

Photoinduced molecular reorientation of absorbing liquid crystals

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The phenomenon of photoinduced molecular reorientation of absorbing nematic liquid crystals is analyzed in a macroscopic general framework and with a specific molecular model. The photoinduced torque responsible for the reorientation is shown to describe a transfer of angular momentum from the molecule center-of-mass degrees of freedom to the rotational ones, mediated by molecular friction. As a consequence, a photoinduced stress tensor is predicted to develop together with the torque in the illuminated fluid. A molecular expression of the photoinduced torque is derived with a rigorous procedure, valid both for a pure material and for a dye-liquid-crystal mixture. This torque expression corrects those reported in previous works on the same subject. The photoinduced torque is evaluated analytically in a simple approximate limit.

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I. INTRODUCTION

When light travels through an anisotropic medium, angular momentum is exchanged between matter and optical wave. The mechanism of this exchange is based on the anisotropy of the material polarizability. On one hand, indeed, light polarization and propagation, which determine the angular momentum carried by the electromagnetic wave, are affected by the medium birefringence. On the other hand, since the induced material polarization \mathbf{P} is not parallel to the optical electric field \mathbf{E} , a net torque per unit volume $\mathbf{P} \times \mathbf{E}$ acting on the medium is developed. An explicit calculation shows that the optical torque corresponds exactly to the angular momentum deposited by light in the unit volume, so that the total angular momentum is always conserved.

In most materials, the effect of the optical torque is hardly detectable even when generated by the intense light of a laser beam. In nematic liquid crystals (LC), on the contrary, the optical torque of a laser beam can easily induce a large change of the molecule average orientation. This effect, known as light-induced molecular reorientation, is at the basis of the LC giant optical nonlinearity, and was the object of extensive investigations in the last fifteen years [1].

The above picture of angular momentum exchange between light and matter breaks down when applied to an effect discovered a few years ago by I. Jánossy *et al.* [2], which attracted considerable interest [3–15]. It was found that a small amount of dye dissolved in a nematic LC in order to make it light absorbing can change the optical torque by a large factor. Depending on the specific dye utilized, the optical torque can be enhanced by one or two orders of magnitude, or it can be canceled out, or even sign-inverted [3–6]. In all cases, however, the birefringence of the material was measured and found approximately unchanged. On the other hand, light absorption by itself does not give rise to angular momentum exchange in a dichroic medium (in the plane-wave limit and for linear polarization). Therefore, the angular momentum lost by light does not correspond anymore to the induced torque. All proposed explanations of the dye effect based on a macroscopic approach, for

example, using thermal phenomena, have been ruled out by experiments. The following two main questions are therefore left open: first, what is the microscopic mechanism responsible for the large change in the optical torque, and second, where does the angular momentum come from?

In Ref. [7], Jánossy presented a molecular model of the dye effect. The physical picture behind his model provides, in our opinion, a plausible answer to the first of the above questions. However, we think instead that the answer to the second question given in Ref. [7] is not correct. As a consequence, we believe that the expression of the anomalous dye-induced optical torque deduced in Ref. [7] is also slightly incorrect. Moreover, the analysis of Ref. [7] is limited to the case of LC-dye mixtures, but we believe that the phenomenon would be qualitatively unchanged in the case of pure light-absorbing LC. In this work, we analyze theoretically the absorption effects to find a satisfactory answer to the question of angular momentum conservation and to correct and generalize the expression of the anomalous optical torque published in Ref. [7].

This paper is organized as follows. First, in Sec. II, our analysis is carried out at a macroscopic level. We use symmetry and continuum theory to obtain general results, valid whatever the correct microscopic picture of the effect is. Next, in Sec. III, we present an extended version of Jánossy's molecular model, which includes explicitly the LC molecule rotational dynamics (in the model of Ref. [7], only dye molecules are considered explicitly). This extension allows us to deduce the LC torque balance from the model itself, with no additional assumptions, as shown in Sec. IV. Each term in the molecular balance of torques is then identified with a phenomenological torque. The correct molecular expression of the torque resulting from the model is thus determined with a rigorous procedure. Our expression is valid also for a pure absorbing material. In Sec. V, the torque expression is cast in a form suitable for explicit calculations. In Sec. VI, the energy balance is discussed briefly. Finally, in Sec. VII, the model is solved in an approximate limit where an analytic approach is possible.

II. MACROSCOPIC ANALYSIS

In a transparent nematic LC, the optical electromagnetic torque acting on the molecular director \mathbf{n} (due to polarizability anisotropy) is given by

$$\boldsymbol{\tau}_{\text{em}} = \langle \mathbf{P} \times \mathbf{E} \rangle = \frac{\epsilon_a}{4\pi} \langle (\mathbf{n} \cdot \mathbf{E})(\mathbf{n} \times \mathbf{E}) \rangle, \quad (1)$$

where $\epsilon_a = n_e^2 - n_o^2$ is the optical dielectric anisotropy, n_e and n_o being the extraordinary and ordinary refractive indices, respectively, and the angular brackets denote time average over an optical cycle.

As reported in the Introduction, when the LC is light absorbing, the total optical torque $\boldsymbol{\tau}_o$ is not given anymore by Eq. (1). The difference $\boldsymbol{\tau}_{\text{ph}} = \boldsymbol{\tau}_o - \boldsymbol{\tau}_{\text{em}}$, accounting only for the additional anomalous effect related to light absorption, is here named photon absorption-induced torque, or in brief ‘‘photoinduced’’ torque. All experimental results are consistent with the following expression [2–5]:

$$\boldsymbol{\tau}_{\text{ph}} = \frac{\zeta}{4\pi} \langle (\mathbf{n} \cdot \mathbf{E})(\mathbf{n} \times \mathbf{E}) \rangle, \quad (2)$$

which is identical to that given in Eq. (1) except for the substitution of ϵ_a with a new dimensionless material constant ζ . This constant is proportional to dye concentration and depends on the molecular structures of both dye and LC. In some guest-host systems it may reach values 400 times larger than ϵ_a for a dye concentration below 1% in weight. Moreover, ζ can also be negative, contrary to ϵ_a , which is always positive at optical frequencies.

The similarity between Eq. (2) and Eq. (1) is not accidental: the dependence of the optical torque on the electric field \mathbf{E} and director \mathbf{n} is fully constrained by symmetry, in the limit of small light intensity and assuming that the material response is local and nonmagnetic. Symmetry alone, however, does not tell us the physical meaning of the constant ζ , and it does not allow us to estimate its value or find its relationship with other material constants. For transparent liquid crystals, all this can be achieved using thermodynamics and the constitutive equations of a uniaxial dielectric. A thermodynamic approach is, however, useless in the case of the photoinduced torque, because the effect is the result of light absorption, which is an irreversible process. A microscopic molecular model is therefore required to determine the physical meaning of ζ and to estimate its value. Nevertheless, it is useful to set first the problem in the model-independent frame of continuum theory.

The torque balance equation controlling the molecular director dynamics in the presence of fields and light can be written as follows [16,17]:

$$I_1 \mathbf{n} \times \frac{d^2 \mathbf{n}}{dt^2} = \boldsymbol{\tau}_{\text{el}} + \boldsymbol{\tau}_v + \boldsymbol{\tau}_{\text{em}} + \boldsymbol{\tau}_{\text{ph}}. \quad (3)$$

The left-hand side of this equation describes the inertial contribution, usually negligible in practice, but included here to make the physical meaning of the equation more evident. On the right-hand side we included the following: the elastic torque $\boldsymbol{\tau}_{\text{el}}$, which is a complicated function of the molecular director gradients [16,17], the viscous torque, given by

$\boldsymbol{\tau}_v = -\gamma_1 \mathbf{n} \times (d\mathbf{n}/dt)$, the electromagnetic torque $\boldsymbol{\tau}_{\text{em}}$, including the polarization optical torque and eventually the static electric and/or magnetic torques, and the photoinduced torque $\boldsymbol{\tau}_{\text{ph}}$.

Equation (3) describes the change in time of the angular momentum associated with molecular orientation, within a given volume element in the LC. To have angular momentum conservation, each torque appearing on the right-hand side of Eq. (3) must obey the following equation [17]:

$$(\boldsymbol{\tau})_i = \frac{\partial}{\partial x_j} (\epsilon_{ihk} n_h s_{jk}) + \epsilon_{ihk} t_{hk}, \quad (4)$$

where ϵ_{ihk} is Levi-Civita antisymmetric tensor, t_{hk} is a stress tensor associated with fluid displacement with no director rotation, and s_{jk} is another material tensor. Equation (4) states that each torque acting on the molecular director has two possible origins: (i) an angular momentum exchange directly with the director field in the surroundings, as in the term given by a total divergence; (ii) an angular momentum exchange, within the current volume element, with other degrees of freedom that transport linear momentum and therefore appear in the expression of the stress tensor. These are essentially the fluid flow, i.e., the molecule center-of-mass degrees of freedom, and the electromagnetic field.

Only the elastic torque $\boldsymbol{\tau}_{\text{el}}$ has both kinds of contributions. The viscous torque $\boldsymbol{\tau}_v$ is given by the antisymmetric part of the viscosity stress tensor, and therefore it describes an angular momentum exchange with the fluid flow. The electromagnetic torque can be included entirely in the stress-tensor term, with $t_{ij}^{\text{em}} = (D_i E_j + B_i H_j)/4\pi - \delta_{ij}(D_h E_h + B_h H_h)/8\pi$ [18]. Not depending on spatial gradients, the photoinduced torque $\boldsymbol{\tau}_{\text{ph}}$ must also correspond to a stress tensor. Therefore, angular momentum conservation requires that a photoinduced stress tensor t_{ij}^{ph} should also exist in the illuminated absorbing LC. When it is not spatially uniform, such a stress tensor could give rise to an anomalous photoinduced flow. We have no experimental information on the symmetric part of t_{ij}^{ph} . Its antisymmetric part is instead determined by Eqs. (2) and (4):

$$t_{ij}^{\text{ph}} = \frac{\zeta}{8\pi} \langle (\mathbf{n} \cdot \mathbf{E})(n_i E_j - n_j E_i) \rangle. \quad (5)$$

Although it depends on the optical electric field, this photoinduced stress tensor cannot be associated with a momentum flux carried by the electromagnetic wave, which is already fully taken into account by t_{ij}^{em} . Therefore, it must be a ‘‘mechanical’’ stress tensor, describing short-range forces exchanged through the material surfaces, similar to those giving rise to pressure or viscosity, and acting on molecule center-of-mass degrees of freedom. The photoinduced torque, therefore, must correspond to an angular momentum transfer from the molecule center-of-mass degrees of freedom (flow) to the orientational ones (director).

The difference between the electromagnetic torque and the photoinduced torque becomes even more evident at the sample boundaries. The electromagnetic stress tensor does not vanish outside the sample and is approximately continuous across the boundary. The volume integral of the electromagnetic torque over the whole LC sample can be therefore

traced back to the entering flux of angular momentum carried by the electromagnetic wave outside the sample. On the contrary, the photoinduced stress tensor vanishes suddenly when crossing the sample boundaries, because the constant ζ is zero outside the sample. The discontinuity of the stress tensor corresponds to a mechanical force acting on the sample bounding walls. If such mechanical force is not compensated by the elastic and/or viscous contributions, it must be finally balanced by the sample holder. If the illuminated LC cell is suspended so that nothing opposes its free rotation, the angular momentum that enters the system as a whole will be given by the ordinary electromagnetic torque only, with no anomalous enhancement.

III. MICROSCOPIC MODEL

Consider a linearly polarized light wave passing through an absorbing nematic LC obtained by dissolving a small amount of dichroic dye in a transparent host. For simplicity we will assume that the system is spatially uniform. We suppose that host and dye molecules are rodlike, and denote their main molecular axis with a unit vector s . Moreover, we assume that only one excited electronic state of the dye is important. Therefore we have to consider three populations of molecules, i.e., ground and excited state dye molecules and nematic host molecules, which will be identified with the index $\alpha = g, e, h$, respectively. The number of α molecules per unit volume and solid angle at time t and orientation s is denoted as $f_\alpha(s, t)$. The total number of α molecules per unit volume is therefore given by $N_\alpha = \int d\Omega f_\alpha$. The total number of dye molecules per unit volume is denoted as $N_d = N_g + N_e$.

Although we are considering here the case of a dye-LC mixture, it should be emphasized that the model is valid also in the case of a pure light-absorbing LC, i.e., to a LC made of dye molecules. All equations in the model can be applied to such case just by setting $f_h = 0$ and $N_h = 0$ (except for Sec. VII, where the replacement $h \rightarrow g$ must be done, instead).

Dynamical equations for the f_α can be obtained starting from the continuity equations in angle space:

$$\frac{\partial f_\alpha}{\partial t} + \bar{\nabla} \cdot \mathbf{J}_\alpha = W_\alpha, \quad (6)$$

where $\bar{\nabla}$ is the angular part of the ordinary ∇ differential operator, the vectors $\mathbf{J}_\alpha(s)$ are the rotational currents, and $W_\alpha(s)$ are the light-induced net transition rates between different α 's [19]. The host molecules are not subject to transitions, i.e., $W_h = 0$. W_e (W_g) is the rate of electronic transitions giving rise to excited-state (ground-state) dye molecules at orientation s minus the rate of transitions removing excited-state (ground-state) dye molecules at the same orientation.

Next, we need ‘‘constitutive’’ equations for the W_α and \mathbf{J}_α . For the former, let us suppose that dye molecules have a transition dipole for light absorption parallel to their axis s . The absorption probability per unit time of a molecule in the ground state is then given by $p(s) = \sigma \langle (s \cdot \mathbf{E})^2 \rangle$, where σ is a molecular constant. The decay probability per unit time is instead given by the excited-level lifetime τ_e , independent of orientation. Immediately after absorption or decay, a mol-

ecule undergoes a fast internal relaxation involving vibrational and conformational degrees of freedom. We make the assumption that this relaxation does not perturb significantly the orientation s of the molecule. Moreover, we assume that the molecule relaxation brings the excited electronic level off resonance with light, so that stimulated emission can be neglected. Under these hypotheses the transition rates are given by

$$W_e(s) = -W_g(s) = p(s)f_g(s) - \frac{1}{\tau_e}f_e(s). \quad (7)$$

For the \mathbf{J}_α , we assume that the molecule orientational dynamics can be described as a rotational Brownian motion, with rotational diffusion constants D_α [20–22]. The rotational diffusion is considered here in the Einstein-Smoluchowski limit, where the angular-velocity distribution follows adiabatically its quasiequilibrium asymptotic limit [22], and therefore needs not be considered explicitly. Moreover, we assume that the molecule orientation drifts under the effect of a potential energy $U_\alpha(s)$ describing the interaction both with neighbor molecules and with external fields. The environment is supposed to be still, on average; i.e., there is no fluid flow. These assumptions lead to the following expression:

$$\mathbf{J}_\alpha = -D_\alpha \bar{\nabla} f_\alpha - \frac{D_\alpha}{kT} (\bar{\nabla} U_\alpha) f_\alpha \quad (8)$$

(no sum over α is implied here) where the first term accounts for the orientational random walk and the second term for the rotational drift under the effect of the potential.

To make Eq. (8) fully defined, however, we also need an explicit expression for the orientational potential energy U_α . We may set $U_\alpha = U_\alpha^{(i)} + U_\alpha^{(\text{em})}$, where $U_\alpha^{(i)}$ is the potential describing the orientational intermolecular interactions, and $U_\alpha^{(\text{em})}$ is the potential energy due to external electromagnetic fields. The latter is independent of the distributions f_α (if local-field effects are neglected), and therefore can be considered as given. The intermolecular interactions are here described with a mean-field approach. Assuming additivity of intermolecular interactions, we have

$$U_\alpha^{(i)}(s) = \sum_{\beta=h,g,e} \int d\Omega' f_\beta(s') U_{\alpha\beta}(s, s'), \quad (9)$$

where $U_{\alpha\beta}(s, s')$ is the potential for the interaction of molecules of the kind α and β , respectively oriented as s and s' . In $U_{\alpha\beta}$, the interaction energy has been already averaged over all relative center-of-mass molecular positions. Independently of the specific intermolecular interactions, $U_{\alpha\beta}$ has the following general symmetry properties: (i) it depends on s and s' only through the scalar $s \cdot s'$; (ii) it is symmetric for molecule exchange, i.e., $U_{\alpha\beta}(s, s') = U_{\beta\alpha}(s', s)$.

Substituting Eqs. (7) and (8) in Eq. (6), we obtain a closed set of nonlinear integral-differential equations for the molecule orientational dynamics. They generalize the model reported in Ref. [7], as they include explicitly the orientational degrees of freedom of host molecules.

IV. MOLECULAR TORQUE BALANCES

The rotational current \mathbf{J}_α at a given orientation \mathbf{s} is related to the molecule average angular velocity $\boldsymbol{\omega}_\alpha$ by

$$\boldsymbol{\omega}_\alpha(\mathbf{s}) = \mathbf{s} \times \frac{\mathbf{J}_\alpha(\mathbf{s})}{f_\alpha}. \quad (10)$$

The angular velocity $\boldsymbol{\omega}_\alpha$ considered here can be formally defined as the average over the partial angular velocity quasiequilibrium distribution for a given orientation \mathbf{s} . Note that this definition is not equivalent to the time-averaged angular velocity of a molecule followed along its motion.

Rewriting Eq. (8) in terms of $\boldsymbol{\omega}_\alpha$, we obtain

$$-\frac{kT}{D_\alpha} \boldsymbol{\omega}_\alpha - \mathbf{s} \times \bar{\nabla} [U_\alpha + kT \ln f_\alpha] = 0. \quad (11)$$

This equation has a simple physical interpretation: it is the average torque balance for all α molecules oriented as \mathbf{s} . The first term in Eq. (11) is the microscopic friction torque experienced by a rotating molecule having average angular velocity $\boldsymbol{\omega}_\alpha$; the second term is the torque due to the free energy $U_\alpha + kT \ln f_\alpha$. Since the potential $U_\alpha = U_\alpha^{(em)} + U_\alpha^{(i)}$, the free-energy torque includes the external torque due to electromagnetic fields and the internal torque due to the equilibrium interaction with surrounding molecules. The entropy contribution $kT \ln f_\alpha$ accounts for the orientational diffusion of molecules. Inertial terms are neglected in the balance, consistently with the use of Einstein-Smoluchowski equations of rotational diffusion.

To obtain the balance of the average torques acting on all molecules per unit volume, we multiply the left side of Eq. (11) times f_α , integrate the result over the whole solid angle, and then sum over $\alpha = h, g, e$. Thus we obtain

$$\boldsymbol{\tau}_f + \boldsymbol{\tau}_{em} + \boldsymbol{\tau}_i + \boldsymbol{\tau}_d = \mathbf{0}, \quad (12)$$

where

$$\boldsymbol{\tau}_f = - \sum_{\alpha=h,g,e} \int d\Omega f_\alpha \frac{kT}{D_\alpha} \boldsymbol{\omega}_\alpha \quad (13)$$

is the total molecular friction torque,

$$\boldsymbol{\tau}_{em} = - \sum_{\alpha=h,g,e} \int d\Omega f_\alpha \mathbf{s} \times \bar{\nabla} U_\alpha^{(em)} \quad (14)$$

is the total electromagnetic external torque,

$$\boldsymbol{\tau}_i = - \sum_{\alpha=h,g,e} \int d\Omega f_\alpha \mathbf{s} \times \bar{\nabla} U_\alpha^{(i)} \quad (15)$$

is an internal torque due to intermolecular interactions, and

$$\boldsymbol{\tau}_d = - \sum_{\alpha=h,g,e} \int d\Omega f_\alpha \mathbf{s} \times \bar{\nabla} kT \ln f_\alpha \quad (16)$$

is a torque associated with orientational diffusion.

We now prove that $\boldsymbol{\tau}_d = \mathbf{0}$ and $\boldsymbol{\tau}_i = \mathbf{0}$. The first result descends from the mathematical identity

$$\int d\Omega \mathbf{s} \times \bar{\nabla} a(\mathbf{s}) = 0, \quad (17)$$

valid for any function $a(\mathbf{s})$. To prove that $\boldsymbol{\tau}_i$ vanishes we make use of the general symmetry properties of intermolecular interaction potential $U_{\alpha\beta}$. By Eq. (9), indeed, we have

$$\begin{aligned} \boldsymbol{\tau}_i &= \sum_{\alpha,\beta} \int d\Omega \int d\Omega' f_\alpha(\mathbf{s}) f_\beta(\mathbf{s}') \mathbf{s} \times \bar{\nabla} U_{\alpha\beta}(\mathbf{s} \cdot \mathbf{s}') \\ &= \sum_{\alpha,\beta} \int d\Omega \int d\Omega' f_\alpha(\mathbf{s}) f_\beta(\mathbf{s}') \mathbf{s} \times \mathbf{s}' \frac{dU_{\alpha\beta}}{d(\mathbf{s} \cdot \mathbf{s}')} \\ &= \sum_{\beta,\alpha} \int d\Omega' \int d\Omega f_\beta(\mathbf{s}') f_\alpha(\mathbf{s}) \mathbf{s}' \times \mathbf{s} \frac{dU_{\beta\alpha}}{d(\mathbf{s}' \cdot \mathbf{s})} \\ &= - \sum_{\alpha,\beta} \int d\Omega \int d\Omega' f_\alpha(\mathbf{s}) f_\beta(\mathbf{s}') \mathbf{s} \times \mathbf{s}' \frac{dU_{\alpha\beta}}{d(\mathbf{s} \cdot \mathbf{s}')} \\ &= - \boldsymbol{\tau}_i. \end{aligned}$$

Therefore $\boldsymbol{\tau}_i = \mathbf{0}$. The vanishing of $\boldsymbol{\tau}_d$ and $\boldsymbol{\tau}_i$ corresponds to the statement that the sum of all internal torques exchanged between molecule orientational degrees of freedom vanishes. Note that $\boldsymbol{\tau}_i$ would not vanish exactly anymore if spatial gradients were included in the mean-field potential. The residual nonzero value would then account for the elastic torque.

We are thus left with the balance between the average external electromagnetic torque and the average friction torque, i.e.,

$$\boldsymbol{\tau}_f + \boldsymbol{\tau}_{em} = \mathbf{0}. \quad (18)$$

This equation, obtained from the molecular model, must correspond to the macroscopic Eq. (3) for the balance of torques. In the latter, we set $\boldsymbol{\tau}_{el} = \mathbf{0}$, because we assumed that there are no spatial gradients, and we neglect the inertial term on the left-hand side. Identifying the molecular expression of the electromagnetic torque appearing in Eq. (18) with the macroscopic one appearing in Eq. (3), we obtain

$$\boldsymbol{\tau}_f = \boldsymbol{\tau}_v + \boldsymbol{\tau}_{ph}. \quad (19)$$

At a molecular level, therefore, both viscous and photoinduced torques must be interpreted as friction torques. The reason why the photoinduced torque is associated to friction is that light absorption results in a continuous rotational drift of dye molecules, as will be shown in the next section. A molecular friction torque corresponds to an angular momentum transfer between a rotating molecule and its neighbor molecules, due to intermolecular interactions. For a single molecule, we might expect such exchange to be both with center-of-mass and orientational degrees of freedom of neighbor molecules. However, the total average friction torque $\boldsymbol{\tau}_f$ is entirely exchanged with the center-of-mass degrees of freedom. Indeed, it plays the role of an external torque in Eq. (18), which describes the balance of angular momentum for all molecule orientational degrees of freedom. This interpretation of the photoinduced torque is clearly consistent with the results of the macroscopic analysis of Sec. II.

V. PHOTOINDUCED TORQUE MOLECULAR EXPRESSION

To simplify our analysis, let us suppose now that an external field, for example, a static magnetic field, balances everywhere the optical torque (including the photoinduced contribution), so that the molecular director is at equilibrium, i.e., $d\mathbf{n}/dt = \mathbf{0}$. The electromagnetic torque $\boldsymbol{\tau}_{em}$ will then include both the static magnetic torque and the ordinary optical torque due to polarization. Moreover, the viscous torque $\boldsymbol{\tau}_v$ vanishes. Therefore, the photoinduced torque molecular expression is given by the whole friction torque, i.e., $\boldsymbol{\tau}_{ph} = \boldsymbol{\tau}_f$, where $\boldsymbol{\tau}_f$ is given by Eq. (13).

The molecular director being still, the system can reach a steady state. The equations describing the steady state are obtained from Eqs. (6) by setting $\partial f_\alpha / \partial t = 0$. Let us consider first the case of zero light intensity and external fields. Then we have $W_\alpha = 0$ and $U_\alpha^{(em)} = 0$, and Eqs. (6) are formally solved by the Boltzmann distribution

$$f_\alpha^{(eq)} = A_\alpha e^{-U_\alpha^{(i)}/kT}, \quad (20)$$

where A_α are normalization constants. In particular $A_e = 0$ and $f_e^{(eq)} = 0$, as without light no dye molecules are excited, while A_g and A_h are fixed by the dye and host number densities N_d and N_h . Actually, Eqs. (20) are a set of self-consistent Maier-Saupe integral equations, since the distributions $f_\alpha^{(eq)}$ appear also in the mean-field expression, in Eq. (9). If Eq. (20) is inserted into Eq. (8), we obtain $\mathbf{J}_\alpha = \mathbf{0}$ and therefore $\boldsymbol{\omega}_\alpha = \mathbf{0}$ and $\boldsymbol{\tau}_{ph} = \mathbf{0}$, as expected.

Let us now introduce the light wave and the external magnetic field. It is convenient to set $f_\alpha = f_\alpha^{(0)} + f'_\alpha$, where the $f_\alpha^{(0)}$ are a set of auxiliary Boltzmann distributions defined as

$$f_\alpha^{(0)} = B_\alpha e^{-U_\alpha/kT}, \quad (21)$$

where U_α are now the total potentials. The normalization constants B_α are defined in the same way as the A_α ; in particular $A_e = 0$, so that $f_e^{(0)} = 0$. We point out that the auxiliary functions $f_\alpha^{(0)}$ are not exactly equal to the equilibrium distributions $f_\alpha^{(eq)}$. The contribution to the rotational currents \mathbf{J}_α due to the Boltzmann terms $f_\alpha^{(0)}$ vanishes identically. Therefore, the currents can be written as

$$\mathbf{J}_\alpha = -D_\alpha \bar{\nabla} f'_\alpha - \frac{D_\alpha}{kT} (\bar{\nabla} U_\alpha) f'_\alpha. \quad (22)$$

For host molecules $W_h = 0$ and Eq. (6) is satisfied by setting simply $f'_h = 0$; i.e., the total distribution is given exactly by a Boltzmann function $f_h = f_h^{(0)}$. Therefore $\mathbf{J}_h = \mathbf{0}$ and $\boldsymbol{\omega}_h = \mathbf{0}$. This is not the case of dye molecules. In fact, the photoinduced transition terms W_e and $W_g = -W_e$ provide a nonzero source to the current fields \mathbf{J}_α , in Eq. (6). Consequently the dye currents \mathbf{J}_e and \mathbf{J}_g and the corresponding angular velocities $\boldsymbol{\omega}_e$ and $\boldsymbol{\omega}_g$ do not vanish, even at steady state, as pointed out already in Ref. [7]. This implies that dye molecules are continuously rotating as a result of photoinduced transitions and of intermolecular interactions. We emphasize that such rotation is totally unrelated to the angular velocity of the molecular director (which vanishes at steady state). A steady-state nonzero rotational current, and there-

fore molecule angular velocity, is not at all incompatible with stationary orientational distributions f_α . Even with no light absorption, the average angular velocity of molecules is not equal to the angular velocity of the molecular director, except when they are both zero.

Since at steady state $\boldsymbol{\tau}_{ph} = \boldsymbol{\tau}_f$ and $\boldsymbol{\omega}_h = \mathbf{0}$, from Eq. (13) we obtain the following molecular expression of the photoinduced torque:

$$\begin{aligned} \boldsymbol{\tau}_{ph} &= - \int d\Omega \left(f_g \frac{kT}{D_g} \boldsymbol{\omega}_g + f_e \frac{kT}{D_e} \boldsymbol{\omega}_e \right) \\ &= - \frac{kTN_g}{D_g} \bar{\boldsymbol{\omega}}_g - \frac{kTN_e}{D_e} \bar{\boldsymbol{\omega}}_e, \end{aligned} \quad (23)$$

where the overbar here denotes average over all orientations. If the dye diffusion constant is independent of the electronic state, i.e., $D_e = D_g = D$, then we have $\boldsymbol{\tau}_{ph} = -(kTN_d/D) \bar{\boldsymbol{\omega}}$ where $\bar{\boldsymbol{\omega}} = (N_e \bar{\boldsymbol{\omega}}_e + N_g \bar{\boldsymbol{\omega}}_g) / N_d$ is the average angular velocity of all dye molecules. For typical values of the photoinduced torque achieved in the experiments, we estimate $\bar{\boldsymbol{\omega}} \approx 10^3$ rad/s.

Equation (23) could be used to calculate explicitly the photoinduced torque by solving Eq. (6) to find the distributions f_α and then using Eqs. (8) and (10) to calculate the angular velocities $\boldsymbol{\omega}_\alpha$. However, this is a very difficult task if no approximations are introduced. We do it now by assuming that the system deviation from equilibrium is small. More precisely, we require that f'_e and f'_g be very small compared to $f_h^{(0)}$ or $f_g^{(0)}$. This is verified in two cases: (i) if the total dye concentration is small, i.e., $N_d \ll N_h$, for any value of light intensity; (ii) if light intensity is small, so that $f'_e \ll f_g$ and $f'_g \ll f_g$, for any value of dye concentration, and in particular in the case of a pure light-absorbing LC. Since the functions f'_α are small, they can be completely neglected when calculating the mean-field potentials $U_\alpha^{(i)}$. Moreover, the photoinduced torque is also small and therefore the magnetic field used to balance it is weak. This implies that $U_\alpha^{(em)}$ can be also neglected with respect to $U_\alpha^{(i)}$. Therefore, the approximation $f_\alpha^{(0)} \approx f_\alpha^{(eq)}$ is valid, and the mean fields $U_\alpha^{(i)}$ can be identified with their equilibrium limit. The potentials $U_\alpha^{(i)}$ calculated using the equilibrium distributions $f_\alpha^{(eq)}$ are independent of the functions f'_α and can be considered as given functions of s .

Another expression for the torque $\boldsymbol{\tau}_{ph}$ can be obtained from Eq. (23), with the help of Eqs. (10), (17), and (22), and neglecting $U^{(em)}$ with respect to $U^{(i)}$:

$$\boldsymbol{\tau}_{ph} = \int d\Omega \mathbf{s} \times (f'_e \bar{\nabla} U_e^{(i)} + f'_g \bar{\nabla} U_g^{(i)}). \quad (24)$$

With the same approximations, Eqs. (6) are rewritten as

$$D_e \bar{\nabla}^2 f'_e + \frac{D_e}{kT} \bar{\nabla} \cdot (f'_e \bar{\nabla} U_e^{(i)}) = -p(f_g^{(eq)} + f'_g) + \frac{1}{\tau_e} f'_e, \quad (25)$$

$$D_g \bar{\nabla}^2 f'_g + \frac{D_g}{kT} \bar{\nabla} \cdot (f'_g \bar{\nabla} U_g^{(i)}) = p(f_g^{(eq)} + f'_g) - \frac{1}{\tau_e} f'_e.$$

Since the mean fields $U_e^{(i)}$ and $U_g^{(i)}$ can be considered as given, Eqs. (25) are linear in the unknown functions f'_e and f'_g . They can be solved rather easily, either with numerical methods [7], or with approximate analytical methods as shown in Sec. VII. Next, inserting the solutions in Eq. (24) and calculating the integral we may obtain the photoinduced torque value.

Equation (24) is equal to the ‘‘naive’’ expression that one would write immediately by considering the populations of dye molecules involved in the photoinduced electronic transitions as an ‘‘external field’’ acting on the molecular director. This ‘‘naive’’ point of view was adopted by several authors working on this subject, but it was rejected in Ref. [7]. Moreover, the ‘‘naive’’ argument cannot be applied in a straightforward way to the case of a pure absorbing LC, as in the experiments reported in Ref. [10]. In this work, we justify the ‘‘naive’’ approach with a rigorous derivation, valid also for a pure LC.

We point out that the expression of τ_{ph} given by Eq. (24) is not exactly the same as that reported in Ref. [7] [at Eq. (17)]. In Ref. [7], an additional factor μ was introduced, due to an analysis of angular momentum conservation, which in our opinion is not correct because it does not take into account rotational friction and the center-of-mass contribution to the angular momentum balance. Our expression is instead substantially the same as that given in Eq. (10) of Ref. [7], where it is interpreted as an internal torque between dye and host molecules, but not identified with the observable photoinduced torque.

VI. MICROSCOPIC ENERGY BALANCE

Being associated with a continuous rotational drifts of dye molecules, the photoinduced torque requires a continuous dissipation of free energy in the system. This energy is supplied by the absorbed light. To see it, consider the power dissipated per unit volume by the friction torques:

$$P = \sum_{\alpha=g,e} \int d\Omega \frac{kT}{D_\alpha} \omega_\alpha^2 f_\alpha = \sum_{\alpha=g,e} \int d\Omega \frac{kT}{D_\alpha} \mathbf{J}_\alpha \cdot \frac{\mathbf{J}_\alpha}{f_\alpha}. \quad (26)$$

Next, the factor $\mathbf{J}_\alpha/f_\alpha$ is calculated by means of Eq. (8). The result is then integrated by parts, obtaining

$$P = \sum_{\alpha=g,e} \int d\Omega (U_\alpha^{(i)} + kT \ln f_\alpha) \bar{\nabla} \cdot \mathbf{J}_\alpha. \quad (27)$$

At steady state, according to Eqs. (6), we can substitute the transition rate W_α for the divergence of \mathbf{J}_α , obtaining

$$P = \int d\Omega [(U_e^{(i)} + kT \ln f_e) - (U_g^{(i)} + kT \ln f_g)] W_e. \quad (28)$$

This equation states that the power dissipated in the system to sustain the photoinduced torque is equal to the orientational free energy provided per unit time by the light-induced electronic transitions. Of course this energy is only a fraction of the total energy absorbed from light in the system.

VII. APPROXIMATE ANALYTICAL EXPRESSION OF PHOTOINDUCED TORQUE

In this section, an analytical expression of the photoinduced torque parameter ζ is obtained in the limit of small dye anisotropy and small light intensity. To this purpose, we need first to introduce an explicit expression of the mean fields $U_e^{(i)}$ and $U_g^{(i)}$. A reasonable choice is provided by the standard Maier-Saupe form

$$U_\alpha^{(i)} = -\frac{1}{2} u_{\alpha h} S N_h (\mathbf{s} \cdot \mathbf{n})^2, \quad (29)$$

where S is the host order parameter and u_{eh}, u_{gh} are coefficients describing the dye-host orientational interaction strength. Equation (29) and the following equations in this section can be applied also to the case of a pure absorbing LC if the label h is replaced with g .

The limit of small dye anisotropy is here obtained as a truncated power expansion in the parameters Su_{eh} and Su_{gh} , supposed small. To first order, the mean fields $U_e^{(i)}$ and $U_g^{(i)}$ in Eqs. (25) can be completely neglected, when calculating the functions f'_e and f'_g . Moreover, for small light intensity, the term f'_g can be neglected compared to $f_g^{(\text{eq})}$ on the right-hand side of Eqs. (25). After these approximations are introduced, the solution to Eqs. (25) can be sought in the form $f'_\alpha = a_\alpha + b_\alpha (\mathbf{s} \cdot \mathbf{e})^2$, where \mathbf{e} is a unit vector oriented as the optical electric field. Three of the four coefficients a_α and b_α are then determined by the equations themselves. The last one can be determined by imposing the conservation of the total dye number density N_d . Thus, we obtain

$$\begin{aligned} f'_e &= \frac{N_d}{4\pi} \sigma \langle E^2 \rangle \frac{\tau_e}{1 + 6D_e \tau_e} [2D_e \tau_e + (\mathbf{s} \cdot \mathbf{e})^2] + O(u_{eh} S), \\ f'_g &= -\frac{N_d}{4\pi} \sigma \langle E^2 \rangle \frac{\tau_e}{1 + 6D_e \tau_e} \left[2D_e \tau_e + \frac{1}{3} \left(1 - \frac{D_e}{D_g} \right) \right. \\ &\quad \left. + \frac{D_e}{D_g} (\mathbf{s} \cdot \mathbf{e})^2 \right] + O(u_{gh} S). \end{aligned} \quad (30)$$

Substituting Eqs. (29) and (30) into Eq. (24), we obtain the photoinduced torque. As expected τ_{ph} turns out to be given by Eq. (2), with the material constant ζ given by

$$\zeta = \frac{16\pi}{15} \sigma N_d S \frac{\tau_e N_h}{1 + 6D_e \tau_e} \left(u_{eh} - \frac{D_e}{D_g} u_{gh} \right) + O(u_{h\alpha} S)^2. \quad (31)$$

The factor σN_d is related to the absorption coefficients α_e and α_o for extraordinary and ordinary waves, respectively, by the following relationship:

$$\sigma N_d = \frac{c(n_e \alpha_e + 2n_o \alpha_o)}{8\pi h \nu}. \quad (32)$$

We are now in the position of identifying the molecular parameters, which are most important in determining the strength of the photoinduced torque, for a given dye concentration N_d . One is the absorption cross section σ , which can be easily determined from linear absorption measurements. Another one is the characteristic decay time τ_d of the non-

equilibrium dye distributions, which in our approximation is given by $\tau_d = \tau_e / (1 + 6D_e \tau_e)$, and which can be determined by means of time-resolved fluorescence experiments [23]. A third parameter quantifies the change Δu occurring in the intermolecular interactions of a dye molecule with its environment when it is electronically excited. In our approximation it is given by $\Delta u = [u_{eh} - u_{gh}(D_e/D_g)]N_h$; i.e., it depends on both the mean-field change and the change in the rotational diffusion coefficients D_α or equivalently in the friction coefficients kT/D_α . Preliminary experimental results indicate that the contribution of D_e/D_g (not considered in Ref. [7]) can be quite important. The factor Δu is clearly the most sensitive to the molecular structures of the dye guest and also of the nematic host. It could be obtained independently using time-resolved fluorescence and absorption experiments. If the reasonable values $\Delta u \sim 0.1$ eV, $\tau_d \sim 1$ ns, and the absorption coefficient $\alpha \sim 100$ cm⁻¹ are assumed, we obtain $\zeta \sim 100$, which is the observed order of magnitude in the most effective guest-host mixtures.

The role of friction was recognized already in Ref. [10], where the study of light-induced reorientation of a bidimensional nematic Langmuir film of absorbing molecules is reported. The material constituting the film is pure, not a mixture. The reported effect can be considered as the bidimensional analog of the effect studied in this paper. However, the model presented in Ref. [10] is also not quite correct. Indeed, it is based on the incorrect assumption that the average angular velocity of the molecules is equal to the angular velocity of the molecular director, i.e., of the center of the orientational distribution. By applying our Eq. (24) to the problem of Ref. [10], a different expression for the light-induced friction torque Γ_a is obtained [instead of Eq. (17) of Ref. [10]]. In the notations of Ref. [10], we obtain

$$\Gamma_a = \frac{I\sigma\tau_e}{2h\nu} (W_0^* - W_0) \sin(2\psi_0) \Delta^2. \quad (33)$$

Note that in Eq. (33) only the energy difference $W_0^* - W_0$ [corresponding in our notations to $(u_{eh} - u_{gh})N_h$] is relevant,

while rotational diffusion or friction is not. This is the consequence of the implicit assumption made in Ref. [10] that rotational diffusion is very slow, and therefore that $f'_g = -f'_e$ [this assumption is used in Eqs. (12) and (13) of Ref. [10]]. Note that, within this approximation, the ground state population f_g is never really at steady state, because its relaxation is actually controlled only by diffusion. This is not a realistic approximation for continuous-wave illumination. Note, moreover, that the ‘‘friction coefficient’’ η defined in Ref. [10] [Eq. (6)] is not a true friction coefficient, but rather a ratio between friction and mean-field strength.

VIII. CONCLUSIONS

In summary, the main results of the present work are as follows: (i) we have shown that the law of angular momentum conservation imposes the existence of a photoinduced stress tensor, acting on the LC flow variables, together with the photoinduced torque acting on the molecular director; if spatial modulations of light are present so that the stress-tensor gradients give rise to volume forces, a measurable photoinduced flow should be possible; (ii) a molecular expression of the photoinduced torque valid also in the case of a pure absorbing LC has been derived from a microscopic model with a rigorous procedure; this expression corrects that reported in Ref. [7]; (iii) we identified the role of molecular friction behind the angular momentum transfer described by the photoinduced torque; (iv) an approximate analytical expression of the photoinduced torque has been derived.

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