Bleaching and stimulated recovery of dyes and of photo-cantilevers

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We examine how intense optical beams can penetrate deeply into highly absorbing media by a non-linear, photo-bleaching process. The role of stimulated recovery to the dye ground state can be important and is delineated. This analysis of non-linear absorption processes is applicable in general to situations where chromophores are irradiated, for instance in biology. We examine the implications for the bending of cantilevers made of heavily dye-loaded nematic photo-solids, that is nematic glasses and elastomers that have large mechanical reactions to light. In particular we describe the bending of cantilevers sufficiently absorbing that they would not bend if Beer’s Law were applicable. We quantify the role of optically-generated heat in determining the mechanical response and conclude that in general it is minor in importance compared with optical effects.

I. INTRODUCTION

Nematic solids are principally elastomeric or glassy. In each case they are composed of nematic polymers, but either loosely or tightly crosslinked. Their moduli are accordingly low or high and they are capable of either huge or modest extensions. They form unique solids in that, when their order is changed, they can change their dimensions considerably and these mechanical responses can be steered in many ways. The order can either be redirected (director rotation under the influence of electric, mechanical or optical fields) or reduced. In this paper, for simplicity we concentrate on changing the magnitude of order, achievable by heating or cooling, or by the absorption of light into photo-active rods when they are a component of the nematic solid. The natural elongation of the oriented polymers making up the networks is modified by order change, with the result that macroscopic mechanical changes are induced. Reversible thermal strains of hundreds of percent have been observed in elastomers. Smaller changes arise in glasses, where subtle arrangements of director have been employed to achieve more complex mechanical responses. Since light and heat have analogous effects, one expects and indeed finds that optical absorption leads to analogous mechanical strains, both in photo-elastomers and in photo-glasses. Such a mechanism of mechanical change offers the possibility of micro-opto-mechanical systems (MOMS) where elements can be optically-induced to bend as elastomeric photo-swimmers or as glassy cantilevers. The bend arises because the contraction is differential with depth since the optical beam is absorbed and is hence weaker with depth. How the beam intensity varies with depth because of non-linear absorption processes, and how this variation is translated into bending even in situations where absorption is so high that penetration would be negligible in the linear case, are the two questions that concern this paper. A schematic, Fig. 1, of the penetration and of the differential contraction leading to bend establishes the coordinate (x) of penetration, the thickness (w), and the curvature (1/R) of the cantilever.

Light disrupts nematic order when molecular rods which are also chromophores, that is dye molecules, bend on absorbing a photon in their straight (trans) ground state and make an indirect transition to their bent (cis) excited state. The orientational order of tightly packed rods is thereby reduced by the cis fraction. We shall assume for simplicity that the mechanical contractile strain is proportional to the cis volume fraction. It is a vexed question as to whether heat released by these optically-induced transitions is the actual cause of the order change. This question has been addressed by irradiating polydomain nematic photo-glasses with polarized light. One finds that the mechanical contraction occurs along the light polarization direction, a response that is therefore simply tuneable by rotating the light polarization. Domains closely aligned to the optical electric field absorb, and thus also contract, preferentially over domains that are misaligned. Moreover, since the domain size is small, heat diffusion is fast and domains neighboring an absorbing region quickly reach similar temperatures. If temperature were the mechanism for contraction, it would thus under these conditions of fast diffusion not distinguish a preferred direction and there would be no overall effect (just as when one simply heats a polydomain nematic solid). Evidently, optical effects dominate. We discuss thermal effects at length in this paper and find their influence small, even across a whole monodomain cantilever, because of the diffusional
rates that arise.

Since photons are absorbed by the dye components in the nematic, then light penetrating the face of a nematic photo-cantilever will be attenuated and hence the contractions generated diminish with depth. Curvature of the cantilever results, Fig. 1. It is important in micro-optomechanical systems (MOMS) where elements can be optically-induced to bend as elastomeric photo-swimmers or as glassy cantilevers.

Weak beams decay exponentially with depth (Beer's law). The conversion of straight to bent (trans → cis) forms of the dye molecules is also exponential in this limit. For a linear connection (valid for small strains) between cis population and contraction, in the Beer limit maximum cantilever curvature is predicted \( w/d \sim 2.63 \) where \( w \) is the thickness of the cantilever and \( d \) is the exponential decay length: if \( w \gg d \), only a thin skin of network contracts and its contractile stresses are insufficient to make the unstrained part of the cantilever.

Experimentally, cantilevers are commonly heavily dyed but still show appreciable mechanical effects. The above arguments suggest that this bending is unexpected: high dye concentrations mean strong absorption and hence small \( d \). In this thin skin limit, \( d \ll w \), bend is expected to disappear. Evidently non-linear effects lead to deep penetration of light and thus lead to bending. We shall explain these related effects by making two assumptions for simplicity to illustrate the underlying principles.

We take the straight forward case of no photo-induced director rotation, that is for nematic glasses and constrained systems (for instance where surface effects might be strong, where the director seems to be immobile under elongations imposed at an angle and also probably don’t rotate during photo processes). However, photosomerisation in glasses has additional subtleties; we derive the non-linear penetration of intense beams into glass as well. Secondly we assume that there is not appreciable reduction in the magnitude of the nematic order parameter under illumination. This assumption is reasonable in glasses, but in liquid and elastomeric nematics, this assumption is too restrictive. Indeed a description of polydomain nematic elastomer response invokes both order reduction and rotation.

An initial attack on this problem invoked photobleaching, that is depletion of the trans form, letting light through to greater depths than would be expected by Beer’s law. Here we derive these non-linear effects fully, paying attention to two additional influences that are potentially important. The optically-stimulated back reaction cis → trans can alter the non-linear processes considerably and is of importance when the cis absorption line is not widely separated from that of the trans species. Secondly, thermal effects could be considerable, all the more so because of a possibly nearby nematic to isotropic transition where giant thermo-mechanical effects are known to occur, especially in elastomers.

The remainder of this paper is organized as follows. In section II we derive equations which describe the attenuation of light passing through a region with photo-active chromophores. Our analysis of non-linear absorption is thus relevant to a wide range of situations where dye is irradiated, and is not limited to mechanics, which is our ultimate aim here. Our methods and results are similar to a penetrating analysis, experimental and theoretical, of Statman and Janossy. In section IV we show how optical attenuation leads to cantilever bending and calculate the radius of curvature as a function of the incident flux of light. In section V we investigate the distribution of strain throughout the bent sample, and in particular we demonstrate that there can be several planes within the cantilever on which the net strain is zero. In section VI we discuss the possible effects of temperature change owing to absorption of photons on the results presented thus far. We find that, for intense illumination, temperature distributions are symmetric about the cantilever mid-plane and hence do not contribute to bend, only contraction. Finally in VII we present our conclusions.

II. ATTENUATION

We consider the situation of Fig. 1(b) of a long, slender cantilever of thickness \( w \) illuminated by light with incident flux \( I_0 \). The absolute number density of chromophores is \( \rho_{ph} \). At a time \( t \) after the onset of illumination and depth \( x \) within the cantilever, the fraction of these chromophores in the straight trans state is \( n_t(x,t) \) and the fraction in the bent cis state is \( n_c(x,t) = 1 - n_t(x,t) \). The magnitude of the Poynting flux at \( x \) and \( t \) is \( I(x,t) \). The dynamics of the trans fraction is determined by three processes, (i) an optically stimulated trans → cis reaction with rate \( \Gamma_1 I(x,t) n_t(x,t) \), (ii) an optically stimulated cis → trans back-reaction with rate \( \Gamma_2 I(x,t) n_c(x,t) \) and (iii) a spontaneous, thermally activated, cis → trans back-reaction with characteristic time \( \tau \). \( \Gamma_1 \) and \( \Gamma_2 \) subsume absorption cross sections per chromophore and the quantum efficiencies \( \Phi_{tc} \) and \( \Phi_{ct} \) of the stimulated trans-cis reaction and cis-trans back-reaction respectively, see \( \Gamma_1 \) for the rate equations in full with such factors explicitly given. We take the absorption cross sections to be independent of nematic order – as discussed above, changing nematic order is itself another source of non-linearity. Combining these three rates we obtain for the rate of change of the trans fraction:

\[
\frac{\partial n_t}{\partial t} = -\Gamma_1 I(x,t) n_t(x,t) + \left( \frac{1}{\tau} + \Gamma_2 I(x,t) \right) n_c(x,t) \tag{1}
\]

In this paper we confine ourselves to the steady-state, that is \( \frac{\partial n_t}{\partial t} = 0 \). Setting this condition in eqn. (1) and
taking out a factor of \( \tau \) gives the steady state \( \text{trans} \) and \( \text{cis} \) populations:

\[
\begin{align*}
n_t(x) &= \frac{1 + \gamma I}{1 + \gamma I + \Gamma_c I} ; \quad n_c(x) &= \frac{\Gamma_c I}{1 + \gamma I + \Gamma_c I} \tag{2}
\end{align*}
\]

where \( I \) is now \( I(x) \) simply, and will be determined below. We can identify two characteristic, material intensities, \( I_t = 1/(\Gamma_t \tau) \) and \( I_c = 1/(\Gamma_c \tau) \). It is convenient to scale the flux by its incident value, thus \( I(x,t) = I_t(x,t)/I_0 \).

The reduced intensity is thus \( I = 1 \) at the entry surface \( x = 0 \), see Fig. 1(b). We also define dimensionless quantities \( \alpha = I_0/I_t \) and \( \beta = I_0/I_c \). These are the incident flux reduced by fluxes \( I_t \) or \( I_c \) characteristic of \( \text{trans} \) or \( \text{cis} \) molecules respectively. We refer to \( \alpha \) and \( \beta \) subsequently as reduced incident fluxes. Ignoring for the moment attenuation, \( \alpha \) measures how much a beam intensity \( I_0 \) leads to \( \text{trans} \) conversion, eqn (1), by comparing \( I_0 \) to \( I_t \), that is the ratio of the forward rate to the thermal backward rate, \( \alpha = I_0/I_t = I_0\Gamma_t/(1/\tau) \). Likewise, \( \beta \) is the ratio of the induced to the thermal back rates.

In terms of the reduced incident intensities \( \alpha \) and \( \beta \), the steady state \( \text{trans} \) and \( \text{cis} \) populations are given by:

\[
\begin{align*}
n_t(x) &= \frac{1 + \beta x}{1 + (\alpha + \beta) x} ; \quad n_c(x) &= \frac{\alpha x}{1 + (\alpha + \beta) x} \tag{3}
\end{align*}
\]

Here \( I \) is just \( I(x) \) since we have the equilibrium case. In the Eisenbach experiments [18] the average conversion was \( n_c \approx 0.84 \). His measurements of attenuation suggested \( \beta \approx 0 \), and thus one can deduce from eqn (1) that his \( \alpha \approx 5 \). Note that \( \alpha \) and \( \beta \) are independent of chromophore concentration, but do depend on the choice of the light polarization [17]. Experimentally it is easiest to determine \( \alpha \) for a system diluted in chromophores, where one can ignore the complications arising when attenuation is significant. These estimates for \( \alpha \) are lower bounds on actual values; including the effects of attenuation through the cantilever will lead to higher values of \( \alpha \). In later work [19] one can deduce that \( \alpha \approx 0.8 \).

The divergence of the Poynting flux, \( \frac{\partial I}{\partial x} \), at any point through the cantilever is equal to the amount of energy taken out of the beam per unit volume per unit time. For simplicity, we ignore curvature leading to obliquity factors for the intensity of light falling on the surface. That is, we consider small deflections or diffuse light. Energy is taken out of the beam both by the optically induced \( \text{trans} \rightarrow \text{cis} \) reaction and by the stimulated \( \text{cis} \rightarrow \text{trans} \) back-reaction, terms (i) and (ii) above. The divergence of the Poynting flux is thus related to the sum of the rates of these two processes. Thus:

\[
\frac{\partial I}{\partial x} = -\gamma_1 \Gamma_t I(x,t) n_t(x,t) - \gamma_c \Gamma_c I(x,t) n_c(x,t) \tag{4}
\]

where the constant \( \gamma \) in each case subsumes the energy of an incident photon, \( h\omega \), the reciprocal of the quantum efficiency \( \Phi \) for the relevant transition, and the absolute number density of chromophores, \( n_{ph} \) (which could differ between \( \text{trans} \) and \( \text{cis} \) forms since bent molecules pack less efficiently). The appearance of \( \Phi \) as an inverse is required since for each successful transition in the rate \( \Gamma_{t_i} n_i \) (i = t,c) there will be unsuccessful absorptions that do not contribute to \( \partial n_i/\partial t \) in (1), but nevertheless still deplete the optical beam and contribute to \( \partial I/\partial x \) in (4).

Eqns (1) and (4) are a pair of coupled, non-linear, first order partial differential equations for \( I(x,t) \) and \( n_t(x,t) \). Solving these equations subject to the boundary conditions \( I(0,t) = I_0 \) and \( n_c(x,0) = 1 \) is in general complex, though analytically possible in some limits. We return to this problem elsewhere [18] and here take the time-independent, equilibrium state. Thus, using \( n_c = 1 - n_t \), dividing through by the incident intensity \( I_0 \), and letting \( d_t = 1/(\gamma_t \Gamma_t) \) and \( d_c = 1/(\gamma_c \Gamma_c) \) denote the characteristic lengths for optical attenuation by \( \text{trans} \) and \( \text{cis} \) chromophores respectively, one obtains [16, 17]:

\[
\frac{dI}{dx} = -\left( \frac{1}{d_t} - \frac{1}{d_c} \right) n_t + \frac{1}{d_c} I(x) \tag{5}
\]

In terms of the parameters \( \alpha \) and \( \beta \), the ratio of the \( \text{trans} \) and \( \text{cis} \) lengths is \( d_t/d_c = (\gamma_c/\gamma_t) (\beta/\alpha) \). The ratio \( \eta = \gamma_c/\gamma_t \) is the ratio of the quantum efficiencies for the \( \text{trans} \rightarrow \text{cis} \) and \( \text{cis} \rightarrow \text{trans} \) reactions, that is \( \eta = \Phi_t/\Phi_c \). We shall take \( \eta = 1 \) in the numerical illustrations in this paper. We have ignored any attenuation by the host material; one could include such effects by adding a simple Lambert-Beer term \( -I(x,t)/d_h \) to the RHS of eqn (4) or eqn (5). See section IIIA for an analysis.

Inserting the steady-state expression for \( n_t \) from eqn (3) into eqn (5), and then integrating w.r.t. \( x \), subject to \( I(x = 0) = 1 \), we obtain (see also [17]):

\[
\ln I + \left( \frac{\alpha - \beta \eta}{\beta^t} \right) \ln \left( 1 + \beta^t I \right) = -\frac{x}{d_t}, \tag{6}
\]

where \( \beta^t = \beta(1 + \eta) \). In general this expression is very different from Beer’s Law, \( I(x) = \exp(-x/d) \).

Deviations from Beer’s Law come about because at high intensities the \( \text{cis} \) population increases (bleaching) and is generally less absorbing than the \( \text{trans} \) species. Optical penetration is then more effective and is of great significance for photo-mechanics. To most simply see how non-linearity (bleaching) manifest themselves, consider the limit \( \beta \to 0 \) [16] that arises when stimulated \( \text{cis} \) back-conversion is weak (for instance in the work of Eisenbach). Under those circumstances \( \Gamma_c \to 0 \) in eqn (1), and then (5) takes the form:

\[
\frac{dI}{dx} = -\frac{n_t}{d_t} I(x) \tag{7}
\]

A non-Bern form arises because \( n_t = 1/(1 + \alpha I) \) itself depends on \( I \), eqn (3). Integration gives

\[
\ln I + \alpha(I - 1) = -x/d_t, \tag{8}
\]

also a \( \beta \to 0 \) limit of (6). A formal solution of which is

\[ I(x) = \frac{1}{\alpha} W_L(\alpha e^{x/d_t}), \]

where \( W_L(x) \) is the Lambert-W
function \( \alpha \mathcal{I} \). The non-exponential decay persists until around \( \alpha \mathcal{I} \ll 1 \), whereupon \( n_t \) becomes independent of \( \mathcal{I} \) and (7) reverts to simple exponential form.

The limiting cases of absorptions are important.

(i) \( (\alpha + \beta) \mathcal{I} \ll 1 \). Now \( n_t \approx 1 \) and \( n_c \approx 0 \) which renders (5) trivially of the Beer form. The limit obtains when \( \alpha = I_0/I_i \) and \( \beta = I_0/I_c \) are both \( \ll 1 \) (since \( \mathcal{I} \) is bounded by 1), that is, the incident beam is weak compared with both material fluxes \( I_i \) and \( I_c \). It also obtains when \( \alpha \) and \( \beta \) are not small, but when \( \mathcal{I} \ll 1/(\alpha + \beta) \), that is when the beam has diminished (albeit linearly rather than exponentially, see the sketch below and also the high intensity traces of Fig. 2) to the point that \( n_t = \text{const} \approx 1 \) and Beer behavior is finally recovered.

From (8) one sees in fact \( I(x) \sim \exp[\frac{-(x - d_t \alpha)}{d_t}] \) for \( x > d_t \alpha \), a shifted Beer form.

(ii) The high flux limit \( \alpha \mathcal{I} \gg 1 \) (with \( \beta \sim 1 \)) is where the forward reaction dominates over thermal back reaction. Photo-equilibrium is highly biased away from trans, that is in eqn (3) \( n_t \ll 1/(\alpha \mathcal{I}) \). Eqn (7) reduces to \( \mathcal{I} \sim 1/(\alpha \mathcal{I}) \). This linear penetration for \( x \lesssim \alpha d_t \) is evident in Fig. 2 at the higher \( \alpha \) values and is at the heart of why even highly absorbing systems can be responsive. When \( x \gtrsim \alpha d_t \), decay is again exponential, see above.

(iii) The high flux limit, \( \beta \mathcal{I} \gg 1 \), that is \( \mathcal{I} \ll 1/\tau \), is where the stimulated back-reaction dominates over the thermal back-reaction. In that case \( n_t \sim \beta/(\alpha + \beta) \approx \beta/(\alpha + \beta) \) are again constants and again (4) takes a Beer form in the equilibrium limit:

\[
\frac{d\mathcal{I}}{dx} = -\mathcal{I}\beta(1 + \eta)/(d_t(\alpha + \beta)).
\] (9)

The decay is exponential, \( \mathcal{I} = \exp(-x/d_t) \) with an effective decay length \( d_{\text{eff}} = d_t(\alpha + \beta)/(\beta(1 + \eta)) \). Thus, except for \( \beta \ll 1 \), profiles start in a Beer-manner, have an intermediate non-exponential behavior if we have \( \alpha > 1 \) with \( \beta \ll \alpha \), and then conclude with another Beer decay. The intermediate regime, \( \beta \mathcal{I} \sim 1 \), is where the stimulated back reaction rate is comparable to the thermal rate.

(iv) When the decay lengths accidentally coincide, \( d_t = d_c = d_t \), that is \( \gamma_i \Gamma_t = \gamma_c \Gamma_c \), one can easily see in either (1) or (5) that a Beer form pertains at all intensities or depths into the photoisomerizing medium:

\[
\mathcal{I} = \exp(-x/d).\]

Statman and Janossy [17] investigated photoisomerization of solutions of the commercially available azodye Disperse Orange (DO3). They obtained a ratio of \( \alpha/\beta \sim 5 \) while the accessible range of \( \alpha \) is up-to \( 80 \) (corresponding to an incident flux of \( 15 \mu \text{W/mm}^2 \)). The spectral bands for trans \( \rightarrow \) cis and cis \( \rightarrow \) trans overlap quite strongly for DO3; one might thus expect much smaller ratios of \( \beta/\alpha \) to be accessible when using dyes with more separated absorption bands. Indeed, Eisenbach’s attenuation study showed that, for his systems, \( d_c \gg d_t \) and thus that \( \alpha \gg \beta \), possibly \( \alpha \sim 100 \times \beta \).

We thus show results initially for high ratios \( \alpha/\beta \) for a range of incident intensities \( \alpha \) and then look at smaller ratios where the non-linear region is not so pronounced.

As can be seen from eqn (3), the cis population is always reduced when \( \beta \) is finite. Thus for non-zero \( \beta \) we require a larger value of \( \alpha \) to achieve a particular value of \( n_c \). Similarly attenuation will lead to reduced intensities lower than unity in eqn (5), again requiring larger values of \( \alpha \) to achieve the same cis concentration. Thus estimates of \( \alpha \) from absorption are lower bounds on true values.

### A. CASE 1 - \( \alpha/\beta = \infty \)

We recall the case in which the illuminating light doesn’t excite the cis \( \rightarrow \) trans back-reaction at all, i.e. \( \beta = 0 \). Thus the intensity is described by eqn (5). Plots are given in [16], but Fig. 2 for the case \( \alpha/\beta = 50 \) of relatively small \( \beta \) also shows how for low \( \alpha \) the decay from the surface intensity is exponential, but that penetration is much deeper for higher \( \alpha \), being initially a linear decay until finally decaying as an off-set exponential beyond the characteristic depth \( d_t \), that is for \( x > d_t \alpha \).

Such non-exponential behavior suggests caution when trying to establish an extinction length from the attenuation of a light beam on traversing a cantilever. For instance [14] an attenuation of 99% on traversing a cantilever of thickness 1\( \mu \)m, were Beer’s Law being followed, would result from an extinction length of \( d_{\text{Beer}} = 1\mu \text{m}/(2\text{ln}(10)) \sim 0.22\mu \)m. But if \( \alpha \) is not small, much more light penetrates to \( x = w \) (Fig. 2 is a guide). The \( d_{\text{Beer}} \) value derived is a gross over-estimate of \( d_t \). Solving for \( d_t \) from eqn (5) for a given attenuation \( T(w) \) on reaching the back face at \( x = w \) yields for 99% attenuation: \( d \sim w/(\alpha + 4.6) = 1\mu \text{m}/(\alpha + 4.6) \to 0.04\mu \)m for \( \alpha = 20 \). The true \( d_t \) associated with a possible exponential decay may thus be much lower than the value \( d_{\text{Beer}} \) estimated as above, an indication that light has penetrated much further into the sample than would be expected for a simple exponential profile. Quantitative measurements of light attenuation varying with thickness or varying with incident intensity would resolve this ambiguity about \( d_t \) and also allow a determination of \( \alpha \). Attenuation at one thickness can only give an upper bound on \( d_t \).

The reasons for departures from Beer’s law for the intensity can be seen by returning the solution \( I(x) \) to eqn (3) to obtain the spatial variation of the cis concentration. Fig. 3 for the case \( \alpha/\beta = 50 \) is a guide to the \( \beta = 0 \) plots (see [16]) and displays exponential decay in \( n_c(x) \) following \( I(x) \) for low intensity (\( \alpha = 0.1, 0.5 \)). High incident intensity not only lifts \( n_c(x = 0) \) at the surface, but also flattens the decay with depth – high \( n_c \) means low \( n_i = 1 - n_e \) and hence fewer trans dye molecules in a state to deplete the incoming beam (a photo-bleached state). With photo-bleached surface layers, radiation penetrates well beyond \( x \sim d_t \), and equally, contraction extends deep into the bulk, certainly beyond
the Beer penetration depth \(d_t\).

For \(\alpha = 0.5\) a point of inflection first appears at the surface, and moves inwards with increasing incident intensity \(\alpha\). The \(\text{cis}\) fraction at the inflection is always \(n_c = 1/3\) in this model. In the general case where \(\beta \neq 0\) we find that the value of \(\alpha\) at which the point of inflection first appears at the front surface is a complicated function of the constant ratio \(\beta/\alpha\), and the value of the \(\text{cis}\) fraction at the inflection point is no longer \(1/3\). From eqn (9), the surface \(\text{cis}\) concentration is \(n_c(0) = \alpha/(1+\alpha)\), since there \(T = 1\), and rises to saturation, \(n_c = 1\), as intensity increases. The precise form of the cantilever bend depends critically on the shape of these \(n_c(x)\) curves. In particular the development of a point of inflection allows three intercepts of the straight, geometric strain curves, and thus three neutral surfaces, we will later see. Since \(n_c(x)\) changes shape with increasing intensity, we will find an elastic response that is highly non-linear with intensity.

**B. CASE 2 - \(\alpha/\beta = 50\)**

We now consider the case with a weakly stimulated back-reaction, \(\beta = \alpha/50\), and henceforth take \(\eta = 1\). Fig 2 shows plots of the reduced intensity as a function of \(x/d_t\). The reduced intensity curves are largely identical to the \(\beta = 0\) case. Once again, for small values of \(\alpha (=0.1, 0.5)\) the decay is essentially exponential, with a characteristic length given by \(d_t\). Increasing \(\alpha\) leads to deeper penetration, with the initial decay being essentially linear. However close inspection of the \(\alpha = 10\) curve reveals a slight upwards curvature, a result of the higher order corrections in \(\beta\) that we take from [3] to [9]. Eventually \(t(x)\) becomes exponential at penetration depths \(x \sim d_t\alpha\) significantly greater than \(d_t\).

As we show above, for \(\beta \geq 1\), that is here \(\alpha \gtrsim 50\), the initial behavior should (briefly) revert to being exponential before attaining the linear decay associated with non-Beer. This point is easier to display below when we consider smaller \(\alpha/\beta\) ratios.

The \(\text{cis}\) profiles as a function of depth are shown in Fig 2. For the values of \(\alpha\) plotted, the curves are essentially identical to those in the \(\beta = 0\) case. High incident intensities result in larger \(\text{cis}\) fractions near the surface, and a flatter decay as before. The point of inflection occurs for a \(\text{cis}\) fraction less than the \(1/3\) found in the \(\beta = 0\) case, but it is still of importance that inflections exist for the character and number of neutral surfaces we explore later.

**C. CASE 3 - \(\alpha/\beta = 5\)**

Increasing the stimulated back reaction further we take \(\alpha/\beta = 5\). The curves for the reduced intensity as a function of depth, see Fig 1, now differ somewhat from those in the small \(\beta\) limit, e.g. as in Fig 2. For the smaller values of \(\alpha\) the curves remain exponential with a characteristic length \(d_t\). Increasing \(\alpha\) leads to some increased penetration, without showing the long linear decay in reduced intensity seen in Fig 2. For \(\alpha = 10\) we have \(\beta t = 2\) at most, a value evidently insufficient to satisfy limit (iii). We do not have a finite initial region for small \(x\) where the decay is exponential with \(d_{\text{eff}}\) given in and below eqn (9). For these values of \(\alpha\) and \(\beta\) one would have \(d_{\text{eff}} = 3d_t\). The dashed line shows the infinite \(\alpha\) limit, and corresponds throughout its range to eqn (9), i.e. an exponential with characteristic length \(d_{\text{eff}} = d_t(\alpha + \beta)/(\beta(1 + \eta)) = 3d_t\). Note that the initial of the \(\alpha = 10\) curve is close to that of the \(\alpha = \infty\) curve.
FIG. 5: The decay in cis depth for various reduced incident intensities α with α/β = 5.

FIG. 4: The decay in reduced light intensity with reduced the backreaction, mophores will also absorb light. For simplicity ignoring α depth for various reduced incident intensities in influence the non-linear absorption for intense beams. The isomerisation processes can be biased by mechanical plex effect is that of the host medium when it is a solid. Another, more com-plex effect is that of the host material that is not a chromophore. In prin-ciple this is the simplest form of absorption and for weak beams where both processes are Beer-like the effect can simply be divided out. W e examine how this procedure translates to the non-linear case. Another, more complex effect is that of the host medium when it is a solid. The isomerisation processes can be biased by mechanical effects, as is well-known from linear experiments. These influence the non-linear absorption for intense beams.

III. OTHER ABSORPTION PROCESSES

At least two other influences are important in non-linear absorption. How does one deal with the absorption of the host material that is not a chromophore. In prin-ciple this is the simplest form of absorption and for weak beams where both processes are Beer-like the effect can simply be divided out. We examine how this procedure translates to the non-linear case. Another, more complex effect is that of the host medium when it is a solid. The isomerisation processes can be biased by mechanical effects, as is well-known from linear experiments. These influence the non-linear absorption for intense beams.

A. Beer-Lambert host absorption

It will always be the case that the host for the chromophores will also absorb light. For simplicity ignoring the backreaction, β = 0, the absorption equation [5] be-

\[
\frac{dI}{dx} = -\left(\frac{n_t h}{d_t} + \frac{1}{d_h}\right) I(x). \tag{10}
\]

The absorption length \(d_t\) of course emerges naturally by measuring the absorption of a sample without dye, \(-\ln(I_w) = w/d_h\). Using \(n_t = 1/(1 + \alpha I)\), and denoting the ratio of absorption lengths \(\psi = d_t/d_h\), integration yields:

\[
\ln(I_w) + \frac{1}{\psi} \ln \left(1 + \frac{1 + \psi(1 + \alpha I_w)}{1 + \psi(1 + \alpha)}\right) = -w/d_{\text{eff}} \tag{11}
\]

where the effective absorption length is \(1/d_{\text{eff}} = 1/d_t + 1/d_h\). The relation \(\psi\) for \(I_w\) has close similarities to that for the profile with a back reaction, eqn (10). The limit \(\psi \to 0\) of eqn (11) of no host absorption leads to the previous Lambert-W expression given below eqn (8). In the conclusions we discuss how host absorption can be allowed for in measurements.

B. Absorption of intense beams in solid hosts

The role of the host has been much studied in dynamical studies of absorption. When the host, typically a polymer or a network, is below the glass temperature then it is observed that there is more than one characteristic decay time for the cis population of guest chromophores. Eisenbach [21] clearly observed two times, the relative weight of the processes being dependent upon temperature. The slower process was analogous to that observed in a liquid host and becomes the only pro cess present at elevated temperatures. The faster process was speculated to arise from the strained state of a cis isomer; a fraction of the molecules when in a bent state are in conflict with the solid matrix around them and thereby decay more quickly to the trans form. Other authors [22] suggest that there is a spectrum of relaxation times corresponding to a range of environments that cis chromophores find themselves in. Eisenbach also found that, when above its glass temperature, rubber provides a liquid-like environment for its chromophore guests. There was only one relaxation time and this was comparable to that found when chromophores were dissolved in liquids, a fact of considerable importance since elastomers are used as photo-mechanical media.

Ignoring for simplicity photo-induced back reactions (as shown to be the case for instance in the Eisenbach study), the dynamical equation (11) is modified in that in principle the forward rate \(\Gamma_t\) could become a function its environment (denoted by \(p\)) and the thermal back reaction rate \(1/\tau\) is certainly a function of \(p\). The result is that the characteristic reduced intensity is now a function of environment and we denote it by \(\alpha_p = \Gamma_p/\tau I_0\). The equilibrium trans number fraction for chromophores in the environment \(p\) is thus \(n^p_t = 1/(1 + \alpha_p I)\), see the original equation (8). Let the probabilities of finding a chromophore in the \(p\) environment be \(a_p\). Then
the total \emph{trans} volume fraction of chromophores is \( n_t = \sum_p a_p/(1 + \alpha_p I) \), and it is this \( n_t \) that must appear in eqn (24):

\[
\frac{1}{I} \frac{dI}{dx} = -\frac{1}{d_t} \sum_p \frac{a_p}{1 + \alpha_p I} \tag{12}
\]

\[-w \frac{dt}{dt} = \int_0^1 \frac{dI}{I} \left( \frac{a}{1 + \alpha I} + \frac{1 - a}{1 + \alpha I} \right) \tag{13}
\]

\[-w \frac{dt}{dt} = \frac{1}{\alpha} \left( \alpha_1 + \alpha_2 - \alpha - \frac{\alpha_1 \alpha_2}{\alpha} \right) \ln \left( \frac{1 + \alpha}{1 + \alpha_1} \right) + \ln I - (1 - I) \frac{\alpha_1 \alpha_2}{\alpha} \tag{14}
\]

The first equation is general, the second two have been specialised to the Eisenbach case of two decay rates and thus \( \alpha_1 \) and \( \alpha_2 \) with weights \( a \) and \( 1 - a \) respectively. Here \( \alpha = \alpha_1 + (1 - a) \alpha_2 \); note that this is not an averaged \( \alpha_p \). Again, this result has similarities of form with the specialised to the Eisenbach case of two decay rates and thus \( \alpha_1 \) and \( \alpha_2 \) with weights \( a \) and \( 1 - a \) respectively. Here \( \alpha = \alpha_1 + (1 - a) \alpha_2 \); note that this is not an averaged \( \alpha_p \). Again, this result has similarities of form with the

\[
\int_0^w \sigma(x) dx = \int_0^w \left( \frac{x}{R} + K + n_c(x) \right) dx = 0,
\]

\[
\int_0^w x \sigma(x) dx = \int_0^w x \left( \frac{x}{R} + K + n_c(x) \right) dx = 0. \tag{15}
\]

When the modulus is constant it drops out, but must generally be retained (for some photo-glasses \( E \) is known to vary with illumination \( I \)). Performing these integrations we have:

\[
\frac{w^2}{2R} + Kw = -\int_0^w n_c(x) dx \tag{16}
\]

\[
\frac{w^3}{3R} + K w^2 = -\int_0^w x n_c(x) dx. \tag{17}
\]

Simplifying between these two expression we obtain for the radius of curvature:

\[
\frac{1}{R} = \frac{12}{w^3} \int_0^w \left( \frac{w}{2} - x \right) n_c(x) dx \tag{18}
\]

Eqn (18) can be rearranged to give an expression for \( n_c(x) \), recalling \( d_t/d_c = \eta \beta/\alpha, \eta = \gamma_c/\gamma_t, \) and \( n_t = 1 - n_c \):

\[
n_c(x) = \frac{1}{1 - \eta \beta^2/\alpha} + \frac{d_c}{d_t} \frac{1}{1 - \eta \beta^2/\alpha} \frac{dI}{I} \tag{19}
\]

Inserting this expression into eqn (18) and changing integration variables \( \int_0^w dx \to \int_{x_0}^w dx \) we have:

\[
\frac{d_t}{R} = 12 \left( \frac{d_c}{w} \right)^3 \left( 1 - \eta \beta^2/\alpha \right) \int_{x_0}^w \left( \frac{w}{2d_t} - x \right) \frac{dI}{I}. \tag{20}
\]

Substituting for \( x/d_t \) and \( w/d_t \) from eqn (6) and integrating, we obtain (with \( \beta' = \beta(1 + \eta) \)):

\[
\frac{d_t}{R} = \frac{12 \alpha}{\beta' (w/d_t)^3} \left[ L_{k2}(-\beta') - L_{k2}(-\beta'I_w) - \frac{1}{2} \ln(I_w) \ln[(1 + \beta'I_w)(1 + \beta')] \right] \tag{21}
\]

where \( L_{k2}(x) = \int_x^0 dt \ln[(1 - t)/(1 - t)] = \sum_{k=1}^\infty \frac{x^k}{k^2} \) is the dilogarithm. The limit \( \beta' \to 0 \) within this expression recovers our earlier expression for the curvature:\n
\[
\frac{d_t}{R} = \frac{12 \alpha d_t^3}{w^3} \times \left[ \frac{w}{d_t} I_w - (1 - I_w) \left( 1 - \frac{w}{2d_t} \right) - \frac{3}{2} \alpha (1 - I_w^2) \right] \tag{22}
\]

At low incident light intensity, \( \alpha \to 0 \), analysis for exponential decay gave maximal reduced curvature \( w/\alpha R \) for \( w/d \sim 2.63 \). In this limit \( 1/R \sim \alpha \sim I \), hence the division by \( \alpha \) to obtain results universal for all (low) intensities of incident light. As intensity increases, the maximum in \( w/\alpha R \) moves to larger \( w/d \) because the radiation penetrates more deeply.

The non-linear regime, at fixed Beer’s Law penetration \( d_t \), is best revealed by reducing \( R \) by \( d_t \) instead of by \( w \), and by not reducing \( 1/R \) by \( \alpha \). Fig. 6 plots \( d_t/R \) against \( w/d_t \) to reveal maxima in \( d_t/R \) at greater \( w \) as intensity \( \alpha \) and thus penetration increases. At a given \( w/d_t \), one sees curvature increase initially with intensity, the Beer limit, and then reduce as penetration increases and gradients of strain are reduced. Thus appreciable curvature arises experimentally even in cantilevers thick...
FIG. 6: Curvature reduced by 1/\(d_t\) against reduced cantilever thickness \(w/d_t\) for various incident reduced light intensities \(\alpha\), with \(\alpha/\beta = 50\) (upper) and \(\alpha/\beta = 5\) (lower). For high intensities, bleached surface layers let light penetrate more deeply and hence a significant fraction of the cantilever has its natural bleached surface layers let light penetrate more deeply and where back reaction is purely thermal, and are seen at ever smaller thicknesses than in the \(\beta = 0\) case where back reaction is purely thermal, and are seen at ever smaller thickness as \(\beta\) increases.

in the sense \(w \gg d_t\); in \[11\] it appears that curvature is induced even though the cantilevers involved (with \(w = 10\mu m\)) are apparently at least 100 times thicker than their extinction length! (See also \[14\] on.) The curvatures against thickness for various intensities \(\alpha\) in the case of \(\alpha/\beta = 50\) studied above are practically identical to those in the \(\beta = 0\) limit of \[14\]. As the back-reaction rate increases relative to the forward rate, \(\alpha/\beta = 5\), the penetration is less and the curvature maxima move to noticeably smaller reduced thicknesses \(w/d_t\), see lower pane.

In the limit of intense illumination, that is \(\alpha \gg 1\), the intensity profile simplified to \(I \approx 1 - x/(\alpha d_t)\) for penetration \(x < \alpha d_t\) and hence intensity such that \(\alpha I > 1\). Under these circumstances \(n_c \approx 1 - 1/(\alpha I)^2\) and, importantly for the curvature, \(n_c' \approx -1/(d_t(\alpha I)^2)\). If the thickness \(w \ll \alpha d_t\), then the largely linear profile of \(I(x)\) obtains through most of the thickness of the cantilever and also \(I \approx 1\). One can then approximate \(n_c' \approx -1/(d_t(\alpha I)^2)\). While the strain follows \(n_c(x)\) linearly, then there will be a linear change of photo-strain, that is new natural state of the cantilever, through the thickness. If the geometric bend follows this exactly, then there is no effective internal stresses in the material. This condition fixes the curvature as \(d_t/R = A/\alpha^2\). We thus see that this definition of very strong irradiation involves the thickness \(w\) in relation to \(\alpha d_t\). It is a condition that penetration is so deep that light emerges from the other side of a heavily dye-loaded sample since there is no region of exponential decay of \(I(x)\). Moreover, because of the deep penetration, the curvature now diminishes with increasing intensity (like \(1/\alpha^2\)), rather than increasing. The time taken for the profile to reach the highly bleached form above can be long, a problem we return to in modeling the non-linear dynamics of intense absorption \[19\].

Quantitative measurements of reduced curvature \(w/R\) with \(L_e\) are required to probe this complex dependence of curvature on thickness and incident intensity. Particular care must be taken to irradiate long enough for equilibrium to be reached, and possibly curvature to reduce from high intermediate values.

V. STRAIN DISTRIBUTIONS

In the linear case \[13\] of bend induced by exponentially decaying optical intensity, two neutral surfaces arise, that is surfaces of zero stress where the geometric strains arising from curvature happen to match the local photo-strain: \(x_n/R + K + n_c(x_n) = 0\). A classical cantilever bent by imposed terminal torques has a single neutral surface at its mid-point \(x_n = w/2\), so that stresses that are equal and opposite about the \(x = w/2\) sum to zero to give no net force. In the current case of cantilevers bending because of strains generated internally by light, rather than by external imposition of torques, the additional constraint of no net torque leads to a more complex distribution of stresses which gives rise to more than one neutral surface.

The maximum values for both the curvature \(1/R\) and contraction \(K\) are intimately related to the positions of the neutral surfaces. Differentiating eqns \[16\] and \[17\] with respect to the cantilever thickness \(w\) and solving between the resulting equations, we obtain the relationship:

\[
\frac{dR}{dw} = 3R^2 \frac{dK}{dw},
\]

thus both \(1/R\) and \(K\) are maximized for the same cantilever thickness. Furthermore, returning \(\frac{dR}{dw} = dK/dw = 0\) to either of the differentiated equations, one finds that the thickness at which this happens, \(w^*\), satisfies \(w^* R + K + n_c(w^*) = 0\), i.e. the straight line of geometrically induced strain intersects the photo-strain \((\sim n_c(x))\) curve at the back surface of the cantilever. The back surface is a neutral surface when the curvature is maximized. The curve \(n_c(x)\) is always a strictly decreasing function of \(x\); however there is a fundamental difference between the curves in the \(\beta = 0\) case for \(\alpha < 0.5\) and those for \(\alpha > 0.5\) – the latter \(n_c(x)\) curves have a point of inflection \((n_c''(x) = 0)\). The straight line of geometrically generated strain imposed from curvature,
\[-(x/R + K),\text{ can intersect the } n_c(x)\text{ curve at most twice if there is no point of inflection, and at most three times if there is a single point of inflection. It is not possible for the strain to satisfy the constraints of vanishing force and torque, that is satisfy eqns } (15) \text{, and have a neutral surface at the back surface of the beam with only two neutral surfaces; thus there is no maximum for the curvature unless the underlying neutral surfaces; thus there is no maximum for the curvature.}\]

\[\beta \neq 0 \text{ the } \alpha \text{ value that divides the curves into those with and those without an inflection point is no longer exactly } \alpha = 0.5 \text{ but, as can be seen in Fig 3, for small } \beta \text{ the division is still at an } \alpha \text{ close to 0.5.}\]

To illustrate the significance of inflections, two sample curvature strains of purely geometric origin are superimposed in Fig 3. On the \( \alpha = 10, \beta = 0.2 \) curve is also plotted the straight line \(- (x/R + K)\) for a cantilever of thickness \( w = 12.5d_t \), a thickness that is before the inflection point in the \( n_c(x) \) curve. As can be seen, the straight line intersects the underlying \( n_c(x) \) curve only twice in satisfying eqns (15) and locates only two neutral surfaces. On the \( \alpha = 5, \beta = 0.1 \) curve is also plotted \(- (x/R + K)\) for the critical thickness \( w = w^c = 9.313d_t \), where the third neutral surface first appears. One sees that this line intersects the underlying \( n_c(x) \) curve three times, internally twice with the third intersection (neutral surface) coinciding with the back surface. This line is that of maximal possible slope, \( dR/dw = 0 \). With further increasing thickness, \( d/R \) decreases. Eventually a neutral surface migrates to the front face and is lost. The cantilever continues to have only 2 neutral surfaces thereafter. Fig. 7 shows how the neutral surfaces change with increasing thickness at fixed illumination \( \alpha = 5, \alpha/\beta = 50 \). Features are slightly shifted to smaller \( w \) in comparison with the \( \beta = 0 \) case of [16]. With two regions of compression and two of elongation, one expects subtle behavior when considering compression-induced director rotation [24] in such cantilevers, to which we return elsewhere.

**VI. TEMPERATURE EFFECTS**

We have neglected the effect of heat generated by absorption of light. Gradients of optical intensity in the cantilever might be expected to generate gradients of temperature and thus of thermal contraction, leading to thermal bend. Experiments where polydomain elastomers bend in the direction of the polarization of light [11] show directly that optical effects dominate (see the analysis of polydomains in [12]) over thermal component of bend. We here quantify the relative size of optical and thermal effects. Let the temperature distribution in the beam be \( \theta(x,t) \), and take the origin of the temperature scale be such that the ambient temperature outside the cantilever is zero, \( \theta = 0 \). The temperature distribution satisfies a continuity equation in which the heat flux contains the usual thermal gradient term \(- \kappa \frac{\partial \theta}{\partial x} \hat{\mathbf{x}} \) and the divergence of the Poynting flux, \( I(x)\hat{\mathbf{x}} \), is a source term:

\[
C \frac{\partial \theta}{\partial t} - \kappa \frac{\partial^2 \theta}{\partial x^2} = -I_0 \frac{\partial I}{\partial x} \tag{24}
\]

where \( C \) is the specific heat of the the cantilever per unit volume and \( \kappa \) is the thermal conductivity perpendicular to the director, that is along the normal to the flat surface of the cantilever. The diffusion co-efficient \( D \) is given by the ratio \( \kappa/C \). Typical values for elastomers are around \( \sim 10^{-7} \text{m}^2\text{s}^{-1} \) [25], with some anisotropy in \( D \) arising in nematic elastomers from anisotropy in the conductivity that we ignore here since thermal effects will in any case turn out to be small. The time taken for heat to diffuse across the thickness of the cantilever is \( \approx w^2/D \sim 0.001 \text{s} \) for a 10\( \mu \text{m} \) sample [11, 26]. For times significantly longer than this, one obtains the steady state solution \( \theta(x) \). At the front and back surfaces there are convective losses which are described by Newton’s law of cooling, that is the heat flux carried away from a surface is \( \delta \theta/\delta t \) (the temperature outside is \( \theta = 0 \)), where \( \delta \) is the convective heat transfer co-efficient. For free convection in air, \( \delta \approx 5 \text{ W m}^{-2} \text{K}^{-1} \). These convection losses are equal to the thermal flux of heat at the respective surfaces:

\[
\theta(0) - \frac{\kappa}{\delta} \frac{\partial \theta}{\partial x} \bigg|_{x=0} = 0
\]

\[
\theta(w) + \frac{\kappa}{\delta} \frac{\partial \theta}{\partial x} \bigg|_{x=w} = 0, \tag{25}
\]

where the signs reflect the direction of the outward surface normal. The thermal conductivity is \( \kappa \approx 0.2 \text{ W m}^{-1} \text{K}^{-1} \) [27]. The solution to eqn (24) satisfying boundary conditions is:

\[
\frac{\theta(x)}{\theta} = 1 - \frac{\left( 1 + \frac{\delta x}{\kappa} \right) \left( 1 + \int_0^1 I(wy)dy \right)}{(2 + \frac{\delta x}{\kappa} \int_0^1 I(wy)dy)}
\]

\[
+ \frac{\delta w}{\kappa} \int_0^1 \hat{\mathbf{y}} I(wy)dy \tag{26}
\]

The characteristic temperature \( \tilde{\theta} = I_0/\delta \) is the temperature that the sample surface would need to attain in
order to lose by Newton cooling all the heat equivalent to the incident Poynting energy. Both of the integrals appearing in this expression have been scaled such that their value is bounded by unity. The scale of their contributions is thus set by their pre-factor $\delta w/\kappa$. This dimensionless quantity compares the thickness of the sample $w$ with the thermal penetration length set by the boundary conditions $\kappa/\delta$.

There are several interesting limits to this equation:

(i) Using the values for $\kappa$ and $\delta$ given above and assuming a cantilever thickness $w \sim 10\mu m$ we obtain $\frac{w}{\kappa} \approx 2.5 \times 10^{-4} \ll 1$, and thus the temperature distribution is essentially constant throughout the sample, that is:

$$\frac{\theta(x)}{\theta} = \left(1 - \frac{I_w}{2}\right) + O(\delta w/\kappa) \quad (27)$$

A constant temperature through the sample leads to contraction along the long axis of the cantilever, but it will not induce bending, since this requires differential contractions. Therefore in this limit, which is close to experimental reality, bending effects in the steady state are due to the optical effects discussed previously, rather than heating.

(ii) Heat is produced proportionately to the rate optical intensity diminishes. There are regimes in which intensity $I(x)$ decays linearly with depth into the cantilever, such as the $\alpha = 10, \beta = 0$ case of [10] where there is linearity throughout if $w \leq 10d_t$, and here in Fig 2, for $\alpha = 10, \beta = 0.2$ where the range of thicknesses where the entire profile is linear is slightly reduced by the influence of stimulated back reactions ($\beta \neq 0$), say $w \leq 8d_t$. For these conditions, that is where $dI/dx = \text{const.}$, then heat is generated at the same rate through the cantilever. In the steady state it diffuses to the surfaces, symmetrically if the surfaces are at the same temperature, and hence heat does not contribute at all to the bending. One sees this since now eqn (26) becomes:

$$\frac{\theta(x)}{\theta} = \left(1 - \frac{I_w}{2}\right) \left[1 + \frac{\delta w}{4\kappa} - \frac{\delta}{\kappa w} \left(x - \frac{w}{2}\right)^2\right], \quad (28)$$

a temperature distribution which is indeed symmetric about the mid-point of the cantilever. Since the thermally-induced strains are also symmetric, they will not produce bending, although once again they will produce an overall contraction. If the cantilever thickness $w$ is increased beyond the linear profile interval in e.g. Fig 2 then asymmetry in the heat production starts to occur, with less heat generated towards the back face. However, the magnitude of the asymmetry is reduced by diffusion and the thermal contribution to bend sets in only slowly with increasing $w$, see (i) above.

The neglect of heat is thus justified in two limits, firstly the convective heat losses from the boundary are likely to result in a uniform temperature distribution through the sample for experimentally realistic values of the thermal conductivity $\kappa$ and the convective heat transfer coefficient $\delta$. Further, in the regime of linear (i.e. non-exponential) decay of intense beams there is no thermal component of bend.

Thermal effects become more extreme, especially in elastomers, if an interior region of the cantilever’s temperature exceeds the nematic-isotropic transition temperature. At this temperature an extremely large strain can develop in elastomers, and possibly in glasses. If it occurs in a region symmetrically disposed about the cantilever mid plane, it could lead to pronounced contractions, but still not to bend. If it occurs in an asymetrically disposed region, it could lead to large bends – an extreme case we return to in considering specifically elastomers and thus at the same time considering director rotation. Additionally one would there consider the displacement of neutral planes due to volumes of the cantilever suffering large contractions of their natural lengths.

VII. CONCLUSIONS

We have shown that non-linear absorption (that is, non-exponential profiles) can be invoked to explain how
bending can arise in cantilevers where, within Beer’s law, one would otherwise expect no response. At high enough incident light intensities, there can be photo-bleaching and thereby penetration of radiation and thus elastic response even in cantilevers so heavily loaded with dye that the Beer penetration depth of the linear regime is insignificant compared with the cantilever’s thickness. The non-linear response in the high dye-loaded limit is possibly of the greatest experimental relevance. We have explored the roles of optically-stimulated de-excitation of dyes and of optically-generated heat in mechanical processes. Stimulated decay can be very important, but the role of heat seems minor.

An experiment [17] to explore the non-linear absorption processes we have described measures the intensity emergent at the back surface for a sample of fixed width w illuminated at the front surface. Altering the incident intensity is equivalent to varying the parameter $\alpha$. Taking a fixed depth (the thickness itself) $w/d_c$ in Fig.2 and increasing reduced incident power $\alpha = I_c/I_t$ is to take a slice through these figures to reveal increasing relative penetration, that is an increased reduced exit intensity $I_w(\alpha) = I_{w}/I_0$, see Fig. [5(a)]. Scaling the output intensity by its incident value would produce a horizontal line $I_w = \exp(-w/d_c)$ as a function of $\alpha$ for simple Beer law attenuation; deviations from this line as power increases away from $\alpha = 0$ are thus signs of non-Beer attenuation processes. In thin cantilevers $w/d_c = 0.1$, $I_w$ is close to unity, and only increases slowly as $\alpha$ is increased – for thin cantilevers nearly all of the incident flux is transmitted in any case. Conversely for thick cantilevers $w/d_c = 10$ we see that there is very little transmittance for small $\alpha$. For larger incident intensities, such that $\alpha \gtrsim 5$, the transmittance begins to increase rapidly with $\alpha$ - a consequence of the increased penetration due to non-linear absorption processes. For two particular sample thicknesses, $\beta \neq 0$ cases are shown too. The curves show that a finite induced back reaction rate reduces enhanced penetration, as one would expect. For the thickest sample, the higher $\beta$ value is sufficient to effectively eliminate penetration of the beam. Deviation from Beer absorbance is perhaps better seen from plots of non-linear absorbance itself, see Fig. [8(b)]. An experimental example, and its relation to their equivalent of our eqn (6), is discussed at length by Statman and Janossy [17].

Despite host and dye absorptive processes being mixed in a non-linear differential equation, an approximate allowance by division by the host transmittance seems to work well: $C_w = I_w/e^{-w/d_h}$ by substitution in eqn (11) yields:

$$\ln(C_w) + \frac{1}{\psi} \ln \left( \frac{1 + \psi (1 + \alpha e^{-w/d_h} C_w)}{1 + \psi (1 + \alpha)} \right) = -w/d_t.$$  

(29)

We plot in Fig.3 the corrected exit intensity $C_w$ implied by (29). For very intense beams, $\alpha \gg 1$, the corrected intensity tends to 1. The dye is bleached and absorption is predominantly by the host. The true profile is then Beer-like and the correction is accurate. At lower intensities the correction is also seen to work surprisingly well. The upper of each curve for a given reduced thickness $w/d_c$ is for no host absorption, representing the pure system being examined. The corrected curve (lower in each case) is close to the ideal curve, even for the very heavy absorption $w/d_h = 0.3$ in the illustration. For smaller absorptions the corrected and the ideal curves are practically indistinguishable. Thus the straightforward correction method should give a good estimate of the underlying non-linear absorptive processes.

Much of the discussion has been of intensities with reference to the ideal Beer intensity, for instance Fig.8(a). Beer behavior obtains when intensities are low enough that the trans population is little reduced. This also obtains at short times when as yet little conversion has taken place. An output power $I_w = \exp(-w/d_c)$ must emerge and has the value of the vertical axis intercept in Fig.8(a) (and is also the same as the reduced weak-beam emergent power). Thus, for a given power $\alpha$ and thickness $w/d_c$, the initial emergent power must rise to the higher value characteristic of the curve in question. The dynamics by which a spatial bleaching pattern is established is non-linear and complicated, see comments below eqn (4).

One can also propose that bleaching can lead to an emergent power that diminishes in time from the initial, Beer value if the cis species have a higher absorption than the trans. A higher cis absorption arises if the incident light frequency is shifted to be closer to the cis absorption line. One can rearrange eqn (4) by evaluating it at $x = w$ and noting that $-w/d_c = \ln(I_B)$, where $I_B$ denotes the Beer, $t = 0$ reduced intensity. Thus denoting by $R$ the ratio $I_w/I_B$, one has:

$$\ln(R) = \frac{1 - \alpha/\beta}{(1 + \eta)/\eta} \ln \left( \frac{1 + \beta I_B R}{1 + \beta R} \right).$$  

(30)
It is evident that the ln on the right hand side is always negative since $I_B R = I_w \leq 1$ and hence if $\alpha < \eta \beta$ then the left hand side is also negative, that is $R < 1$ – the intensity drops below the Beer value rather than rising with time and increasing power. The criterion, referring back to the ratio of the quantum efficiencies, amounts to $d_c < d_t$, that is, attenuation due to cis is greater than that due to trans. Sample thickness is encoded in $I_B = \exp(-w/d_t)$. Solutions to eqn (30) are shown in Fig 10. Care is needed in interpreting this figure: as thickness increases, the absolute amount of light passing through the sample is greatly reduced since the Beer normalisation to $I_w$ in $R$ is becoming exponentially small. This reverse effect of photo-bleaching maybe useful in occasions where at high intensities it is desirable to have a smaller fraction of the light transmitted (but as noted above, the absolute amount of light transmitted is still increasing with incident power). It is possible that biological systems depend on this behavior.

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