aligned along the optical field, part perpendicular to it, and a part remains aligned along the initial orientation. When the optical field is removed, the initial configuration is recovered unless the light-induced anchoring is strong enough to stabilize the new director orientation. In the former case, according to the model presented above, ϕ relaxes to 0. Let us indicate by t^* the irradiation time, and by $\Phi=\phi(t^*)$. For $t>t^*$, in the following we put $t^*=0$, $\phi(t)$ is the solution of the differential equation

$$\eta\frac{d\phi}{dt} = -\{\nu\phi+\alpha\sin(2\phi)\}, \tag{15}$$

as it follows from Eq. (11). Equation (15) has to be solved with the initial condition $\phi(0)=\Phi$. From Eq. (15) we get that the condition $d\phi/dt=0$ implies $\nu\phi_f^*+\alpha\sin(2\phi_f^*)=0$, whose solution is $\phi_f^*=0$, as expected. When the optical field is removed, $\phi(t)$ relaxes to zero as

$$\int_\Phi^{\phi(t)} \frac{d\xi}{\nu\xi+\alpha\sin(2\xi)} = -\frac{t}{\eta}. \tag{16}$$

If the surface anchoring energy, due to the surface treatment is negligible, the relaxation time for the surface orientation is found to be $\tau=\eta/\nu$, whereas in the case in which the coupling with the bulk is negligible, the relaxation time is given by $\tau=\eta/(2\alpha)$.

VI. INTRINSIC TIME FOR THE OPTICALLY INDUCED EASY DIRECTION: THE CASE OF THE SURFACE COVERED WITH PHOTOPOLYMER

In the previous section we assumed that the anisotropy induced by the light is a very fast phenomenon, whose typical time is very small with respect to the one connected with the viscous movement of the surface director induced by the new easy direction. However, in some case this is not true. The aim of this section is to take into account in the model presented above the case in which the two times are comparable.

Let us consider first the case in which the substrate is a photopolymer. In the absence of the optical field, let $N_i(0)$ be the number of photosensitive pairs, per unit area, along a direction forming with the polarization of the light an angle ψ_i. We have the condition of normalization

$$\sum_{i=-M}^{M} N_i(0) = \mathcal{N}_p, \tag{17}$$

where $\mathcal{N}_p$ is the total number of photosensitive pairs, per unit area. We assume that in the absence of the optical field the pairs are uniformly distributed. We divide them in $2M$ classes in such a manner that $N_i(0)=\mathcal{N}_p/(2M)$, and $\psi_i = i\pi/(2M)$.

In the presence of the optical field there is an increase of the number of photosensitive pairs along the direction (or perpendicular to the direction, according to the photosensitive substrate) of the polarized optical field [23]. The probability of transition is proportional to $\sin^2\psi_i$. The decreasing of N_i in dt is given by $dN_i = -aN_i \sin^2\psi_i dt$, where $1/a$ is a characteristic time depending on the photopolymer and on the intensity of the light. Consequently $N_i(t) = N_i(0)\exp(-at\sin^2\psi_i)$. The number of pairs formed in the direction of the optical field coming from the direction ψ_i is $N_i^*(t) = N_i(0) - N_i(t)$. The total number of pairs in the direction of the optical field is

$$N_0(t) = N_0(0) + \sum_{i=-M}^{M} N_i^*(t), \tag{18}$$

from which it follows that:

$$N_0(t) = \mathcal{N}_p - \sum_{i=-M}^{M}{}' N_i(0) e^{-at\sin^2\psi_i}, \tag{19}$$

where the prime means that in the sum the contribution coming from $i=0$ is excluded. The average value of a function $g=g(\psi)$ is defined by

$$\langle g \rangle = \frac{1}{\mathcal{N}_p} \sum_{i=-M}^{M} g_i N_i(t), \tag{20}$$

where $g_i = g(\psi_i)$. By taking into account Eq. (19) it is possible to rewrite Eq. (20) as

$$\langle g \rangle = g_0 + \frac{1}{\mathcal{N}_p} \sum_{i=-M}^{M} (g_i - g_0) N_i(0) e^{-at\cos^2\psi_i}. \tag{21}$$

In the case in which $g=\cos^2\psi$ from Eq. (21) we get, by taking into account the expression of $N_i(0)$ reported above,

$$\langle \cos^2\psi \rangle = 1 - \frac{e^{-at}}{2M} \sum_{i=-M}^{M} \sin^2\psi_i e^{-at\sin^2\psi_i}. \tag{22}$$

In the continuum limit we get

$$\langle \cos^2\psi \rangle = 1 - \frac{e^{-at/2}}{2}\{\mathcal{I}_0(at/2) + \mathcal{I}_1(at/2)\}, \tag{23}$$

where $\mathcal{I}_0$ and $\mathcal{I}_1$ are modified Bessel functions of the zeroth and first order. As expected, for $t=0$, $\langle\cos^2\psi\rangle = \langle\sin^2\psi\rangle = 1/2$. We can introduce a scalar order parameter $\mathcal{Q}$ for the polymer defined as

$$\mathcal{Q} = 2\langle\cos^2\psi\rangle - 1. \tag{24}$$

It is such that in the absence of irradiation $\mathcal{Q}=0$ and tends to 1 for large irradiation time. Since the degree of order is increasing with the irradiation time along the direction of the polarization of the light **e** the equivalent director of the polymer is **e**. The orienting field of the polymer on the nematic molecules is proportional to $\mathcal{Q}$. It follows that in Eq. (11) the coefficient $\gamma \propto \mathcal{Q}$, and hence $\gamma = \gamma(t)$. We put $\gamma(t) = h\mathcal{Q}(t)$, where h is a parameter connected to the intensity I of the optical field responsible for the photopolymerization. In this case, by taking into account that $\mathcal{Q}(0)=0$, we have $(d\phi/dt)_0 = 0$, instead of Eq. (7). Now in the differential Eq. (11) the variables are no longer separable, and the time evolution of $\phi=\phi(t)$ can be determined only numerically. In the case when $1/a$, which is the typical time for the appearance of the surface easy direction, is small with respect to the typical time appearing in Eq. (11), we can assume that the anisotropy induced by the light is a rapid phenomenon, and to use the analysis presented in Sec. IV. On the contrary if $1/a$ is very large with respect to the typical time in Eq. (11), it is possible to integrate Eq. (11) by assuming γ time independent, and after integration to take into account the time dependence of this parameter. In the special case in which the coupling with the bulk is negligible ($\nu=0$), as well as the surface anchoring energy connected with the surface anisotropy ($\alpha=0$), the dynamic equation describing the evolution of $\phi=\phi(t)$ is

$$\eta\frac{d\phi}{dt} = -\gamma(t)\sin[2(\phi - \phi_e)], \tag{25}$$

whose solution vanishing for $t=0$ is

$$\phi(t) = \phi_e - \tan^{-1}\left\{\tan\phi_e \exp\left(-\frac{2}{\eta}\int_0^t \gamma(t')dt'\right)\right\}. \tag{26}$$

In Fig. 2(a) we show the time dependence of the surface order parameter $\mathcal{Q}$. Since in our analysis we assume that the induced orientation always increases with the intensity of the light, for large t, $\mathcal{Q}\to 1$. In Fig. 2(b) the time evolution of the surface twist angle ϕ is reported for the case in which $1/a$ is comparable to γ/η, when the terms connected to α and ν can be neglected. In this case, for large t, $\phi \to \phi_e$.

In the analysis presented above, we do not take into account the fact that, in time there is a damaging effect induced by the irradiation light, and there is also an increasing difficulty of pairing nonpolymerized side chains. These facts introduce in the expression for dN_i written above an exponential decreasing factor $\exp(-t/\tau_D)$, where τ_D is a phenomenological parameter introduced by Ionescu *et al.* [23]. It follows that our analysis is valid when $1/a \gg \tau_D$. The

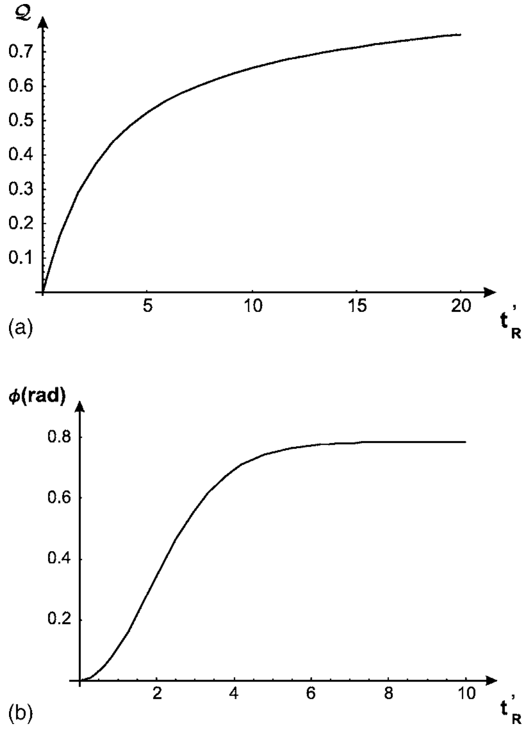

FIG. 2. (a) Time evolution of the surface surface order parameter due to the photosensitive pairs $\mathcal{Q}$ vs the dimensionless time $t'_R=at$. (b) Time evolution of the surface twist angle ϕ vs the dimensionless time $t'_R=at$, when $1/a=\eta/h$. Note that in the present case $(d\phi/dt)_0=0$, due to the absence of order in the photopolymer at $t=0$.

more rigorous analysis where this simplifying hypothesis is removed, does not change, for finite irradiation time, our conclusions. The most important result connected with this damaging effect due to the light is that the degree of order, induced by the light, is no longer a monotonic increasing function of the irradiation time [14,24].

VII. INTRINSIC TIME FOR THE OPTICALLY INDUCED EASY DIRECTION: THE CASE OF DYE MOLECULES DISSOLVED IN THE LIQUID CRYSTAL

Let us consider the case in which the molecules of dye are dissolved in the liquid crystal. As before, we assume that one surface is giving strong planar anchoring, whereas the other one weak anchoring, along the easy direction imposed by the reference surface. After some time depending on the thickness of the sample and on the diffusion coefficient of the dye molecules in the liquid crystal, some of the dye molecules are adsorbed by the surfaces limiting the sample [11]. We assume, even if this hypothesis is not fundamental, that the adsorption energy of the dye molecules is very large with respect to one of the liquid crystal molecules. In this framework, practically all dye molecules are adsorbed to form a monolayer [25]. We assume, furthermore, that when the light is sent on the sample the adsorption-desorption phenomena of dye molecules at the surface are not perturbed [12]. Since the dye molecules, in the ground state, are similar to the nematic molecules, at the surfaces they are oriented along the easy axis $\mathbf{v}$. Let us suppose now that an optical field, forming an angle ϕ_e with the initial nematic orientation, along the x axis of our reference frame, is sent on the sample at $t=0$. The effect of the optical field on the dye molecules is to induce a transformation with dye molecules along the optical field A and a transformation with dye molecules normal to the field B [26]. We indicate by $\mathcal{N}_d$, $\mathcal{N}$, $\mathcal{N}_A$, and $\mathcal{N}_B$ the total surface density of dye molecules, the surface density of dye molecules oriented along the x axis, the surface density of molecules of dye in the state A, and the surface density of molecules of dye in the state B, respectively. The kinetic equations for the formation of the dye molecules in the states A and B are assumed of the type

$$\frac{d\mathcal{N}_A}{dt}=p_A\mathcal{N}-\lambda_A\mathcal{N}_A,$$

$$\frac{d\mathcal{N}_B}{dt}=p_B\mathcal{N}-\lambda_B\mathcal{N}_B, \qquad (27)$$

where $p_A \propto \cos^2\phi_e$, $p_B \propto \sin^2\phi_e$ are the probability of excitation of the dye molecules, whereas λ_A and λ_B are connected with the probability of deexcitation. Since the number of dye molecules is fixed, $\mathcal{N}_A(t)+\mathcal{N}_B(t)+\mathcal{N}(t)=\mathcal{N}_d$. Equations (27) have to be solved with the boundary conditions $\mathcal{N}_A(0)=\mathcal{N}_B(0)=0$, stating that for $t=0$ all dye molecules are oriented along the x axis, in the fundamental state. From Eqs. (27) it follows that $(d\mathcal{N}_A/dt)_0=p_A\mathcal{N}_d$ and $(d\mathcal{N}_B/dt)_0=p_B\mathcal{N}_d$. These relations state that the initial rapidity of formation of the dye molecules in the states A and B only depend on the probability of excitation p_A and p_B, repectively. Furthermore, in the steady state, for $t\to\infty$, where $(d\mathcal{N}_A/dt)_{\text{eq}}=(d\mathcal{N}_B/dt)_{\text{eq}}=0$, $\mathcal{N}_A^{\text{eq}}=(p_A/\lambda_A)\mathcal{N}^{\text{eq}}$, $\mathcal{N}_B^{\text{eq}}=(p_B/\lambda_B)\mathcal{N}^{\text{eq}}$, and hence $\mathcal{N}_A^{\text{eq}}/\mathcal{N}_B^{\text{eq}}=(p_A\lambda_B)/(p_B\lambda_A)$. In our analysis we will assume that $\phi_e=\pi/4$, that implies $p_A=p_B$. In this framework $\mathcal{N}_A^{\text{eq}}/\mathcal{N}_B^{\text{eq}}=\lambda_B/\lambda_A$. From this relation it follows that for $\lambda_B>\lambda_A$, $\mathcal{N}_A^{\text{eq}}>\mathcal{N}_B^{\text{eq}}$, i.e., the density of dye molecules in the state A is larger than the one in the state B, in the state of equilibrium.

We look for a solution of Eqs. (27) of the type $\mathcal{N}_A(t)=\mathcal{N}_A^{\text{eq}}+\delta\mathcal{N}_A(t)$ and $\mathcal{N}_B(t)=\mathcal{N}_B^{\text{eq}}+\delta\mathcal{N}_B(t)$, where $\mathcal{N}_A^{\text{eq}}$ and $\mathcal{N}_B^{\text{eq}}$ are the values of equilibrium for $\mathcal{N}_A(t)$ and $\mathcal{N}_B(t)$, for $t\to\infty$. A simple calculation gives

$$\mathcal{N}_A^{\text{eq}}=\frac{p_A\lambda_B}{(p_A+\lambda_A)(p_B+\lambda_B)-p_Ap_B}\mathcal{N}_d,$$

$$\mathcal{N}_B^{\text{eq}}=\frac{p_B\lambda_A}{(p_A+\lambda_A)(p_B+\lambda_B)-p_Ap_B}\mathcal{N}_d,$$

$$\mathcal{N}^{\text{eq}}=\frac{\lambda_A\lambda_B}{(p_A+\lambda_A)(p_B+\lambda_B)-p_Ap_B}\mathcal{N}_d. \qquad (28)$$

The parts of the solution representing the evolution towards the final state $\delta\mathcal{N}_A(t)$ and $\delta\mathcal{N}_B(t)$ are solutions of the homogeneous system of coupled differential equations

$$\frac{d(\delta\mathcal{N}_A)}{dt} = -(p_A+\lambda_A)\delta\mathcal{N}_A - p_A\delta\mathcal{N}_B,$$

$$\frac{d(\delta\mathcal{N}_B)}{dt} = -(p_B+\lambda_B)\delta\mathcal{N}_B - p_B\delta\mathcal{N}_A. \tag{29}$$

Solutions of Eq. (29) are of the type $\delta\mathcal{N}_A(t)=C_A\exp(-\mu t)$ and $\delta\mathcal{N}_B(t)=C_B\exp(-\mu t)$, where C_A and C_B are constants and $\mu>0$ the characteristic exponent to be determined. Routine calculations give

$$\delta\mathcal{N}_A(t) = C_1e^{-\mu_1 t}+C_2e^{-\mu_2 t},$$

$$\delta\mathcal{N}_B(t) = R_1C_1e^{-\mu_1 t}+R_2C_2e^{-\mu_2 t}, \tag{30}$$

where $\mu_{1,2}$ are the solutions of the equation

$$(\mu-p_A-\lambda_A)(\mu-p_B-\lambda_B)-p_Ap_B=0 \tag{31}$$

and

$$R_1=\frac{\mu_1-p_A-\lambda_A}{p_A}, \quad R_2=\frac{\mu_2-p_A-\lambda_A}{p_A}.$$

The constants C_1 and C_2 are obtained by the boundary conditions $\mathcal{N}_A(0)=\mathcal{N}_B(0)=0$, and are found to be

$$C_1=p_A\frac{\mathcal{N}_B^{\mathrm{eq}}-R_2\mathcal{N}_A^{\mathrm{eq}}}{\mu_2-\mu_1}, \quad C_2=-p_A\frac{\mathcal{N}_B^{\mathrm{eq}}-R_1\mathcal{N}_A^{\mathrm{eq}}}{\mu_2-\mu_1}.$$

We can now evaluate the influence of $\mathcal{N}_A$ and $\mathcal{N}_B$ on the nematic orientation. We assume that the dye molecules in the states A and B tend to orient the nematic director along their directions, parallel and perpendicular to the optical field, respectively, whereas the ones we have indicated with $\mathcal{N}$ stabilize the initial orientation along $\mathbf{v}\parallel\mathbf{x}$. It follows that the average energy per surface nematic molecule due to the dye molecules is

$$f_s=-g_AN_A(\mathbf{v}_A\cdot\mathbf{n})^2-g_BN_B(\mathbf{v}_B\cdot\mathbf{n})^2-g_NN(\mathbf{v}\cdot\mathbf{n})^2 \tag{32}$$

where $\mathbf{v}_A\parallel\mathbf{e}$, $\mathbf{v}_B\perp\mathbf{e}$, $N_A=\mathcal{N}_A/\mathcal{N}_n$, $N_B=\mathcal{N}_B/\mathcal{N}_n$, $N=\mathcal{N}/\mathcal{N}_n$, and g_A, g_B, and g_N are phenomenological parameters describing the interaction of a surface molecule with the easy directions $\mathbf{v}_A$, $\mathbf{v}_B$, and $\mathbf{v}$, respectively [19]. In terms of the twist angle ϕ, f_s reads

$$f_s=-\gamma(t)\cos^2(\phi-\phi_e)-\gamma_N(t)\cos^2\phi, \tag{33}$$

where $\gamma(t)=g_AN_A(t)-g_BN_B(t)$, and $\gamma_N(t)=g_NN(t)$, are the effective orienting energies due to the dye molecules in the A and B states and in the state along the initial orientation, respectively. The interesting point is that now the effective surface energy due to the presence of the dye molecules depends on t. From Eq. (33) the easy axis ϕ_E and the anchoring energy strength w defined by $\partial f_s/\partial\phi=0$ and by $w=(\partial^2f_s/\partial\phi^2)_{\phi=\phi_E}$ are found to be

$$\phi_E=\frac{1}{2}\tan^{-1}\left(\frac{1}{2}\frac{\gamma(t)\sin(2\phi_e)}{\gamma_N(t)+\gamma(t)\cos(2\phi_e)}\right),$$

$$w=2\sqrt{[\gamma_N(t)+\gamma(t)\cos(2\phi_e)]^2+[\gamma(t)/4]^2\sin^2(2\phi_e)}. \tag{34}$$

In the simple case in which the effect of the bulk on the nematic orientation can be neglected, the time evolution of the surface twist angle is given by the ordinary differential equation

$$\eta\frac{d\phi}{dt}=-\gamma(t)\sin[2(\phi-\phi_e)]-\gamma_N(t)\sin(2\phi), \tag{35}$$

that has to solved with the boundary condition $\phi(0)=0$. From Eq. (35) we get that for $t\to\infty$, $\phi\to\phi_f$ is given by

$$\phi_f=\frac{\gamma_{\mathrm{eq}}\sin(2\phi_e)}{\gamma_N^{\mathrm{eq}}+\gamma_{\mathrm{eq}}\cos(2\phi_e)}, \tag{36}$$

where $\gamma_{\mathrm{eq}}=\gamma_A^{\mathrm{eq}}-\gamma_B^{\mathrm{eq}}$. As expected, for $\gamma_N^{\mathrm{eq}}=0$, $\phi_f=\phi_e$ or $\phi_f=\phi_e+\pi/2$, according to the sign of γ_{eq}. If $\gamma>0$, $\phi\to\phi_e$, whereas for $\gamma<0$, $\phi\to\phi_e-\pi/2$. This behavior is in agreement with the experimental observations on combined liquid crystal cells doped with methyl-red [13]. Furthermore, from Eq. (35) by taking into account that $\mathcal{N}_A(0)=\mathcal{N}_B(0)=0$, we get $(d\phi/dt)_0=0$ and

$$\eta\left(\frac{d^2\phi}{dt^2}\right)_0=\left(\frac{d\gamma}{dt}\right)_0\sin(2\phi_e).$$

From the expression for $(d^2\phi/dt^2)_0$ it follows that the curvature of the twist angle for $t=0$ can change sign, according to the sign of $(d\gamma/dt)_0$. In the case where $\gamma_{\mathrm{eq}}>0$ and $(d\gamma/dt)_0<0$, for small t the presence of the dye molecules favors the orientation along the normal to the optical field, but for large t the dye molecules induce an orientation along the optical field, in agreement with the experimental observations.

In Fig. 3 we show the time evolution of $N_A(t)$ (a), $N_B(t)$ (b), and of $N(t)$ (c). For the numerical calculations we suppose $\phi_e=\pi/4$, and hence $p_A=p_B$. In particular we assume $p_A=p_B=0.8$ 1/s, $\lambda_A=0.2$ (1/s), and $\lambda_B=0.6$ (1/s). Since $\lambda_B>\lambda_A$, $\mathcal{N}_A^{\mathrm{eq}}>\mathcal{N}_B^{\mathrm{eq}}$, as it has been discussed above. In Fig. 4 the easy axis ϕ_E (a) and the anchoring energy strength w (b) are reported derived by means of Eq. (34), for $\gamma_A=2\times10^{-21}$ J/molecule, $\gamma_B=4.4\times10^{-21}$ J/molecule, and $\gamma_N=0.1\times10^{-21}$ J/molecule [9]. In the insets of Fig. 4 the time dependencies of ϕ_E and of w are shown for small t. In the considered case $p_A=p_B$ and $\lambda_A<\lambda_B$, and hence $(d\mathcal{N}_A/dt)_0=(d\mathcal{N}_B/dt)_0$ and $\mathcal{N}_A^{\mathrm{eq}}>\mathcal{N}_B^{\mathrm{eq}}$. Since $\gamma_A<\gamma_B$, for small t the nematic orientation is imposed by the dye molecules in the state B, whereas for large t the nematic orientation is along the optical field. The theoretical behaviors of ϕ_E and w reported in Fig. 4 are similar to the ones reported in Ref. [18] for the same quantities (see Figs. 6 and 7 of Ref. [18]). In Fig. 5 the actual surface twist angle $\phi(t)$ is shown for the same set of parameters. The angle ϕ does not coincide with

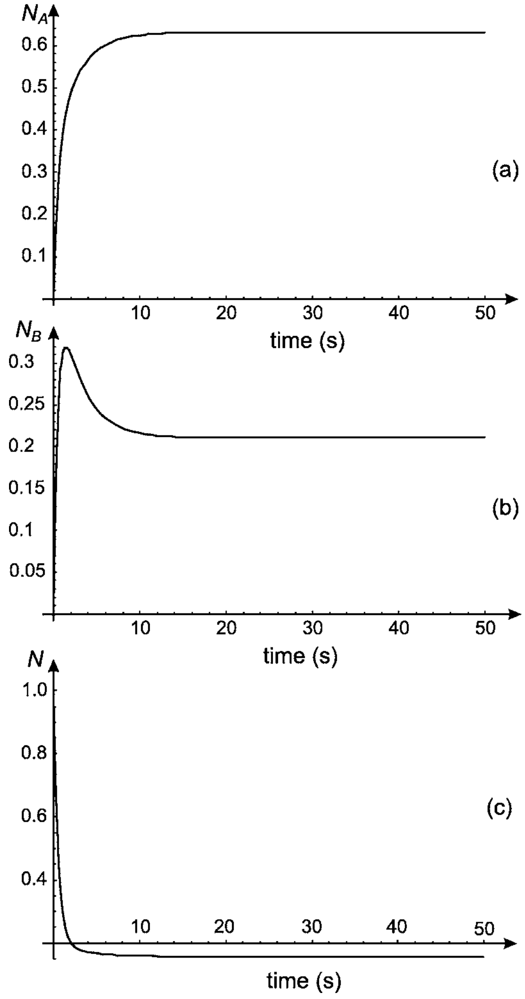

FIG. 3. Time evolution of $N_A=\mathcal{N}_A/\mathcal{N}_n$ (a), $N_B=\mathcal{N}_B/\mathcal{N}_n$ (b), and $N=\mathcal{N}/\mathcal{N}_n$ (c), representing the relative surface densities, with respect to $\mathcal{N}$, of dye molecules along the optical field, normal to the optical field, and along the initial orientation, respectively. The parameters used for the figure are $\mathcal{N}_n=\mathcal{N}_d=10^{20}$ m^2 (Ref. [13]), $p_A=p_B=0.8$ (1/s), $\lambda_A=0.2$ (1/s), and $\lambda_B=0.6$ (1/s).

ϕ_E because the bulk density of the elastic torque, due to the surface characterized by strong anchoring, is not zero. However, for large t, $\phi \rightarrow \phi_e$.

For the molecular viscosity η we used the value obtained in the following manner. As is clear from the discussion reported above, η is a surface viscosity for molecule [28]. In the equations the quantity $\eta_S=\mathcal{N}_n\eta$ usually appears, i.e., the surface density of our molecular surface viscosity [29]. By assuming $\eta_S=6$ Pa s m and $\mathcal{N}_n \sim 10^{20}$ m^{-2}, we get $\eta=6\times 10^{-20}$ Ps s m^3. The theoretical prediction for $\phi=\phi(t)$ reported in Fig. 5 compare well with the experimental data reported in Ref. [5] (see Fig. 2 of Ref. [5]), and in Ref. [18] (see Fig. 4).

In the analysis presented in this section, we have assumed that the adsorption energy for the molecules of dye is very large with respect to the ones for the nematic molecules, in such a manner that all of them are adsorbed. In this framework, we considered just two kinds of orientations of the dye molecules, parallel and perpendicular to the polarization of the light. Of course the real situation is more complicated, because if the adsorption of the dye molecules is not complete, the dye molecules are distributed in the bulk continuously, and the kinetic Eqs. (27) should contain the angular distribution functions of the dye molecules, as in Ref. [27]. The generalization of our model along this line is under study, and will be published elsewhere.

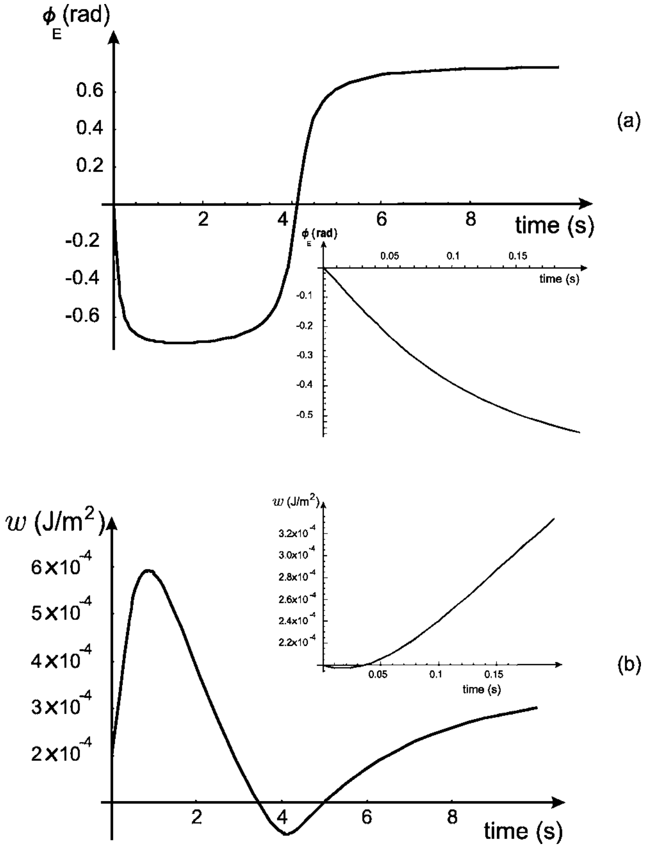

FIG. 4. Surface easy axis ϕ_E (a) and anchoring energy strength w (b) for the surface energy density given by Eq. (34), when $\phi_e=\pi/4$. The insets depict the behavior of ϕ_E and of w for low irradiation dose. The parameters used for the figure are $\gamma_A=2\times 10^{-21}$ J/molecule, $\gamma_B=4.4\times 10^{-21}$ J/molecule, $\gamma_N=0.1\times 10^{-2}$ J/molecule, of the same order of magnitude of KT (Ref. [9]), and $\eta=6\times 10^{-20}$ Pa s m^3 (Ref. [29]). The others parameters are as in Fig. 3.

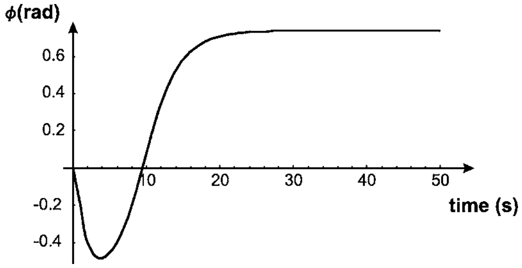

FIG. 5. Surface twist angle ϕ vs t for a nematic cell containing dye molecules, when $\phi_e=\pi/4$. The parameters used for the figure are as in Fig. 4.

VIII. FOKKER-PLANCK EQUATION

In the previous sections we have written an equation for a molecular object in analogy with the dynamic equation valid for a macroscopic body. Of course at molecular level the concept of viscosity is meaningless. The aim of this section is to show that the fundamental equation used in our analysis can be justified starting from an analysis at microscopic level. In this way it will be possible to give a meaning to the rotational viscosity introduced above. In the following we present a simplified version of the model discussed in Ref. [30].

In the absence of the optical field acting on the photosensitive substrate, the nematic orientation is the one fixed by the surface with strong anchoring, inducing an easy axis on the photosensitive surface. In this case, due to a finite value of the temperature, the surface molecules are oscillating around the average orientation, coinciding with the surface director. The probability of the oscillation in the two directions is the same. In the presence of the optical field, the initial symmetry is broken, and a drift of the molecular directions along the optical field appears. In this case, following the procedure discussed in Ref. [21] it is possible to write down a master equation describing the evolution of the molecular orientation along the direction connected with the optical field. By a proper discretization of the molecular orientations, and passing to the continuum description, it is possible to show that the density of probability, $\mathcal{P}(\varphi,t)$, of the surface molecules to be oriented at an angle φ is given by [12]

$$\frac{\partial\mathcal{P}}{\partial t}=D\left\{\frac{\partial}{\partial\varphi}\left(\frac{\partial u}{\partial\varphi}\mathcal{P}\right)+\frac{\partial^2}{\partial\varphi^2}(\mathcal{P})\right\}, \tag{37}$$

known as the Fokker-Planck equation [31]. In Eq. (37) $u(\varphi)$ is the energy per surface molecule, in KT units, and D is the rotational diffusion coefficient. The solution of Eq. (37) in the steady state $\mathcal{P}_s$ can be easily obtained. In fact in this state $\partial\mathcal{P}/\partial t=0$. Consequently from Eq. (37) we get

$$\frac{\partial u}{\partial\varphi}\mathcal{P}_s+\frac{\partial\mathcal{P}_s}{\partial\varphi}=\kappa, \tag{38}$$

where κ is an integration constant to be determined. The normalized solution of Eq. (38) such that $\mathcal{P}_s(0)=\mathcal{P}_s(\pi)$ is

$$\mathcal{P}_s(\varphi)=\frac{e^{-u(\varphi)}}{\int_0^\pi e^{-u(\varphi)}d\varphi}. \tag{39}$$

It coincides with the Boltzmann distribution [31]. We can now determine the evolution of the average value of $\phi=\langle\varphi\rangle$. To this end let us consider an arbitrary function of φ, $f=f(\varphi)$. By definition of average

$$\langle f(\varphi)\rangle=\int_0^\pi f(\varphi)\mathcal{P}(\varphi,t)d\varphi, \tag{40}$$

we have

$$\frac{d}{dt}\langle f(\varphi)\rangle=\frac{d}{dt}\int_0^\pi f(\varphi)\mathcal{P}(\varphi,t)d\varphi. \tag{41}$$

A simple calculation, taking into account that $f(0)=f(\pi)$, as well as $\mathcal{P}(0)=\mathcal{P}(\pi)$, gives

$$\frac{d}{dt}\langle f(\varphi)\rangle=D\left\{-\left\langle\frac{\partial f}{\partial\varphi}\frac{\partial u}{\partial\varphi}\right\rangle+\left\langle\frac{\partial^2 f}{\partial\varphi^2}\right\rangle\right\}. \tag{42}$$

In the particular case in which $f(\varphi)=\varphi$ from Eq. (42) we have $d\phi/dt=-D\langle\partial u/\partial\varphi\rangle$, that can be rewritten as

$$\eta\frac{d\phi}{dt}=-\left\langle\frac{\partial U}{\partial\varphi}\right\rangle, \tag{43}$$

where $\eta=KT/D$ is the rotational viscosity [32]. Equation (43) coincides with Eq. (6) or Eq. (11), depending on the importance of the coupling with the bulk of the surface molecule.

IX. CONCLUSION

We have proposed a phenomenological model for the easy axis optically induced in nematic combined cells whose isotropic surface is covered with a photosensitive polymer, or are doped with an azo-dye. The analysis is based on a dynamic equation containing a surface viscous term and a drift term connected with the optical field. The fundamental equation used to build the formalism is phenomenological. However, to justify it from a microscopical point of view, we have presented a mathematical derivation centered on a master equation describing the evolution of the molecular orientation along the direction of the optical field. We considered, separately, the cases in which the anisotropy connected with the incident light is a fast or slow phenomenon, with respect to the nematic reorientation. The predicted time dependence for the surface twist angle is in agreement with the one experimentally measured.

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