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Nonlinear dynamics of optical absorption of intense beams

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On traversing materials with absorbing dyes, weak optical beams decay exponentially (a Beer profile), while intense beams develop in time a profile that is spatially linear until at great depth it becomes spatially exponential. This anomalous, deep penetration, due to photobleaching of surface layers, is important for heavy dye loading and intense beams, for instance in photo-actuation. We address the problem of the evolution in time from initial Beer's Law to a finally deeply-penetrating optical profile in dyes. Our largely analytic solution of the coupled, nonlinear, partial differential equations governing the spatiotemporal decay of the Poynting flux and the nonlinear population dynamics of the photo-active molecules under intense irradiation has application to optomechanical devices.

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Light absorption can optically switch the nematic phase of liquid crystals to the disordered, isotropic state: rodlike dye molecules transform from their linear *trans* to their bent *cis* isomers and thereby disrupt the orientational order of their nematic hosts. When such a host is part of a nematic elastomer, then the solid responds with stresses [1] or huge (several 100%) optically induced strains [2,3]. Optical actuation offers advantages over electrical, thermal, and solvent mediated response, being of large amplitude, easily reversible, sensitive to polarization and susceptible to remote application.

Two mysteries attend photoisomerization, seen for instance in actuation. The first concerns the magnitude of bend seen in photocantilevers [4]. In practice, the dye loading of these materials is so large that the penetration depth d of the intensity profile $I(x)=I_0 e^{-x/d}$ is significantly smaller than the sample thickness w [5]. In this case only a thin surface layer near the front of the cantilever contracts and the remaining material resists bend. Despite this, significant bending is often observed. Nonlinear absorption at high light intensities, where Beer's law gives way to a linear and more penetrating intensity profile [6,7], have been suggested to explain this phenomenon [8,9]. The second mystery concerns the dynamical response, which is often initially slow and then proceeds quickly [10], especially in heavily dye-loaded systems. It is this second mystery that we address here.

Dye dynamics is a rich and much-studied subject, especially in the nonlinear limit, for instance the reverse saturation absorption (RSA) problem (see [11] and extensive references therein). Systems of molecular levels participating in absorption and decay are complex with a wide range of processes often in the ns to ps range. We are interested in a simpler aspect, namely the dynamics of a dye system characterized by a ground state (t) and a next lowest level (c). The t population is lost by photon absorption to an excited intermediate state which decays quickly to c. The subsequent c → t thermal or stimulated decays are relatively slow, taking ms to minutes (depending on intensity in the stimulated case), whence one ignores the dynamics of the intermediate state and considers an effective two-level system. We show that a largely analytic solution of the slow dynamics is thereby possible, allowing much insight as to how the excited state profile develops (the determinant of mechanical response when isomerization accompanies the dye response). We initially only consider purely thermal c → t back transitions (at rate $1/\tau$). Experimentally this is often the case [12]; see also [7]. We deal with optically stimulated back reaction at the end of the paper. These can modify our NL absorption profiles, but we are not concerned here with the more subtle RSA limit [11] where an excited state cross section can be larger than that of the ground state, thereby acting as a useful limiter of transmission of intense beams—indeed we are exploring the deeper penetration of beams due to bleaching. However, the RSA limit (using light of different color) is used to stimulate the recovery of photostrain; we return to it elsewhere.

Ignoring optical back reaction, the spatial decay of the Poynting flux of a light beam, $I(x)$, is governed by

$$\partial I/\partial x = -\gamma\Gamma n_{\mathrm{t}}(I) I \equiv -n_{\mathrm{t}} I/d, \tag{1}$$

where n_{t} is the local number fraction of t-dye molecules and depends on time t and space x (through I). The Beer length $d=1/(\gamma\Gamma)$ depends on the material parameters γ (proportional to the number density of chromophores and the energy each t → c transition absorbs from the beam) and on Γ which determines the t → c transition rate as also seen in the dynamics of n_{t}:

$$\partial n_{\mathrm{t}}/\partial t = -\Gamma I n_{\mathrm{t}} + n_{\mathrm{c}}/\tau. \tag{2}$$

The c-number fraction is $n_{\mathrm{c}}=1-n_{\mathrm{t}}$. We reduce intensity by the incident value to give $\mathcal{I}(x)=I(x)/I_0$. The combination $I_{\mathrm{t}}=1/(\Gamma\tau)$ gives a characteristic intensity, a material constant related to the t-photo response. If I_0 is reduced by I_{t}, then $\alpha=I_0/I_{\mathrm{t}}$ is a measure of how intense the incident beam is. The above equations then reduce to effectively Eq. (31) of [11]:

$$\partial\mathcal{I}/\partial x = -n_t\mathcal{I}/d, \quad \partial n_t/\partial t = -[(1+\alpha\mathcal{I})n_t - 1]/\tau. \tag{3}$$

At short times conversion has not yet proceeded and $n_t=1$. Then the first of (3) easily integrates to Beer's Law $\mathcal{I}(x,t\sim 0)=e^{-x/d}$.

At long times (equilibrium) $\partial n_t/\partial t=0$ and thus $n_t^\infty = 1/(1+\alpha\mathcal{I})$. For weak beams $(\alpha\sim 0)$ $n_t \approx 1$ and again (3) gives Beer's Law. At high intensities $\alpha \gg 1$, one has nonlinear absorption [7]. Then $n_t \sim 1/(\alpha\mathcal{I})$, at least before depths such that the beam attenuates to $\mathcal{I}\sim 1/\alpha$. Then in (3) one has $\partial\mathcal{I}/\partial x \approx -1/(\alpha d)$ and hence $\mathcal{I}\simeq 1-x/(\alpha d)$ (for $x \lesssim \alpha d$). The intensity profile is initially linear until depths where n_t rises to being significantly greater than $1/\alpha$ and absorption is then important. The surface layer is in effect photobleached and lets much light down to depths $x>d$; see [8,9] for discussion, including of the role of optical back reaction. We consider here for simplicity nonmesogenic dyes and thus avoid dye rotation rather than *cis* formation as a route to bleaching (see [13] for this possibility). With the equilibrium form of n_t inserted into the first part of (3), integration gives the nonlinear, equilibrium profile [6–9]:

$$\ln[\mathcal{I}(x)] + \alpha[\mathcal{I}(x) - 1] = -x/d. \tag{4}$$

The long-time limit ($t \gtrsim 5\tau$ in practice) of our dynamical profiles will display the linear rather than exponential forms until depths much greater than d. The Mathematica defined function ProductLog gives [8,9] the solution: $\mathcal{I}=\frac{1}{\alpha}\text{ProductLog}[\alpha e^{(\alpha-x)}]$.

We are concerned here with the dynamics of the transition from Beer's law initially to the above equilibrium profile for intense beams. The absorbance $\mathcal{A}=\ln[1/\mathcal{I}(w,t)]$ is the usual measured quantity and reflects the absorber number in the optical path. Rearranging the first of Eq. (3) to $\frac{1}{\mathcal{I}}\frac{\partial\mathcal{I}}{\partial x}=-n_t(x,t)/d$ and integrating $\int_1^{\mathcal{I}} d\mathcal{I}$ and $\int_0^w dx$, one obtains for all times and incident intensities [recall $\mathcal{I}(0,t)=1$ for all t]:

$$\mathcal{A}(w,t) = \frac{w}{d}\bar{n}_t \equiv \frac{w}{d}\frac{1}{w}\int_0^w dx\, n_t(x,t), \tag{5}$$

where $\bar{n}_t$ is the mean t-number fraction through the sample. In the nonlinear limit, $\bar{n}_t$ is not independent of w and hence $\bar{n}_t/d$ is no longer a simple, material-dependent extinction coefficient.

The dynamics of $\mathcal{A}$ is often observed and analyzed assuming exponential behavior:

$$\mathcal{A}(w,t) \simeq \mathcal{A}(w,\infty) + [\mathcal{A}(w,0) - \mathcal{A}(w,\infty)]e^{-t/(n_t^\infty \tau)}.$$

Note that $\mathcal{A}(w,0)=w/d$ exactly and that the nonlinear limit of $\mathcal{A}(w,\infty)$ is given by the ProductLog solution to Eq. (4) for $\mathcal{I}(w)$. However, this is not a solution to the differential Eq. (3) and becomes a bad dynamical estimate for thick samples, $w \gg d$, that are only traversed by intense beams because of bleaching. The characteristic time $\tau n_t^\infty = \tau/(1+\alpha\mathcal{I})$ is shorter than thermal times, but clearly $\mathcal{I}(x)$ depends on position in thick samples and there is a spectrum of times, $\tau(x)$, and the overall response is not exponential. To solve the problem exactly, use $\mathcal{A}(x,t)=-\ln(\mathcal{I})$ as the variable. Denote partial spatial and temporal derivatives of X by X' and $\dot{X}$, respectively. Differentiating Eq. (5) with respect to t and using Eq. (3) for $\dot{n}_t$ under the integral yields

$$\dot{\mathcal{A}} = \int_0^x dx[1-(1+\alpha\mathcal{I})n_t]/(\tau d).$$

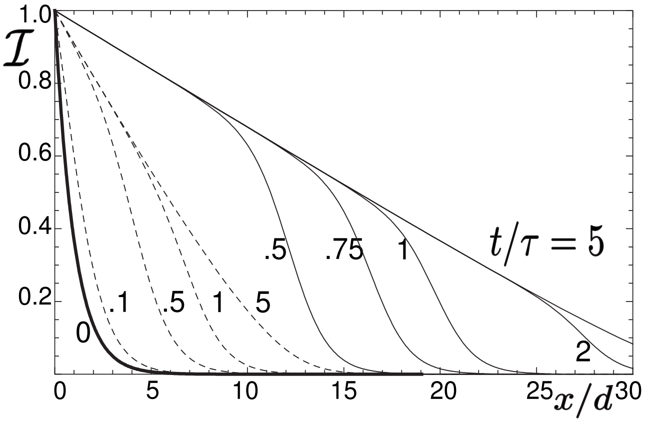

FIG. 1. Intensity against reduced depth for reduced incident intensities $\alpha=10$ (dotted) and 30 (full) at reduced times t/τ marked. Beer's law obtains for any α at $t=0$ (heavy line).

Now use $n_t/d=\mathcal{A}'$, $\mathcal{A}(0,t)=0$, and $\mathcal{A}'=-\mathcal{I}'/\mathcal{I}$:

$$\tau\dot{\mathcal{A}} = x/d - \int_0^x dx(1+\alpha\mathcal{I})\mathcal{A}' \tag{6}$$

$$= \frac{x}{d} - \mathcal{A} + \alpha(\mathcal{I}-1) \equiv \frac{x}{d} - \mathcal{A} + \alpha(e^{-\mathcal{A}} - 1). \tag{7}$$

A final quadrature gives $\mathcal{A}(x,t)$:

$$t/\tau = \int_{x/d}^{\mathcal{A}} \frac{d\mathcal{A}}{x/d - \alpha - \mathcal{A} + \alpha e^{-\mathcal{A}}}. \tag{8}$$

The initial absorption $\mathcal{A}(x,t=0)=x/d$ obtains from the vanishing of each side of (8), and is Beer's Law. The limit $t/\tau \to \infty$ in Eq. (8) is achieved when the denominator in the integrand tends to zero, from which one obtains Eq. (4), that is, the ProductLog solution.

Figure 1 shows $\mathcal{I}(x,t)(\equiv e^{-\mathcal{A}(x,t)})$ for reduced intensity I_0/I_t against x for a set of times t. Initially at $t=0$, the profile $\mathcal{I}(x,0)$ is exponential, and at long times $(t=5\tau)$ the profile is essentially linear out to $x\sim\alpha d=10d$, then decays exponentially. At intermediate times the profile first saturates (bleaches) at small x, that is it approaches the initial part of the equilibrium profile. Then as the surface layers let more light through, the profile deeper down also approaches the non-Beer form. For even higher incident intensity, $\alpha=30$, ultimate penetration is deeper and the approach to the bleached state, as time advances, even sharper. A front of bleaching propagates through the sample. Compare the two graphs at a given $x=5d$. The more intense case, $\alpha=30$, sees a spatially more rapid achievement of the bleached state than the $\alpha=10$ case, and over times considerably shorter than τ,

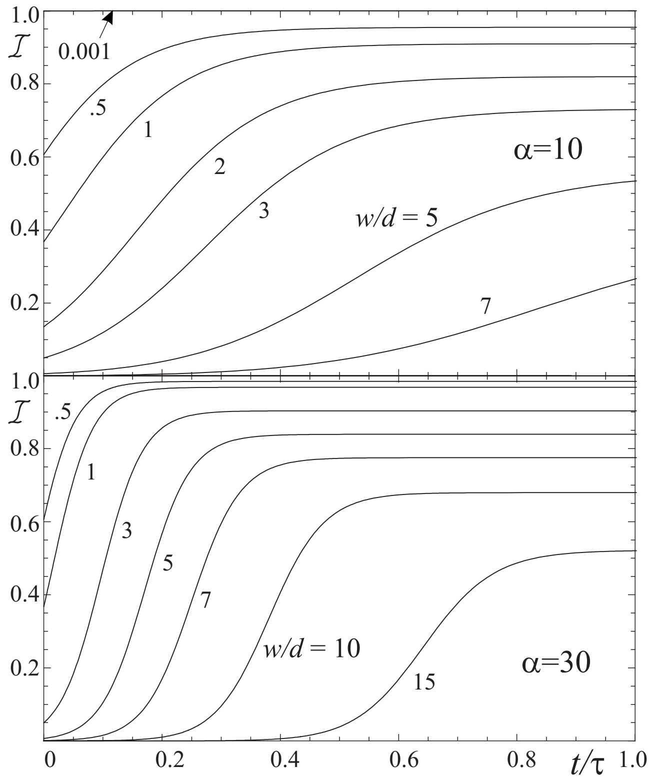

FIG. 2. Emergent reduced intensity $\mathcal{I}=I(w)/I_0$ against time at reduced incident intensity I_0/I_t and 30 for various reduced sample thicknesses w/d.

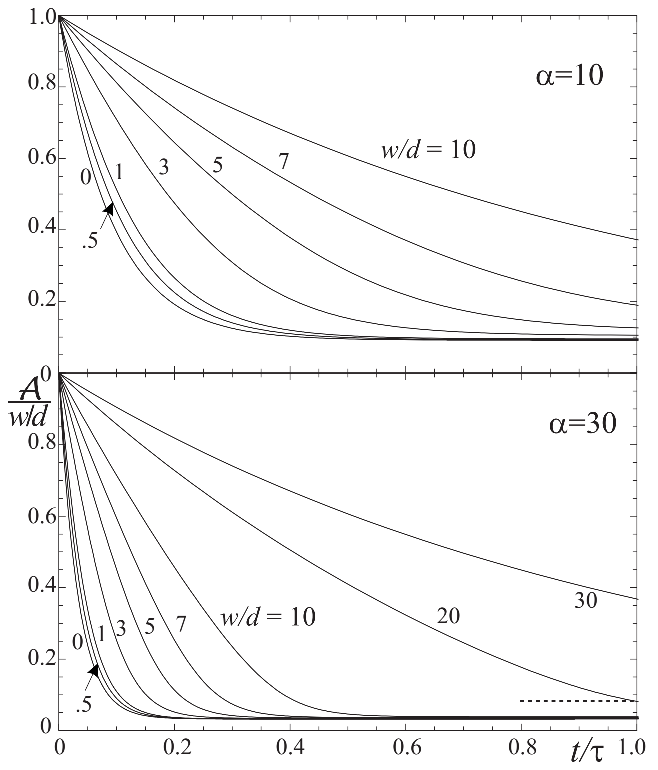

FIG. 3. Nonlinear extinction $\mathcal{A}(w,t)/(w/d)$ against time at reduced incident intensity I_0/I_t and 30 for various reduced sample thicknesses w/d. The dotted line is the asymptote for the $w/d=30$ dynamics.

as the approximate analysis suggested. For either α, the emergent light is far in excess of any Beer expectation, the rate of buildup which we now examine.

Although these curves of Fig. 1 are vital to understanding the buildup (and possible decay) of optically induced curvature in heavily dye-doped solid nematics, the intensity profile is not in general directly observable. It is more feasible to measure the dynamics of the buildup of intensity of the light emerging at the back face $x=w$ of a sample, $\mathcal{I}(w,t)$. Figure 2 reveals $\mathcal{I}(w,t)$ for various fixed thicknesses w, for two reduced incident intensities α. The initial ($t=0$) value is that from Beer penetration, $e^{-w/d}$. Finally, $\mathcal{I}$ rises to the long-time, bleached value $\mathcal{I}(w,t\gg\tau)$ shown at the corresponding $x=w$ in Fig. 1. The rise is naturally slower for thicker samples. Such penetration dynamics has recently been seen [10].

Thick ($w>d$) beams give initially exponentially small emergent fluxes that give way to large fluxes as the linear profile is set up. Such data are accommodated in the usual logarithmic way, here by dividing the absorbance by the thickness which is not a material-dependent constant (an extinction) in this nonlinear limit. Figure 3 shows $\mathcal{A}(w,t)/(w/d)$ for various fixed thicknesses w, for incident intensities $\alpha=10,30$.

The initial increase of intensity away from the Beer value in Fig. 2 is $\dot{\mathcal{I}}(w,t=0)=-\dot{\mathcal{A}}(w,0)e^{-\mathcal{A}(w,0)}\equiv-\dot{\mathcal{A}}(w,0)e^{-w/d}$ whereupon using (7) for $\dot{\mathcal{A}}$ at $t=0$ where $\mathcal{A}=w/d$, one obtains for the initial slope

$$\tau\dot{\mathcal{I}}(w,t=0)=\alpha(1-e^{-w/d})e^{-w/d}. \tag{9}$$

For intense beams ($\alpha\gg1$) on thick ($w\sim\alpha d$) samples, the initial intensities at the back face on irradiating the front face are small, $\mathcal{I}(w,0)=e^{-w/d}$. The rates of increase are also initially very small, $\dot{\mathcal{I}}\sim\alpha e^{-\alpha}/\tau$, but then rise sharply with time, see the example with $\alpha=30$.

Two other processes are sometimes important in nonlinear absorption, those of host absorption and of c absorption, that is, optically stimulated back reaction. Both are discussed in detail in the nonlinear static case [9]. Moderate host absorption can be successfully divided out and plays a limited role. Back reaction occurs if the t→c and c→t absorption lines begin to overlap. This is sometimes the case and has the effect of reducing deep penetration [7].

In Eq. (1), host absorption gives another term, $-I/d_h$, while depletion of the beam by dyes in their c state gives $-\gamma_c\Gamma_c n_c(I)I$. Optical back reaction also affects the dynamics. An additional term $+\Gamma_c I n_c$ from the decay c→t acts in Eq. (2) to replenish the t population. There is a characteristic intensity $I_c=1/(\Gamma_c\tau)$ analogous to that of the t species, and thus another measure $\beta=I_0/I_c$ of the incident beam intensity. Now the coupled, nonlinear partial differential equations (3) become

$$\mathcal{A}'=-\frac{\partial\mathcal{I}/\partial x}{\mathcal{I}}=\left(\frac{1}{d}-\frac{1}{d_c}\right)n_t+\frac{1}{d_c}+\frac{1}{d_h}, \tag{10}$$

$$\tau\dot{n}_t = (1+\beta\mathcal{I}) - [1+(\alpha+\beta)\mathcal{I}]n_t. \qquad (11)$$

The changes, even if only one of these influences is introduced at a time, add difficulty to the solution of the equations. Proceeding as before, one differentiates Eq. (10) with respect to time and uses (11) to eliminate $\dot{n}_t$. Where n_t appears, it can be eliminated in favor of $\mathcal{A}'$ by using Eq. (10) again. Terms do not quite all integrate totally as in going from (6) and (7) because Eq. (10) has additional new constant terms. Spatially integrating gives

$$\tau\dot{\mathcal{A}} = -\mathcal{A} + x/d_{\mathrm{eff}} + (\alpha+\beta)(\mathcal{I}-1) + \left[\alpha\left(\frac{1}{d_c}+\frac{1}{d_h}\right)+\beta/d_{\mathrm{eff}}\right]\int_0^x dx\mathcal{I}, \qquad (12)$$

where $1/d_{\mathrm{eff}}=1/d+1/d_h$ is an effective absorption length arising from the simple combination of dye and host absorptions in the Beer limit. It is interesting that although β (and thus $1/d_c$) and $1/d_h$ enter Eqs. (10) and (11) in entirely different ways, their effects can be scaled on to each other in the resultant equation for dynamical nonlinear absorption (12). Remember, however, that d_{eff} depends on d_h and so lengths are not quite equivalently affected by this interchange of sources of extra absorption. We show just the effect of adding in optical back reaction into the dynamical equations, that is $1/d_h=0$ and lengths are still reduced by d. For $\alpha=10$ and, say, $\beta=0.2$, the $\mathcal{I}(w,t)-t$ curves are indistinguishable from those in upper Fig. 2 which have $\beta=0$. Figure 4 shows the behavior for $\beta=2$ which should be compared with upper Fig. 2. The starting values are of course the same; the final values are lower because β acts to lower the final penetration. The upward curvature at short times is lost. Thicker samples are much more drastically affected. In liquid samples, diffusion of t and c species in the concentration gradient set up optically can occur over our relatively long time scales; an additional diffusive term arises in Eq. (11).

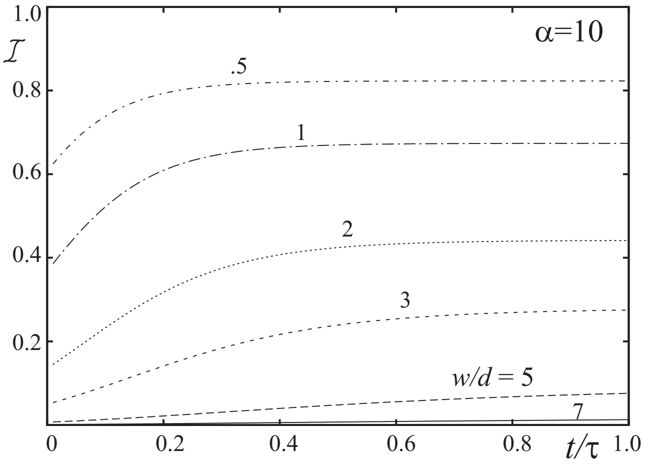

FIG. 4. Emergent reduced light intensity $\mathcal{I}(w,t)$ against time for various reduced sample thicknesses w/d. Reduced incident intensity is $\alpha=I_0/I_t=10$ with a relatively high degree of reduced optical back reaction $\beta=I_0/I_c=2$.

We have shown that the dynamics of penetration of intense light beams into heavily absorbing media is complex and strongly dependent upon incident intensity. We reduced to a simple quadrature the dynamics of the buildup of the nonexponential intensity profile through a material containing absorbing dyes with concentration coupled to the intensity. A practical experiment to observe this effect via the time dependence of the emergent light from the sample is proposed. There is evidence from large amplitude photomechanics that nonlinear dynamical effects are important in practice.

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