PHYSICAL REVIEW E VOLUME 62, NUMBER 3 SEPTEMBER 2000

Director rotation via photoinduced differential depletion in nematic dyes

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(Received 11 January 2000)

We revisit the problem of director realignment induced by photoisomerization of rodlike dye molecules. We find a geometrical basis for the rotational rate, arising by the differential depletion of rods from the nematic distribution. A simple expression, valid for arbitrarily strong, Maier-Saupe-like nematic order, is given for this rate. Contact is made with the weak order scaling limit given in the literature.

PACS number(s): 61.30.Gd, 42.65.−k, 42.70.Df, 64.70.Md

The *trans-cis* photoisomerization of rodlike dye molecules by the absorption of light changes their shape to a more spherical one. If such a dye liquid is nematic, the loss of molecules to a non-nematogenic state by photon absorption perturbs the distribution of the remaining rods. Depletion of rodlike molecules not only changes nematic order; polarized light incident on a nematic dye, or on a nematic with dye guest molecules, causes the director to rotate away from the polarization direction. The large literature of theory and experiment on laser-induced director rotation is discussed in two fundamental theoretical papers [1,2] where an important mechanism of photoalignment is described. Both these papers calculate a photoinduced torque $\boldsymbol{\tau}_{\mathrm{ph}} = \epsilon_o \zeta (\hat{\mathbf{n}} \cdot \mathbf{E})(\hat{\mathbf{n}} \times \mathbf{E})$ where $\mathbf{E}$ is the optical field, by analyzing the angular diffusion flux set up by photon absorption causing molecules to leave the nematic distribution. In particular, it was shown [2] that diffusion itself cannot lead to a torque, a conclusion we shall support. In [2], the torque is instead obtained by setting angular derivatives of the nematic potential equal to a mean molecular angular velocity, ω, times $k_B T/D_r$ where D_r is a rotational diffusion constant. By the fluctuation-dissipation theorem, D_r is related to an angular drag coefficient γ by $D_r \sim k_B T/\gamma$. Osipov and Terentjev [3] identify γ with the appropriate nematic viscosity [6] (Leslie) coefficient, γ_1. Hence the torque is quite plausibly $\tau \sim \gamma_1 \omega$.

Another approach is that of Zolot'ko [4], who considers the torques associated with the molecular potentials between nematic and dye molecules. When dye molecules are photoisomerized, the nematic-dye potential is changed and with it is changed the associated torque. Thus details of the intermolecular potentials are vital for the description. Additionally, one assumes for simplicity that the dye concentration is low. The same subtleties of torques addressed in [1,2] are also present.

We take a rather different view of the mechanism for photoalignment, namely, that photoisomerism causes a depletion of the angular distribution of dye orientations, the depletion having several angular components with differing symmetry—relating to both the director rotation and the angular diffusion of rods. This simple approach does not require the detailed knowledge of or modeling of interatomic potentials [4]. Indeed its attraction is great simplicity and generality in connection with molecular interactions and degree of order.

The depletion of angular distributions was considered long ago by Stolbova [5]. She solved a simpler problem of weak depletion of an initially isotropic distribution of rods. In the direction of the electric vector there are then fewer rods and a static, weakly negative nematic distribution results from this depletion, which is balanced in equilibrium by angular diffusional recovery. We are dealing instead with an anisotropic system; thus there are two directions $\mathbf{E}$ and $\hat{\mathbf{n}}$. Depletion is then more complex than in Stolbova's case—some components can be balanced in equilibrium by the healing of depletion through angular diffusion. Other components of depletion cannot be offset by diffusion—they amount to rotation of the distribution as a whole, that is, to rotation of the director. Our work recognizes the symmetry differences between such components of distortion of the angular distribution.

The probability of photon absorption by a given rod depends on the optical electric field intensity along the rod axis, that is, on $(\mathbf{E} \cdot \hat{\mathbf{u}})^2 = E^2 \cos^2 \psi$ where the unit vector $\hat{\mathbf{u}}$ is the molecular axis, which makes an angle ψ to the optical field $\mathbf{E}$. The rate of photon absorption by a molecule is $\Gamma E^2 \cos^2 \psi$ where Γ is the absorption coefficient. The orientational distribution of rods, $\mathcal{P}(\theta,\varphi)$, is then depleted by absorption at a rate

$$\dot{\mathcal{P}}_{\mathrm{a}} = -\eta [2 P_2(\cos \psi) + 1] \mathcal{P}, \tag{1}$$

where $\eta = \Gamma E^2/3$. The second Legendre polynomial $P_2(\cos \psi) = (3 \cos^2 \psi - 1)/2$ is the appropriate angular function with which to re-express $\cos^2 \psi$. The distribution of rods is centered about the director $\hat{\mathbf{n}}$, the polar angle θ being measured from $\hat{\mathbf{n}}$ itself, the azimuthal angle ϕ being measured from the $\mathbf{E}$-$\hat{\mathbf{n}}$ plane; see Fig. 1.

We denote the two angles defining $\hat{\mathbf{u}}$ with respect to $\hat{\mathbf{n}}$ as $\boldsymbol{\Theta} = (\theta, \phi)$, and similarly $\mathbf{A} = (\alpha, 0)$ defining $\hat{\mathbf{n}}$ with respect to $\mathbf{E}$. The second angle of $\mathbf{A}$ is 0 since the origin of azimuthal angles is taken from the $\mathbf{E}$-$\hat{\mathbf{n}}$ plane. The angles $\boldsymbol{\Psi}$ defining $\hat{\mathbf{u}}$ with respect to $\mathbf{E}$ are the compound of the angles $\underline{\mathcal{A}}$ and $\boldsymbol{\Theta}$, which we denote by $\boldsymbol{\Psi} = \mathbf{A} \otimes \boldsymbol{\Theta}$.

At a given θ, rods with $\phi = 0$ are more aligned with $\mathbf{E}$ (at angle $\alpha - \theta$) than rods with $\phi = \pi$ (which are at angle $\alpha + \theta$). The former are preferentially depleted over the latter. When the nematic order is perfect (all rods aligned to $\hat{\mathbf{n}}$ with $\theta = 0$), there is no dissymetry and, we predict, no director

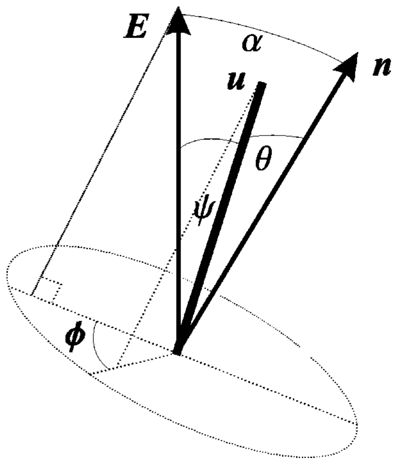

FIG. 1. The director $\hat{\mathbf{n}}$ at an angle α to an optical field $\mathbf{E}$. Rods $\hat{\mathbf{u}}$ are ordered about $\hat{\mathbf{n}}$ with polar angle θ to $\hat{\mathbf{n}}$ and azimuthal angle ϕ measured with respect to the $(\mathbf{E},\hat{\mathbf{n}})$ plane as indicated on the section of plane perpendicular to $\hat{\mathbf{n}}$. The angle between $\mathbf{E}$ and $\hat{\mathbf{u}}$ is ψ.

rotation. Using the Legendre expansion for the compound $\boldsymbol{\Psi}=\mathbf{A}\otimes\boldsymbol{\Theta}$, that is, $P_n(\cos\psi)=P_n(\cos\alpha)P_n(\cos\theta)+\Sigma_{m=1}^{n}(n-m)!/(n+m)!P_n^m(\cos\alpha)P_n^m(\cos\theta)\cos(m\phi)$, where P_n^m denotes associated Legendre polynomials, we obtain

$$\dot{\mathcal{P}}_a=-\eta\bigg(2P_2(\cos\alpha)P_2(\cos\theta)+\frac{1}{3}P_2^1(\cos\alpha)P_2^1(\cos\theta)\cos\phi+\frac{1}{12}P_2^2(\cos\alpha)P_2^2(\cos\theta)\cos2\phi+1\bigg)\mathcal{P}. \tag{2}$$

The other Legendre polynomials are $P_2^1(\cos\theta)=3\sin\theta\,\cos\theta$ and $P_2^2(\cos\theta)=3\sin^2\theta$. The second term in Eq. (2) describes the differential photon-induced depletion, an effect that is clearly lost at $\alpha=0$ and $\alpha=\pi/2$, as can be seen from Fig. 1, and is confirmed by the form of $P_2^1(\cos\alpha)$.

The first and third terms in Eq. (2) represent changes in the uniaxial and biaxial order, respectively. The extent of the order changed by these terms in $\dot{\mathcal{P}}_a$ is determined by the rate of depletion $[-2\eta P_2(\cos\alpha)-(\eta/12)P_2^2(\cos\alpha)]$ compared to the rate of healing by angular diffusion as the rods try to recover their equilibrium distribution of angles. The diffusional rate of return to equilibrium of perturbations like P_l^m is $l(l+1)D_r$, with $l=2$ being of interest here. The net resulting uniaxial and biaxial deviations from the order in the nonilluminated state are easy to calculate and are of order η/D_r. We return to them elsewhere when considering experiments that detect these shifts in order and correlate the shifts with the rate of rotation.

The second term is unaffected by diffusion; it is simply cancelled by rotation of the principal directions of the distribution as a whole, that is, director rotation. The total rate of change of the distribution has several contributors:

$$\frac{D\mathcal{P}}{Dt}=\dot{\mathcal{P}}_a+\dot{\mathcal{P}}_{\rm rot}+\dot{\mathcal{P}}_{\rm diff}+\dot{\mathcal{P}}_{e\to g}. \tag{3}$$

The term $\dot{\mathcal{P}}_{\rm rot}$ represents changes due to rotation and it will be determined by requiring it to cancel the effect of the $\cos\phi$ term in Eq. (2). The change due to diffusion, $\dot{\mathcal{P}}_{\rm diff}$, balances the effect of the first and third terms of Eq. (2), as we discuss above. We delay discussion of order parameter distortions. The gain due to molecules de-exciting and joining the ground state (g) is $\dot{\mathcal{P}}_{e\to g}$. We assume for simplicity (i) that in their bent state the e molecules lose any nematic ordering tendency and (ii) that the rotational rate $D_r^{(e)}$ in the excited state (e) is large enough, and the lifetime $\tau^{(e)}$ of e molecules long enough that the e molecules can randomize. Thus when they decay, they rejoin the g molecules with no angular bias. This is the limit $6D_r^{(e)}\tau^{(e)}>>1$, a combination that is easily identified in, say, Eq. (31) of Ref. [2]. Under these circumstances there is no θ or ϕ dependence in $\dot{\mathcal{P}}_{e\to g}$. The population $\mathcal{P}_e$ is set in quasiequilibrium by the rate of loss, $\dot{\mathcal{P}}_{e\to g}$, equaling the total rate of excitation, the term constant in ϕ in Eq. (2). One can easily relax the simplification of e-state isotropy.

To calculate the rotational rate, we assume that the rate of depletion Γ is sufficiently small that $\mathcal{P}$ remains close to its nematic equilibrium (unilluminated) form, an assumption also made in [2]. We thus ignore the small biaxial order of order η/D_r, induced by photo-isomerization, compared with the uniaxial order. The nematic distribution is then a function only of $(\hat{\mathbf{u}}\cdot\hat{\mathbf{n}})^2\equiv\cos^2\theta$, that is, $\mathcal{P}=\mathcal{P}[P_2(\hat{\mathbf{u}}\cdot\hat{\mathbf{n}})]$, again reverting to P_2 since $(\hat{\mathbf{u}}\cdot\hat{\mathbf{n}})^2$ and P_2 are proportional. The rate of change of a quasiequilibrium $\mathcal{P}$ due to a rotating director, that is, due to a changing angle α, is $\dot{\mathcal{P}}_{\rm rot}=(\partial\mathcal{P}/\partial x)(dx/dt)$. Here $x=P_2(\hat{\mathbf{u}}\cdot\hat{\mathbf{n}})\equiv P_2(\cos\theta)$ changes in time δt due to a change $\delta\alpha$:

$$\begin{aligned}\delta P_2(\hat{\mathbf{u}}\cdot\hat{\mathbf{n}})&=P_2[\cos(\boldsymbol{\delta\alpha}\otimes\boldsymbol{\theta})]-P_2(\cos\theta)\\&=P_2(\cos\delta\alpha)P_2(\cos\theta)\\&\quad+\frac{1}{6}P_2^1(\cos\delta\alpha)P_2^1(\cos\theta)\cos\phi\\&\quad+\frac{1}{24}P_2^2(\cos\delta\alpha)P_2^2(\cos\theta)\cos2\phi-P_2(\cos\theta).\end{aligned} \tag{4}$$

Expanding and taking only the leading terms, of order $(\delta\alpha)$, we obtain $\delta P_2=\frac{1}{2}P_2^1(\cos\theta)\cos\phi\delta\alpha$. It is only the term in $\cos\phi$ that contributes at order $(\delta\alpha)$. The rate of change is thus $dx/dt=\frac{1}{6}P_2^1(\cos\theta)\cos\phi\dot{\alpha}$. We then obtain

$$\frac{D\mathcal{P}}{Dt}=-\frac{\eta}{3}P_2^1(\cos\alpha)P_2^1(\cos\theta)\cos\phi\mathcal{P}+\frac{1}{2}P_2^1(\cos\theta)\cos\phi\dot{\alpha}\partial\mathcal{P}/\partial x+\ldots, \tag{5}$$

where ... refers to the last two contributions of the right-hand side (rhs) of Eq. (3) and to the diffusional terms of

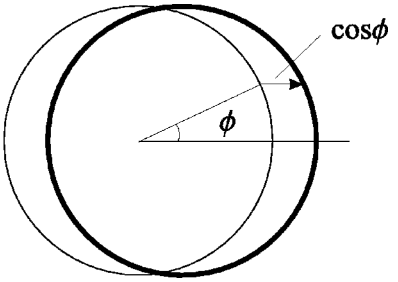

FIG. 2. A circle (light) ''distorted'' by displacements cosϕ to its current position (heavy line) is really only suffering a bodily translation.

Eq. (2) which should be matched to each other for a steady state to obtain. We require that the distribution remain in quasiequilibrium as it rotates. We thus set $D\mathcal{P}/Dt=0$ to obtain the angular velocity.

In the case where the distribution is of the simplest nematic form, $\mathcal{P}\propto\exp[cx]$, the first two terms alone on the right-hand side of Eq. (5) can be balanced to give the rotational rate $\dot{\alpha}$:

$$\dot{\alpha}=\frac{2}{3}\eta P_2^1(\cos\alpha)/(\partial\ln\mathcal{P}/\partial x)\equiv\frac{2}{3}\frac{\eta}{c}P_2^1(\cos\alpha). \tag{6}$$

In this case, $\dot{\alpha}$ does not depend on diffusional rates since it derives exclusively from differential depletion. We stress that the $\mathcal{P}$ in the rhs of Eq. (6) is the quasiequilibrium nematic distribution in which we have neglected the biaxial distortions created by the weak illumination.

We give a geometric illustration of the irrelevance to diffusion of the $P_2^1(\cos\theta)\cos\phi$ term; it is also true in mechanical and elastic problems that such a term does not represent physical effects, but only a shift in origin; see Fig. 2.

For instance, a ''distortion'' $\cos\phi$ of the light circle to the heavy circle is really only a simple linear displacement of the circle as a whole. Such a displacement would have no physical effect, for instance, no restoring force if we were considering all distortions $\mathbf{v}(\phi)$ of an elastic ring that are allowed by continuity, that is, $\mathbf{v}(\phi)=\mathbf{v}(\phi+2\pi)$ giving us 1, $\cos\phi$, $\cos 2\phi,\ldots$.

Consistent with our depletion picture, one immediately sees in Eq. (6) that the rotation vanishes at $\alpha=0$ and $\pi/2$, that is, when the optical field is along or perpendicular to the director. Indeed, given the structure of $P_2^1(\cos\alpha)$ and inserting η, Eq. (6) can be rearranged to

$$\boldsymbol{\omega}=\frac{2}{3}\Gamma(\hat{\mathbf{n}}\cdot\mathbf{E})[\mathbf{E}\times\hat{\mathbf{n}}]/c, \tag{7}$$

where $\boldsymbol{\omega}$ is the rotation vector of $\dot{\alpha}$.

The well-known Maier-Saupe (MS) mean field potential is $U(\theta)=-uQP_2(\cos\theta)$ where the uniaxial order Q is $\langle P_2(\cos\theta)\rangle$. Then the angular distribution of rod axes is given by $\mathcal{P}\propto\exp[uQP_2(\cos\theta)/k_BT]$, whence $c=uQ/k_BT$. We neglect here any small induced differences between the magnitude of Q in the illuminated and dark states. Within this approximation, the explicit expression for $\dot{\alpha}$ is,

$$\dot{\alpha}=\frac{2k_BT}{9}\frac{\Gamma E^2}{uQ}P_2^1(\cos\alpha). \tag{8}$$

We have also restored $\Gamma E^2/3$ in favor of η. The rotational rate diminishes as Q increases and, finally, vanishes for perfect order induced by large coupling $u\to\infty$; see our discussion of differential depletion above Eq. (2). When the nematic order is weak, small deviations from isotropy, depletion has a relatively great effect and the rotation is rapid (but the torque is small; see below). Within this assumption of MS order, the temperature dependence of $\dot{\alpha}$ is fixed as $T/Q_{\rm MS}(T)$, where $Q_{\rm MS}(T)$ is the classical MS variation of order parameter with temperature; see, for instance, [6]. Otherwise, one should correlate $\dot{\alpha}$ with experimentally observed values of $Q(T)$.

Our expression for $\dot{\alpha}$ is valid for arbitrarily strong, Maier-Saupe-like nematic order, provided that the equilibrium state is not strongly distorted by depletion. When the nematic order is weak, the Leslie coefficient scales like $\gamma_1\sim(uQ)^2$; see Ref. [3]. Since the torque $\tau_{\rm ph}$ is $\gamma_1\dot{\alpha}$, the γ_1 scaling and that of $\dot{\alpha}$ in Eq. (8) above combine to give the scaling of Marrucci and Paparo, that is, $\tau_{\rm ph}\sim uQ$ in the limit of weak nematic anisotropy. Thus the torques implied by Eq. (8) vanish as the nematic order is lost.

When the distribution is not of the simplest nematic form, for instance it is $\mathcal{P}\propto\exp[cx+dx^2+\ldots]$, then there are additional terms such as $\sim dP_2^1(\cos\theta)P_2(\cos\theta)\cos\phi+\ldots$ in the coefficient of $\dot{\alpha}$ in Eq. (5). These cannot be matched to the ηP_2^1 first term and are alleviated by angular diffusion as in [1,2]. Then our simple geometric picture is only approximate.

Assembling all the terms in $\boldsymbol{\tau}_{\rm ph}=\gamma_1\boldsymbol{\omega}$ and comparing with the definition of the coefficient ζ, we have for the phototorque:

$$\zeta_{\rm ph}=-\frac{2}{3}\gamma_1\Gamma k_BT/(\epsilon_{\rm o}uQ). \tag{9}$$

The classical torque exerted by a field $\mathbf{E}$ on a nematic is of the same form as in our initial definition, $\boldsymbol{\tau}_{\rm ph}=\epsilon_o\zeta(\hat{\mathbf{n}}\cdot\mathbf{E})(\hat{\mathbf{n}}\wedge\mathbf{E})$, where now $\zeta_{\rm cl}=\Delta\chi$ with $\Delta\chi=\Delta\chi_{\max}Q$ being the anisotropy in dielectric susceptibility and where $\Delta\chi_{\max}$ is the anisotropy extrapolated to the state of perfect nematic order. Note that, for the common case of positive anisotropy $(\Delta\chi>0)$, the sign is the opposite of ours—classical effects align and photo-orientational bleaching effects misalign the director to the field. The relative magnitudes are

$$\frac{|\zeta_{\rm ph}|}{\zeta_{\rm cl}}=\frac{2}{3}\gamma_1\Gamma k_BT/(\epsilon_o\Delta\chi_{\max}uQ^2), \tag{10}$$

which clearly has to be >1 for photobleaching effects to dominate and cause misalignment.

We have calculated simple analytical expressions for the rate of director rotation as a result of photoisomerization depleting the nematic distribution of rods. The side effects of depletion will be small distortions of the degree of order in the (rotating) angular distribution of rods. This should be independently measurable and will be the subject of a future paper. We predict that the rate of rotation should depend simply on the uniaxial nematic order parameter and the nematic coupling, and indeed that the rate of rotation should become very small as these become large. Our results are valid for arbitrarily large nematic orders of the Maier-Saupe type.

ACKNOWLEDGMENTS

The work of S. V. F. was supported by EPSRC. We are indebted to Dr. L. Marrucci and Dr. E.M. Terentjev for critical and incisive comments. Dr. Marrucci also pointed out why our weak nematic limit scaling and his are identical.

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