

Molecular interpretation of the absorption-induced optical reorientation of nematic liquid crystals

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A molecular mechanism is proposed to explain the anomalous optical reorientation observed in nematic guest-host systems. According to the model, light-induced reorientation in these systems is due to the interaction between the excited dye molecules and the nematic host. The model justifies a phenomenological description given earlier. Numerical results, based on the present model, are in agreement with the observed order of magnitude of the effect.

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I. INTRODUCTION

The interaction of light with nematic liquid crystals attracted considerable attention in the past [1–3]. One of the problems studied in detail is the orienting action exerted by an optical field in nematic films. The basic mechanism of the light-induced orientation process in transparent nematics is the interaction between the electric field of the light beam and the induced electrical polarization of the nematic molecules. Similarly to the case of static fields, the volume torque Γ^{opt} exerted by the electromagnetic field on the nematic molecules is

$$\Gamma^{\text{opt}} = \epsilon_0 \epsilon_a (\mathbf{n} \cdot \mathbf{E})(\mathbf{n} \times \mathbf{E}), \quad (1)$$

where \mathbf{n} is the director, \mathbf{E} denotes the electric field strength, $\epsilon_a = n_e^2 - n_0^2$. n_e and n_0 are the extraordinary and ordinary refractive indices, respectively.

Recent experiments with nematics disclosed that in the presence of absorbing dyes another orienting mechanism exists also, which can be much stronger than the “direct” mechanism described above. For example, it was found that doping a nematic host with 1% of 1,8-dihydroxy, 4,5-diamino, 2,7 diisopentyl-anthraquinone reduces the optical Fréedericksz threshold by two orders of magnitude compared to its value in the pure host [4]. Further experiments showed that the dyed systems behave in every aspect as if, due to the dye, the optical torque would have increased by a huge factor [5]. However, the relevant material parameters (i.e., the refractive indices) turned out to be practically unaffected by the doping.

Motivated by the above observations, we proposed that in guest-host systems the light-induced torque is a superposition of the direct optical torque [Eq. (1)] and a “dye-induced” torque, the latter arising from the interaction between the excited molecules and the nematic host [5,6]. In order to give a consistent description of the experimental facts, it was suggested that the dye-induced torque has the same form as the time-averaged optical torque:

$$\Gamma^{\text{dye}} = \eta \langle \Gamma^{\text{opt}} \rangle$$

or

$$\Gamma^{\text{dye}} = \epsilon_0 \zeta \langle (\mathbf{n} \cdot \mathbf{E})(\mathbf{n} \times \mathbf{E}) \rangle \quad \text{with } \zeta = \epsilon_a \eta. \quad (2)$$

Here ζ is a dimensionless new parameter, which—apart from being proportional to the concentration—depends only on the structure of the particular dye, dissolved in the nematic host. According to recent experimental results, the quantity ζ/α (α : absorption coefficient) is of the order of 0.1–1 cm; its sign was found to be positive for some dyes and negative for others [7].

The aim of the present paper is to interpret the effect of absorption on the optical reorientation, using a molecular description. The basic assumption is that the anomalous reorientation of the director results from the interaction between the excited dye molecules and the host. In Sec. II we develop a simple mean-field model to determine this interaction. In the model it is assumed that the strength of the mean field acting on the dye molecules is different in the ground state and in the excited state. The orientational distributions of the ground-state and excited molecules are obtained through two coupled diffusion equations. The coupling arises from the light-induced transitions from the ground state to the excited state and from the inverse transitions, caused by spontaneous emissions.

From the model, we determine the angular velocity of the dye molecules. With no absorbed radiation, the average angular velocity is zero. On the other hand, in the presence of absorption, the angular velocity of the dye molecules does not vanish, not even when the orientational distributions are in steady state. The internal angular momentum of the system associated with this rotation plays a central role in our considerations. In Sec. III we point out that when the dye molecules are set to rotation by the internal interactions, the system as a whole should start to rotate in the opposite sense, because the total angular momentum cannot change. This condition allows us to determine the director angular velocity as a function of the parameters of the model. The dye-induced torque can be formally defined as an equivalent external torque which would produce the same director rotation.

In Sec. IV the limit of small light intensities is discussed. It is shown that in this limit, the theory justifies the phenomenological relation given above [Eq. (2)]. In

Sec. V we demonstrate that, using reasonable numbers for the relevant parameters, the model reproduces the experimentally established order of magnitude of the effect. Finally, in Sec. VI, some further possible experiments are proposed which could help to verify the ideas presented in the paper.

II. THE MODEL

We investigate rodlike dye molecules, dissolved in a nematic host. The interaction energy of the dye molecules with the surrounding nematic host is considered in a mean-field approximation, i.e., it is assumed that it depends only on the orientation of the dye molecules relative to the nematic director \mathbf{n} . In the absence of irradiation, when all dye molecules are in a ground state, the interaction energy of a given molecule with the host material is $U_g(\mathbf{s})$; \mathbf{s} is a unit vector parallel to the rod axis of the dye molecule. Excitation by the optical field transforms a fraction of the dye molecules into a metastable excited state with a lifetime of τ . In the excited state, the electronic structure of the molecule is different from that in the ground state, hence the interaction energy is changed from $U_g(\mathbf{s})$ to $U_e(\mathbf{s})$. We do not specify here the form of the mean-field interaction energies, it is only assumed that they are compatible with the nematic symmetry, i.e., they are invariant to the transformation $\mathbf{s} \rightarrow -\mathbf{s}$ and are axially symmetric around the director.

In the following, we determine the orientational distribution of the excited- and ground-state dye molecules in the presence of a linearly polarized light beam. Three processes are considered: excitation by the optical field, transitions from the excited state to the ground state, and rotational diffusion of the dye molecules. For simplicity, we suppose that no external field acts on the dye molecules, not even the direct optical torque.

We consider dyes of positive dichroism with the transition dipole moment parallel to the rod axis [8]. The probability of excitation per unit time for a ground-state dye molecule with orientation \mathbf{s} can be written as

$$p(\mathbf{s}) = \Lambda \langle E^2 \rangle (\mathbf{e} \cdot \mathbf{s})^2. \quad (3)$$

Here \mathbf{e} is a unit vector in the direction of the light polarization; Λ is a parameter that depends on the molecular structure of the dye and the wavelength of the exciting radiation. The time averaging refers to a time interval long compared to the period of oscillation of the electromagnetic field, but short compared to the characteristic time of the rotational movement of the molecules. The number of excitations per unit time, volume, and solid angle is $p(\mathbf{s})f_g(\mathbf{s})$; the corresponding number of transitions from the excited state to the ground state is $f_e(\mathbf{s})/\tau$. Here $f_g d\Omega_s$ and $f_e d\Omega_s$ gives the number of ground-state and excited molecules, respectively, per unit volume oriented in an element of solid angle $d\Omega_s$ around \mathbf{s} .

In order to describe the rotational movement of the dye molecules, we adopt the diffusion model given by Nordio and Segre [9]. In this model it is supposed that the molecules reorient in the nematic potential through small angular steps. In the limit of infinitesimal steps, the

rotational diffusion of the rodlike dye molecules can be described in the same way as translational diffusion in a continuum [10], with the restriction that the particles can move only on the surface of a unit sphere. The "velocity" of the diffusing particles, \mathbf{v} , is $\boldsymbol{\omega} \times \mathbf{s}$, where $\boldsymbol{\omega}$ denotes the angular velocity vector of the dye molecules relative to the nematic host. The ground-state and excited molecules are considered to be separate components of the system.

Taking into account the transitions between the two states, the orientational distribution functions, f_g and f_e , are determined by the rate equations

$$\begin{aligned} \frac{\partial f_g}{\partial t} + \overline{\text{div}} \mathbf{J}_g &= -p f_g + \frac{f_e}{\tau}, \\ \frac{\partial f_e}{\partial t} + \overline{\text{div}} \mathbf{J}_e &= p f_g - \frac{f_e}{\tau}. \end{aligned} \quad (4)$$

The rotational diffusion currents, \mathbf{J}_g and \mathbf{J}_e , are defined as $f_g \mathbf{v}_g$ and $f_e \mathbf{v}_e$; the subscripts g and e refer to the ground-state and excited molecules, respectively. The currents are given by the constitutive equation:

$$\mathbf{J}_i = -D \overline{\nabla} f_i - D/kT (\overline{\nabla} U_i) f_i \quad (i = g, e). \quad (5)$$

The first term on the right-hand side of the above equation represents the rotational Brownian motion of the molecules, D is the relevant diffusion coefficient. The second term describes the drift motion of the molecules in the mean-field nematic potential with a mobility of D/kT . It is assumed that the diffusion constant is the same in the ground state and the excited state. The $\overline{\nabla}$ and $\overline{\text{div}}$ operators denote the angular part of the usual ∇ and div operators in spherical coordinates. With the help of Eqs. (3)–(5), f_g and f_e can be calculated for any specified form of the mean-field potentials, U_g and U_e .

In the absence of excitation, p and thus f_e are zero. In the steady state ($\partial f_i / \partial t = 0$), the solution of Eqs. (4) and (5) is $\mathbf{J}_g = \mathbf{0}$, which leads to the usual Boltzmann distribution:

$$f_g = f_0 = N_d e^{-U_g/kT} / \int e^{-U_g/kT} d\Omega_s, \quad (6)$$

where N_d denotes the number of dye molecules per unit volume.

In the presence of excitation, the \mathbf{J}_i currents differ from zero. Furthermore, the total rotational current, $\mathbf{J}_g + \mathbf{J}_e$, also has a finite value. In order to demonstrate this fact, we determine the average angular velocity of the dye molecules. Assuming that the component parallel to the rod direction is zero ($\boldsymbol{\omega} \cdot \mathbf{s} = 0$), the angular velocity can be given as

$$\boldsymbol{\omega}_i = (\boldsymbol{\omega}_i \times \mathbf{s}) \times \mathbf{s} = \mathbf{v}_i \times \mathbf{s}, \quad i = g, e. \quad (7)$$

The time average of the angular velocity of an individual dye molecule ($\overline{\boldsymbol{\omega}}_d$) can be obtained through averaging over the different orientations and electronic states:

$$\overline{\boldsymbol{\omega}}_d = \frac{1}{N_d} \int (f_g \boldsymbol{\omega}_g + f_e \boldsymbol{\omega}_e) d\Omega_s. \quad (8)$$

With the help of Eqs. (5), (7), and (8), after a short cal-

ulation one finds

$$\bar{\omega}_d = -\frac{D}{kTN_d}\Gamma^{\text{int}}, \quad (9)$$

where Γ^{int} is the volume torque exerted by the dye molecules on the nematic host:

$$\Gamma^{\text{int}} = -\int (\mathbf{M}_g f_g + \mathbf{M}_e f_e) d\Omega_s. \quad (10)$$

In the above relation, the quantities \mathbf{M}_g and \mathbf{M}_e denote the torques acting on a single ground-state or excited dye molecule, respectively,

$$\mathbf{M}_i = -(\bar{\nabla} U_i) \times \mathbf{s}, \quad i = g, e. \quad (11)$$

In the absence of excitation, $\bar{\omega}_d$ is zero. In the presence of absorption, however, the integral on the right-hand side of Eq. (10) does not vanish. To see this fact more clearly, we note that unless \mathbf{e} is parallel or perpendicular to \mathbf{n} , the f_i functions are not axially symmetric around the director. Consider, e.g., the case when the angle included between the polarization direction and the director is 45° and compare the excitation rates for dye molecules oriented parallel to the polarization ($\mathbf{s} \parallel \mathbf{e}$) and for the direction \mathfrak{s} , obtained through reflection of \mathbf{s} in a line parallel to the director. The angle between the director and the rod direction is in both cases 45° , yet the transition rate has a maximum for the dye molecules aligned along \mathbf{s} , while it is zero for those aligned along \mathfrak{s} (since $\mathfrak{s} \perp \mathbf{e}$). As a consequence of the difference in the excitation rates, the distribution functions belonging to the two directions differ too. On the other hand, the \mathbf{M}_i torques are antiparallel for \mathbf{s} and \mathfrak{s} . Because of the difference in $f_i(\mathbf{s})$ and $f_i(\mathfrak{s})$, the products $\mathbf{M}_i f_i$ in the two directions do not cancel each other and the integral has a finite value.

In general, the f_i functions can be decomposed to a symmetric and antisymmetric part with respect to the $\mathbf{s} \rightarrow \mathfrak{s}$ transformation; only the antisymmetric part contributes to the torque Γ^{int} .

From the above consideration, it follows that under light illumination Γ^{int} is finite, hence *the average angular velocity of the dye molecules does not vanish* [see Eq. (9)]. This fact is a key feature of our model.

The finite value of $\bar{\omega}_d$ implies that the dye molecules are rotating relative to the director. This rather unusual situation is a result of the processes on which our model is based. A crucial point is that the dye molecules exhibit two distinct electronic states and transitions occur between these states. In a "one-component" system, i.e., without transitions, a molecular field could not induce a continuous rotation. The orientationally selective excitation of the dye molecules (dichroism) and the change of the interaction energy upon excitation are also essential to have this effect. Finally, thermal fluctuations, i.e., the rotational diffusion of the molecules, also play an important role. Without thermal diffusion, the dye molecules would be perfectly aligned along the director, both in excited and in the ground state, thus internal rotation would not take place.

We call attention to the following aspects of the phenomenon.

(a) The internal rotation described above refers to individual dye molecules; it does *not* imply that the orientational distribution functions, characterizing the dye system, would also rotate relative to the director. $\bar{\omega}_d$ usually differs from zero even when the orientational distributions have reached a steady state. It should be emphasized that steady state and internal rotation are compatible with each other. In steady state, the number of dye molecules entering a given element of solid angle is equal to the number of dye molecules departing from this element during the same time. The nonvanishing average angular velocity means that slightly more dye molecules enter and depart from this element through (say) a clockwise rotation than through an anticlockwise rotation; nevertheless the number of molecules entering and leaving can be equal.

(b) The orientational distributions and $\bar{\omega}_d$ were determined with respect to a frame attached to the director. If the director rotates relative to the laboratory frame, the dye distribution functions follow the rotation. (This is a well-known effect for guest-host systems and provides the basis of a color display technique.) The average angular velocity of the dye molecules relative to the laboratory frame in this case is $\bar{\omega}_d + \omega_n$, where $\omega_n = \mathbf{n} \times \dot{\mathbf{n}}$ is the director angular velocity.

III. DETERMINATION OF THE ABSORPTION-INDUCED ROTATION OF THE DIRECTOR

A simple way to determine the rotation of the director during excitation would be to consider the field created by the dye molecules as an external one and identify Γ^{int} with the "dye-induced" torque. Such an assumption is, however, not valid, because the motion of the dye molecules is not independent from the director rotation.

In order to determine the director motion under the influence of radiation, we exploit the fact that—in as demonstrated in the preceding section—in the presence of absorption the average angular velocity of the dye molecules does not vanish.

Consider a certain volume of a uniformly oriented nematic sample, illuminated by an optical field. We suppose that initially there is no absorption and the normal optical torque is compensated by, say, a static magnetic field. Under such circumstances the director stays in a steady position. At a certain moment, let us "switch on" absorption, without destroying the balance between the direct optical torque and the magnetic torque. (This could be realized experimentally by shifting abruptly the wavelength of the light from a transparent part of the spectrum to the absorption band of the dye.) According to our considerations, the dye molecules will start to rotate relative to the director with an angular velocity of $\bar{\omega}_d$. Thus the dye gains a certain quantity of angular momentum. However, the rotation of the dye molecules is a result of *internal* interactions within the guest-host system, thus the *total* angular momentum of the system should remain zero. This requirement is fulfilled if, simultaneously with the dye, the director starts to rotate in the opposite sense than the dye.

The angular velocity of the director can be determined from the conservation law of angular momentum:

$$N_d J_d (\bar{\omega}_d + \omega_{\text{abs}}) + N_n J_n \omega_{\text{abs}} = 0. \quad (12)$$

Here J_d and J_n denote the moment of inertia of a dye molecule and of a nematic molecule, respectively, with reference to an axis perpendicular to their long axes. N_n and ω_{abs} are the number of nematic molecules per unit volume and the absorption-induced angular velocity of the director, respectively. Hence

$$\omega_{\text{abs}} = -\bar{\omega}_d \frac{N_d J_d}{N_n J_n + N_d J_d} = \frac{D}{k T N_n} \frac{J_d}{J_n + N_d / N_n J_d} \Gamma^{\text{int}}. \quad (13)$$

One may draw an analogy between the dye-induced reorientation process described above and the situation in the Einstein-de Haas experiment [11]. In the latter, a magnetic field generates a nonvanishing internal angular momentum (spin) in a suspended iron rod. At the same time, the iron lattice gains an equal amount of angular momentum of opposite sign, which can be detected as a torsional displacement of the system. The external magnetic torque, $\mathbf{M} \times \mathbf{H}$, is zero during the process.

In our case, the internal angular momentum is created by the optical field and is attached to the dye molecules, rotating relative to the director. The role of the iron matrix is played by the host material. There are, of course, important differences between the two cases. For example, in the magnetic rod a constant internal angular momentum can exist without continuous energy input. On the contrary, the rotation of the dye in the nematic is a dissipative process, which can only be preserved if there is a permanent transfer of energy from the optical field to the system. Furthermore, in the nematic we assume a pure rotation of the director, without translation, in contrast with the rigid body rotation of the lattice in the Einstein-de Haas experiment. In Appendix A we describe a possible experiment which could prove the validity of this latter supposition.

If external fields or elastic deformations are also present, we can assume that the director motion generated by the external and elastic torques is linearly superposed on the absorption-induced rotation of the director. Hence, according to the laws of nemato-hydrodynamics [12] (assuming no flow), the equation of motion for the director can be written as

$$\gamma_1 (\omega_n - \omega_{\text{abs}}) = \Gamma^{\text{ext}} + \Gamma^{\text{elast}}, \quad (14)$$

where γ_1 is the rotational viscosity of the nematic.

Equation (14) can be formally written also in the form

$$\gamma_1 \omega_n = \Gamma^{\text{ext}} + \Gamma^{\text{elast}} + \Gamma^{\text{dye}}, \quad (15)$$

where the "dye-induced" torque Γ^{dye} is defined as

$$\Gamma^{\text{dye}} = \gamma_1 \omega_{\text{abs}}. \quad (16)$$

(It should be noted, however, that regarding angular momentum transfer, Γ^{dye} cannot be considered as an external torque; see Appendix A.)

From Eqs. (13) and (16) one finds

$$\Gamma^{\text{dye}} = \mu \Gamma^{\text{int}} \quad \text{with} \quad \mu = \gamma_1 \frac{D}{k T N_n} \frac{J_d}{J_n + N_d / N_n J_d}. \quad (17)$$

If the dye and host molecules are not very different, we expect the factor μ to be of the order of unity. For small concentrations ($N_d / N_n \ll 1$) and for $J_d = J_n$, $\mu \approx \gamma_1 D / k T N_n$. The factor $k T N_n / D$ is of the same order of magnitude as the rotational viscosity: e.g., with $D = 2 \times 10^8$ 1/sec [14], $N_n = 2.5 \times 10^{21}$ cm⁻³ [corresponding to 4-cyano-4'-pentyl-biphenyl (5CB)], and at $T = 300$ K, $k T N_n / D = 0.5$ P, while a typical value of γ_1 is 1 P. For $\mu = 1$, the internal and the dye-induced torques are equal. In this special case, the dye-induced torque is equal to the internal torque produced by the dye molecules. In the following, for simplicity, we confine the discussion to this case.

IV. LIMIT OF LOW INTENSITIES

In the absence of illumination, no excited dye molecule is present, therefore $f_e = 0$ and the distribution function of the ground-state molecules, f_g , is equal to the unperturbed distribution function, f_0 :

$$f_0 = N_d e^{-U_g / k T} / \int e^{-U_g / k T} d\Omega_s.$$

In the limit of low intensities, f_e and the function $f_h = f_0 - f_g$ (distribution of "holes") can be expanded in power series of $\langle E^2 \rangle$, i.e., the intensity. Retaining only the linear terms, the rate equations [Eq. (4)] can be approximated as

$$\frac{\partial f_i}{\partial t} + \text{div} \mathbf{J}_i = p f_0 - \frac{f_e}{\tau} \quad (i = h, e), \quad (18)$$

with

$$\mathbf{J}_h = -D \bar{\nabla} f_h - D / k T (\bar{\nabla} U_g) f_h.$$

We use a coordinate system, in which the director is along the z axis and the polarization is in the x, z plane. The functions f_h and f_e can be written in the form

$$f_i = f_i^S + \frac{\Lambda \langle E^2 \rangle}{2D} \sin \Theta \cos \varphi Y_i(\theta) f_0 \quad (i = h, e), \quad (19)$$

where θ and φ are the polar and azimuthal angles, respectively, Θ is the angle between \mathbf{e} and \mathbf{n} . f_i^S is the symmetric part of f_i , which, as explained above, does not contribute to the dye-induced torque. The Y_i functions obey the differential equations

$$\begin{aligned} \frac{1}{D} \frac{\partial Y_h}{\partial t} - \left[\frac{\partial^2 Y_h}{\partial \theta^2} + A_1 \frac{\partial Y_h}{\partial \theta} + A_0 Y_h - \frac{Y_e}{D \tau} \right] &= \sin 2\theta, \\ \frac{1}{D} \frac{\partial Y_e}{\partial t} - \left[\frac{\partial^2 Y_e}{\partial \theta^2} + B_1 \frac{\partial Y_e}{\partial \theta} + \left[B_0 - \frac{1}{D \tau} \right] Y_e \right] &= \sin 2\theta. \end{aligned} \quad (20)$$

The A and B functions are

$$\begin{aligned} A_1 &= \cot \theta + M_g / k T, \quad A_0 = -1 / \sin^2 \theta, \\ B_1 &= A_1 + \frac{M_g - M_e}{k T}, \\ B_0 &= A_0 + \frac{M_g - M_e}{k T} A_1 + \frac{\partial (M_g - M_e) / \partial \theta}{k T}, \end{aligned}$$

where $M_g = -\partial U_g / \partial \theta$ and $M_e = -\partial U_e / \partial \theta$ denote the magnitude of the molecular torques.

The dye-induced optical torque has a y component only which can be expressed as

$$\Gamma_y^{\text{dye}} = -\frac{1}{2} \sin 2\Theta \frac{\Lambda \langle E^2 \rangle}{D} \pi \times \int_0^\pi (-M_g Y_h + M_e Y_e) \sin \theta f_0(\theta) d\theta. \quad (21)$$

One can write also

$$\Gamma^{\text{dye}} = \varepsilon_0 \zeta \langle E^2 \rangle (\mathbf{n} \cdot \mathbf{e}) (\mathbf{n} \times \mathbf{e}),$$

with

$$\zeta = -\frac{1}{2} \frac{\Lambda}{D} \pi \int_0^\pi (-M_g Y_h + M_e Y_e) \sin \theta f_0(\theta) d\theta$$

or

$$\Gamma^{\text{dye}} = \eta \langle \Gamma^{\text{opt}} \rangle \quad (\eta = \zeta / \varepsilon_a). \quad (22)$$

By comparison with Eq. (2), it can be seen that for low intensities the model justifies the phenomenological relation, proposed for the dye-induced torque on the basis of experimental evidence. The above considerations were carried out for a linearly polarized light beam; in Appendix B we prove that Eq. (10) holds for elliptically polarized optical fields too.

For high intensities, the model predicts a breakdown of the linear relation between Γ^{dye} and $\langle \Gamma^{\text{opt}} \rangle$. The breakdown is connected to the saturation of the dye absorption at high excitation rates; it could be observed probably in reorientation experiments with nanosecond pulses.

V. ESTIMATION OF THE ζ COEFFICIENT

In order to estimate the magnitude of ζ , we use the Maier-Saupe form of the mean-field potentials [13], namely, we assume that

$$U_g(\mathbf{s}) = C - u_g (\mathbf{n} \cdot \mathbf{s})^2, \quad U_e(\mathbf{s}) = C' - u_e (\mathbf{n} \cdot \mathbf{s})^2. \quad (23)$$

The magnitude of C and C' is irrelevant in the present context. Regarding the u_i parameters, we suppose that these quantities are of the same order of magnitude as the nematic potential for the host molecules, i.e., they are a few times larger than the thermal energy, kT . For u_g , this assumption is supported by the fact that the orientational order parameter of the ground-state dye molecules is usually comparable to that of the nematic molecules. Although there is no direct experimental information on u_e , it seems reasonable to assume that it is of the same order of magnitude as u_g .

The parameter Λ can be expressed with the help of the (linear) absorption coefficients of the guest-host system. Taking into account that the absorbed electromagnetic energy is equal to the number of excitations, multiplied by the photon energy, we can write

$$\alpha I = h\nu \int p(\mathbf{s}) f_0 d\Omega_s = h\nu \Lambda \langle E^2 \rangle \int (\mathbf{e} \cdot \mathbf{s})^2 f_0 d\Omega_s, \quad (24)$$

where I is the light intensity and α is the absorption coefficient belonging to the polarization direction \mathbf{e} . Taking into account that $I = nc\varepsilon_0 \langle E^2 \rangle$ and applying the

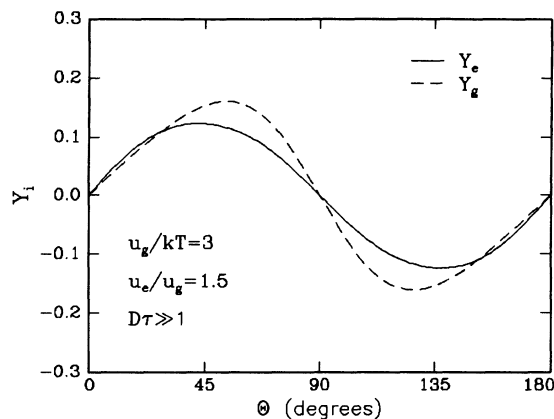


FIG. 1. An example of the Y_i functions.

above relation for the cases $\mathbf{e} \parallel \mathbf{n}$ (ordinary ray, $\alpha = \alpha_{\parallel}, n = n_o$) and $\mathbf{e} \perp \mathbf{n}$ (extraordinary ray $\alpha = \alpha_{\perp}, n = n_e$) leads to the relation

$$\Lambda = \varepsilon_0 \frac{3cn_0 \bar{\alpha}}{h\nu N_d} \quad \text{with } \bar{\alpha} = (2\alpha_{\perp} + n_e/n_o \alpha_{\parallel})/3.$$

From the above result, ζ can be written in the form

$$\zeta = \frac{3cn_0 \bar{\alpha}}{2D} \frac{kT}{h\nu} \xi, \quad (25)$$

with

$$\xi = \frac{1}{kT} \frac{\int_0^\pi (-M_g Y_h + M_e Y_e) \sin \theta e^{-U_g/kT} d\theta}{\int_0^\pi \sin \theta e^{-U_g/kT} d\theta}.$$

Numerical calculations were carried out for steady state ($\partial f_i / \partial t = 0$). In Fig. 1, the Y_i functions are plotted for a particular set of the mean-field parameters. In Figs. 2 and 3, results for the ξ coefficient are shown. The different curves represent different values of u_e/u_g . As the figures show, for $u_e = u_g$ the effect vanishes; ξ (and therefore ζ) is positive for $u_e > u_g$ and negative for $u_e < u_g$. In Fig. 2, the dependence of ξ on the lifetime of the excited state is demonstrated. For short lifetimes, the

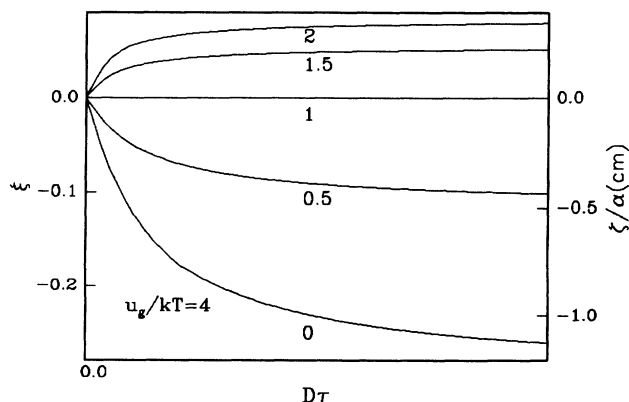


FIG. 2. ξ and ζ/α as a function of the lifetime of the excited state. The numbers at the curves indicate the value of u_e/u_g .

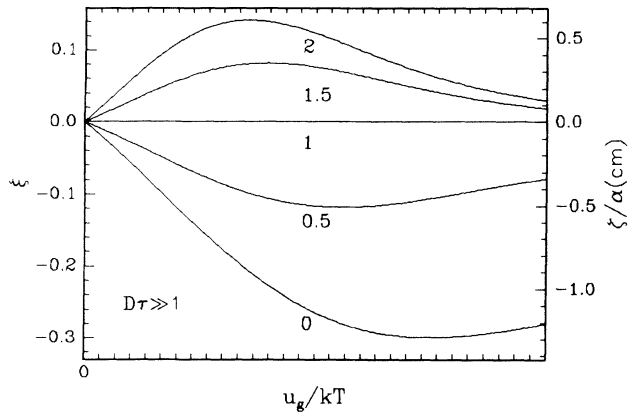


FIG. 3. ξ and ζ/α as a function of the ground-state mean-field potential. The numbers at the curves indicate the value of u_e/u_g .

rotational diffusion of the excited molecules can be neglected and the dye-induced torque is proportional to τ . In the opposite limit, $D\tau \gg 1$, ξ becomes independent from the lifetime. In Fig. 3, ξ is shown as a function of the ground-state potential u_g , in the long-lifetime limit.

On the right-hand scales, the $\zeta/\bar{\alpha}$ values correspond to $h\nu = 1.96$ eV (photon energy of the He-Ne laser), $kT = 0.025$ eV, and to a typical value of the rotational diffusion coefficient $D = 2 \times 10^8$ 1/sec [14]. With these values of the parameters, $\zeta/\bar{\alpha}$ is of the order of 1 cm, which is compatible with the experimentally observed values [7].

VI. CONCLUSIONS

According to the model presented in this paper, the anomalous optical reorientation in dyed nematic liquid crystals is due to the internal interaction between the excited dye molecules and the nematic host. We showed that as a result of this interaction, the dye molecules carry an internal angular momentum. The rotation of the director can be deduced from the law of angular momentum conservation. Regarding macroscopic motions, the absorption-induced rotation is equivalent to the presence of an external torque, Γ^{dye} . Using a mean-field description, we justified the empirical relation, according to which the dye-induced torque is proportional to the direct optical torque. Numerical calculations reproduced the experimentally established order of magnitude of the effect.

The average angular velocity of the dye molecules can be established, for usual experimental circumstances, in a simple way. From Eq. (13) it follows that for $J_n = J_d$ and small concentrations $\bar{\omega}_d = -\omega_{\text{abs}}/c_d$, where c_d is the dye concentration. A typical reorientation time of the director is a few seconds, thus $|\omega_{\text{abs}}|$ is of the order of 1 sec^{-1} . Hence with $c_d = 10^{-2}$ one finds $|\bar{\omega}_d| \approx 10^2 \text{ sec}^{-1}$. This is a very slow motion on a molecular scale; nevertheless, as demonstrated in the paper, this small perturbation is sufficient to have a strong effect on macroscopic phenomena.

The model does not include any detail of the molecular

structure, therefore it gives no direct explanation of the differences found in the magnitude and sign of the ζ parameter for various dyes [7]. According to our considerations, ζ depends on the structure through the mean-field potentials, u_g and u_e . An independent determination of u_g and u_e and a comparison with ζ for different dyes would allow us to check the basic ideas of the present theory. We note that u_g is related to the order parameter of the ground-state dye molecules and thus it can be easily determined. On the other hand, the experimental determination of u_e would require the measurement of the order parameter of the excited dye molecules. To our knowledge, such measurements have not been carried out.

Finally, it should be noted that our discussion refers to bulk reorientation processes and it has no direct connection with the recently reported light-induced surface-alignment phenomenon [15].

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APPENDIX A

Consider a certain volume of a transparent nematic, exposed to external torques. Appropriate boundary conditions are supposed, which prevent flow. Under such circumstances, the molecules constantly gain angular momentum from the external sources and transmit it, through collisions, to the surrounding part of the sample. The angular momentum dissipated from the external fields is finally transmitted to the boundaries of the sample and creates a torque on the walls of the cell.

The situation is different when the reorientation of the director is caused by the internal field of the dye molecules. As there is no angular momentum input to the volume, there cannot be any net transmitted angular momentum to the surrounding. Consequently, no torque should be observed on the walls.

The validity of this statement could be verified experimentally, for example, in the following way. In homeotropic layers, under the influence of circularly polarized radiation, undamped rotation of the director around the layer normal occurs [16]. In transparent nematics, the angular momentum dissipated by the nematic during the rotation is supplied by the light beam and it should correspond to an appropriate torque on the walls. In the presence of absorption, with otherwise unchanged conditions, the speed of the director rotation increases significantly [4]. However, according to our previous considerations, the torque on the walls should not change (i.e., should correspond to the direct part of the optical torque), because the dye-induced part of the rotation does not involve angular momentum transfer.

It may also be of interest to consider the angular momentum balance in static configurations of the director. In the presence of illumination, a static state can be regarded as the superposition of a dye-induced rotation of the director and a compensating rotation in the opposite sense, generated by an appropriate external torque.

The former rotation is not, the latter one is accompanied by angular momentum dissipation. Thus there should be a net angular momentum transfer to the walls (and a corresponding torque on them) even in an undeformed static director configuration. On a molecular level, the source of this torque is the internal angular momentum of the dye molecules, which is continuously transferred by collisions to the host molecules and from them to the boundaries of the cell.

APPENDIX B

The model can be extended to the case of an elliptically polarized optical field in the following way. Let \mathbf{e}_1 and \mathbf{e}_2 denote the unit vectors along the principal directions of the polarization ellipsoid of the light wave. The probability of excitation can be written as

$$p(\mathbf{s}) = p_1(\mathbf{s}) + p_2(\mathbf{s})$$

$$\text{with } p_l(\mathbf{s}) = \Lambda \langle E_l^2 \rangle (\mathbf{e}_l \cdot \mathbf{s})^2 \quad (l = 1, 2),$$

where E_l is the component of the electric field along \mathbf{e}_l . In the linear approximation, valid for low intensities, the dye-induced torque is the linear superposition of the contributions from the p_1 and p_2 terms. Hence

$$\Gamma^{\text{dye}} = \varepsilon_0 \xi \sum_{l=1,2} \langle E_l^2 \rangle (\mathbf{e}_l \cdot \mathbf{n})(\mathbf{e}_l \times \mathbf{n}). \quad (\text{B1})$$

On the other hand, the direct optical torque can be written as

$$\Gamma^{\text{opt}} = \varepsilon_0 \varepsilon_a (\{E_1 \mathbf{e}_1 + E_2 \mathbf{e}_2\} \cdot \mathbf{n})(E_1 \mathbf{e}_1 + E_2 \mathbf{e}_2) \times \mathbf{n}.$$

The time average of the terms containing the product $E_1 E_2$ vanishes, because the phase shift between E_1 and E_2 is $\pi/2$. Hence

$$\langle \Gamma^{\text{opt}} \rangle = \varepsilon_0 \varepsilon_a \sum_{l=1,2} \langle E_l^2 \rangle (\mathbf{e}_l \cdot \mathbf{n})(\mathbf{e}_l \times \mathbf{n}). \quad (\text{B2})$$

Comparing (B1) and (B2) shows that the relation $\Gamma^{\text{dye}} = \eta \langle \Gamma^{\text{opt}} \rangle$ ($\eta = \xi / \varepsilon_a$) is valid for elliptically polarized light waves too.

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