Linear and Nonlinear Photoinduced Deformations of Cantilevers

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Glassy and elastomeric nematic networks with dye molecules present can be very responsive to illumination, huge reversible strains being possible. If absorption is appreciable, strain decreases with depth into a cantilever, leading to bend that is the basis of micro-opto-mechanical systems (MOMS). Bend actually occurs even when Beer's law suggests a tiny penetration of light into a heavily dye-doped system. We model the nonlinear opto-elastic processes behind this effect. In the regime of cantilever thickness giving optimal bending for a given incident light intensity, there are three neutral surfaces. In practice such nonlinear absorptive effects are very important since heavily doped systems are commonly used.

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Nematic elastomers can change their length by large factors on losing or recovering their orientational order. Contraction and elongation, respectively, arise because the disordering or ordering of rods causes the network chains to become more spherical or elongated, on average. Mechanical strains follow the molecular shape changes of the constituent chains. Nematic order can be decreased or increased by heating or cooling, and thus huge thermal strains of up to 500% can be observed [1,2]. Equally, if rods are also chromophores, that is dye molecules, then absorbing a photon will cause molecular bend and thus disruption of the rod ordering characteristic of the nematic state. Photo strains are thus analogous to thermal strains in nematic networks; they are also large and reversible [3,4]. More densely crosslinked nematic networks suffer small strains on illumination. They have large moduli and are perhaps better called nematic glasses [5]. Unlike elastomers, their directors, the ordering direction on average of rods, seem to be immobile under elongations imposed at an angle and also probably do not rotate during photo processes [6].

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 will diminish with depth. Curvature of the cantilever results, Fig. 1(a). It is important in micro-opto-mechanical systems (MOMS) where elements can be optically induced to bend as glassy cantilevers [7] and, e.g., as elastomeric photo-swimmers [8]. Sheets of polydomain nematic photo glass can be induced to bend by absorption, the bend direction being that of the light polarization [9].

Simple absorption gives (Beer's law) an exponential decay of intensity with depth and hence also an exponentially decaying conversion of straight to bent (*trans*→*cis*) forms of the dye molecules. Assuming a linear connection (valid for small strains) between *cis* population and contraction, one can calculate the cantilever curvature. A maximum curvature is predicted [10] for $w/d \sim 3$, 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 below respond. Equally, if $w \ll d$, then there is little variation of photostrain through the thickness, and the cantilever may contract but not differentially with depth and thus will bend little. The extent of bend, for a fixed w/d, was also predicted to be linear with intensity.

The purpose of this Letter is to explain the experimentally common situation where heavily dye-doped cantilevers bend. High dye concentrations mean strong absorption and hence small d. Thus, one is frequently in the thin-skin limit $d \ll w$, where bend might be expected to disappear, and yet appreciable effects are still seen [11]. We shall explain this effect for the more straightforward case of no photo-induced director rotation, that is for nematic glasses, or for elastomers with diffuse illumination. Director rotation has been explored in polydomain photo-elastomers and doped polymer films [12,13], and may be complex. We shall also, for simplicity, ignore anticlastic, that is saddle, effects and also ignore curvature leading to obliquity factors for the intensity of light falling on the surface (that is, we consider the case of small deflections or of diffuse light). For simplicity, we also assume a linear connection between the *cis* fraction of chromophores (n_c) and the photo-contractile strain (ϵ_p), that is $\epsilon_p = -An_c$.

With n_t the *trans* fraction ($n_t = 1 - n_c$), matching the rate of loss of *trans*→*cis* by absorption, $-\Gamma I n_t$, with the rate of gain from the *cis*→*trans* backreaction, n_c/τ, one

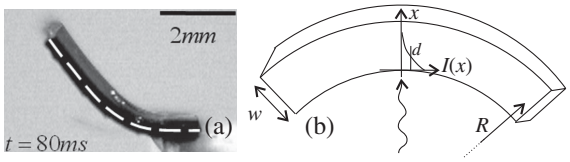

FIG. 1. (a) A cantilever bending towards its side illuminated by a spot (P. Palffy-Muhoray). (b) Radiation penetration with linear absorption length d giving light-induced bend.

obtains the *cis* photo-equilibrium fraction $n_c = \frac{I/I_c}{1+I/I_c}$. The light intensity (Poynting flux) is I, and our constant Γ subsumes an absorption cross section per chromophore (assumed independent of nematic order—itself another source of nonlinearity that is discussed in the polydomain case [12]), and a quantum efficiency [14]. τ is the *cis* state lifetime. The characteristic intensity, $I_c = 1/(\Gamma\tau)$ is a material constant. If we reduce I by its value at the surface, I_0, then with $\mathcal{I}(x) = I(x)/I_0$ and $\alpha = I_0/I_c$, a measure of the incident intensity, one has at depth x

$$n_c(x) = \alpha\mathcal{I}/(1+\alpha\mathcal{I}); \qquad n_t(x) = 1/(1+\alpha\mathcal{I}). \quad (1)$$

The reduced intensity is $\mathcal{I} = 1$ at the entry surface $x = 0$, see Fig. 1(b). Ignoring for the moment attenuation ($I = I_0$), α gives us a measure of how much a beam of intensity I_0 leads to conversion to *cis*, Eqn. (1), by the comparison of I_0 to I_c, that is the balance of the forward to the thermal backward rates $\alpha = I_0\Gamma/(1/\tau)$. In the Eisenbach experiments [15], the average conversion was $n_c \sim 0.84$ and thus $\alpha \sim 5$. Note that α is independent of chromophore concentration, but it does depend on the choice of the light polarization [14]. Experimentally, it is easiest to determine for a system dilute in chromophores, where one can ignore the complications arising when attenuation is significant. Thus, this estimate for α is a lower bound on the actual value; including the effects of attenuation through the cantilever will lead to a higher value of α. In later work [3], one can deduce that $\alpha \sim 0.8$. We ignore photo-induced back-reactions. Eisenbach [15,16] found these to be very weakly stimulated, as in our model. We find for a relatively high back-rate, $\Gamma' = 0.2\Gamma$, our results are qualitatively unchanged for $\alpha \lesssim 5$. We show elsewhere that non-Beer behavior persists for $\alpha \lesssim \Gamma/\Gamma'$.

However, $I(x)$ does diminish because of the forward conversion $-\Gamma I n_t$ of *trans*→*cis*, giving a variation $d\mathcal{I}/dx = -\gamma\Gamma n_t(\mathcal{I})\mathcal{I} \equiv -n_t\mathcal{I}/d$ where γ is another material constant depending on the absolute number density of chromophores and the absorption energy, n_t is given by Eqn. (1), and where $d = 1/(\gamma\Gamma)$ is an exponential decay length obtaining in the $n_t \sim 1$ limit of low incident intensities $\alpha = I_0/I_c \ll 1$ (Beer's Law). Integrating, one obtains the in general nonexponential law [14]

$$\ln[\mathcal{I}(x)] + \alpha[\mathcal{I}(x) - 1] = -x/d. \quad (2)$$

Figure 2 shows how for low α, the decay from the surface intensity is exponential, but that penetration is much deeper for higher α, being initially a linear decay until finally decaying exponentially, well beyond the characteristic depth d, as $\mathcal{I}(x) \sim \exp[-(x - d\alpha)/d]$ for $x > d\alpha$. Such nonexponential behavior suggests caution when trying to establish an extinction length from the attenuation of a light beam on traversing a cantilever. For instance [11], an attenuation of 99% on traversing a cantilever of thickness 1 μm, were Beer's Law being followed, would suggest an extinction length of $d_{\text{Beer}} = 1\ \mu\text{m}/[2\ln(10)] \sim 0.22\ \mu$m. But if α is not small, much more light penetrates to $x = w$ (Fig. 2), and one could grossly overestimate d: solving for d from Eqn. (2) for a given attenuation $\mathcal{I}(w)$ on reaching the back face at $x = w$ yields for 99% attenuation: $d \sim w/(\alpha + 4.6)$. The d associated with exponential decay may thus be much lower than the value d_{Beer} estimated 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 and also allow a determination of α. Attenuation at one thickness only gives an upper bound on d.

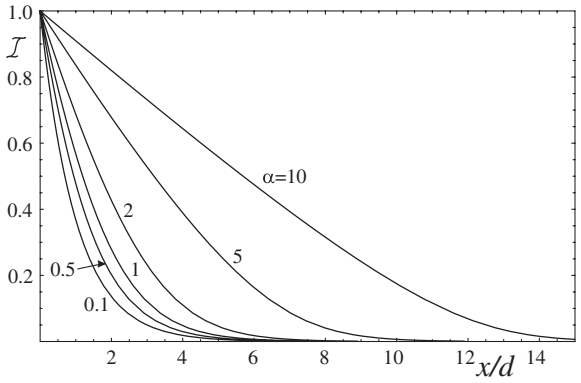

FIG. 2. The decay in reduced light intensity with depth for various reduced incident intensities α.

The reasons for departures from Beer's law for the intensity can be seen by returning the solution $\mathcal{I}(x)$ to Eqn. (1) for the *cis* concentration. Figure 3 displays exponential decay in n_c following $\mathcal{I}(x)$ 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

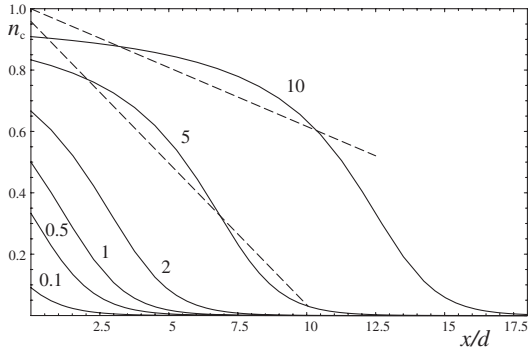

FIG. 3. Number fraction $n_c(x)$ of dye molecules converted to *cis* against reduced depth x/d for various reduced incident light intensities, $\alpha = I_0/I_c$. Increasing α extends the conversion to greater depths because of photo bleaching of the surface layers. Reduced geometric bend strain for $\alpha = 5$, 10 are straight lines. For cantilevers of thickness $w = w* = 10.053d$ and $w = 12.5d$, respectively, there are three and two intersections (neutral surfaces) with the photo-strain curves.

depth—high n_c means low $n_t = 1 - n_c$ 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 $x \sim d$, and equally, contraction extends deep into the bulk, certainly beyond the Beer penetration depth d.

For $\alpha = 0.5$, a point of inflection first appears at the surface and moves inwards with increasing intensity. The *cis* fraction at the inflection is always $n_c = 1/3$ in this model. The surface *cis* concentration is $n_c(0) = \alpha/(1 + \alpha)$ 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. Since $n_c(x)$ changes shape with increasing intensity, we will find an elastic response highly nonlinear with intensity.

Figure 1(b) shows a cantilever with radius of curvature R. The geometric strain from bending is $x/R + K$, where R and K are constants to be determined for a given thickness w and illumination α. The actual strain relative to the new natural length created by illumination is $x/R + K - \epsilon_p$ which, if we further reduce throughout by the dimensionless constant connecting photo-strain and *cis* concentration, that is A, we obtain $x/R + K + n_c(x)$ for the effective reduced strain. When we take Young's modulus, E, not to vary with illumination, strain directly gives the stress. Mechanical equilibrium requires vanishing total force and moment across a section, thus

$$0 = \int_0^w \left[\frac{x}{R} + K + n_c(x)\right] dx = \int_0^w x\left[\frac{x}{R} + K + n_c\right] dx, \tag{3}$$

with $n_c(x)$ given by Eqns. (1) and (2). The constant modulus drops out, but must be retained generally (for some photo-glasses E is known to vary with illumination [6]). Using $d\mathcal{I}/dx$, one can change variable to integrate the n_c terms and obtain the equilibrium conditions

$$0 = \frac{w^2}{2Rd} + \frac{Kw}{d} + \alpha(1 - \mathcal{I}_w), \tag{4}$$

$$0 = \frac{w^3}{3Rd^2} + \frac{Kw^2}{2d^2} + \alpha\left[1 - \mathcal{I}_w + \frac{1}{2}\alpha(1 - \mathcal{I}_w^2) - \frac{w}{d}\mathcal{I}_w\right] \tag{5}$$

where $\mathcal{I}_w$ is the intensity at the back surface of the cantilever. Elimination gives $1/R$ and K; for instance,

$$\frac{1}{R} = \frac{12\alpha d^2}{w^3}\left[\frac{w}{d}\mathcal{I}_w - (1 - \mathcal{I}_w)\left(1 - \frac{w}{2d}\right) - \frac{\alpha}{2}(1 - \mathcal{I}_w^2)\right]. \tag{6}$$

$1/R$ and K depend on w and α directly and through $\mathcal{I}_w = \mathcal{I}(w/d; \alpha)$, itself a nonlinear function of both w/d and α as revealed by Eqn. (2).

At low incident light intensity, $\alpha \to 0$, analysis [10] for exponential decay gave maximal reduced curvature $w/\alpha R$ for $w/d \sim 2.63$. In this limit, $1/R \sim I_o$, hence the division by α to obtain universal results. As intensity increases, the maximum in $w/\alpha R$ moves to larger w/d because the radiation penetrates more deeply.

The nonlinear regime, at fixed Beer's Law penetration d, is best revealed by reducing R by d instead of by w, and by not reducing $1/R$ by α. Figure 4 plots d/R against w/d to reveal maxima in d/R at greater w as intensity α and thus penetration increase. At a given w/d, 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 in the sense $w \gg d$: in [9], it appears that curvature is induced even though the cantilevers involved (with $w = 20\ \mu$m) are apparently at least 100 times thicker than their extinction length. (See also [11].) Quantitative measurements of reduced curvature w/R with I_o are required to probe this complex behavior. Deflections of long cantilevers can be misleading since they can already be large for small curvatures.

We have neglected the effect of heat generated by absorption of light. Gradients of 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 [9] show that optical effects dominate (see the analysis of polydomains in [12]), but how great is any thermal component of bend compared with the nonlinear optical effects we report here? Heat is produced proportionately to the rate intensity diminishes. Thus, in Fig. 2, if the thickness $x = w$ falls into the interval where intensity varies linearly, $d\mathcal{I}/dx = $ 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. As w falls beyond the linear interval, then asymmetry in the heat production starts to occur, with less heat generated towards the back face. However, the temperature distribution loses some of its asymmetry by diffusion, and the thermal contribution to bend sets in only slowly with increasing w. Thus, the neglect of heat is justified in the limit of intense absorption of strong beams. Equally, we have neglected absorption of the nondye component of the elastomer. Background absorption turns out to renormalize the intensity but otherwise not change our results qualitatively.

In the linear case [10], 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 torques simply has a single neutral surface at its mid point $x_n = w/2$, so the stresses that are equal and opposite about $x = w/2$ sum to zero to give no net force. Here, we have the additional constraint of no net torque, and as a result, a more complex distribution of stresses is

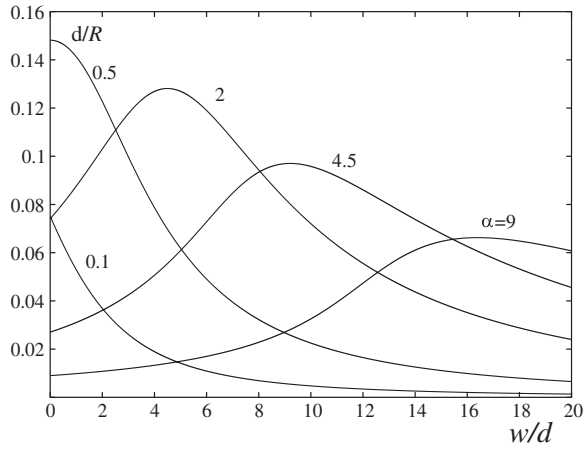

FIG. 4. Curvature reduced by $1/d$ against reduced cantilever thickness w/d for various incident reduced light intensities α. For high intensities, bleached surface layers let light penetrate more deeply, and hence a significant fraction of the cantilever has its natural length contracted. Bend occurs even for cantilevers much thicker than the linear penetration depth d.

required that gives rise to more than one neutral surface. An example is shown in the $\alpha = 10$ plot of Fig. 3 for a cantilever of thickness $w = 12.5d$. The straight line $x/R + K$ intersects $n_c(x)$ twice to satisfy both of Eqns. (3). For $\alpha < 0.5$, there is no point of inflection, $n_c'' = 0$, and there can only ever be two neutral surfaces. One can show that for $\alpha > 0.5$ and thin enough cantilevers, there remain only two neutral surfaces as in the $\alpha = 10$, $w = 12.5d$ example above. Remarkably, however, increasing thickness to a critical value $w^*(\alpha)$ dependent on $\alpha(>0.5)$, the curvature reaches a maximum with w, and a third neutral surface appears at the back face of the cantilever. This sequence of neutral planes can be proven analytically by differentiating (4) and (5) with respect to w. On the $\alpha = 5$ plot of Fig. 3 is shown the (negative) bending strain, the straight line $-(x/R + K)$, for the case where $w = w^*(\alpha = 5) = 10.053d$. One can see the two internal intersections, and

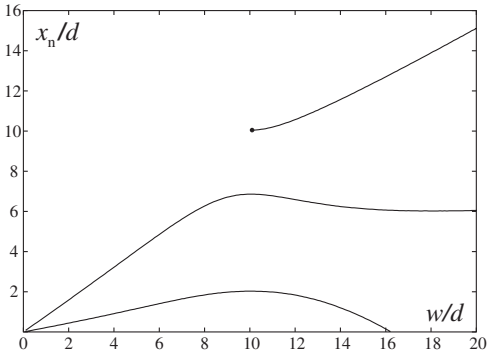

FIG. 5. Neutral surfaces for fixed incident light intensity $\alpha = 5$ as cantilever thickness w changes. At the w maximizing curvature, a third neutral surface appears from the rear face; at greater w, a neutral surface is lost at the front face.

a third at the end point w^*, that is at the rear face. This line is that of maximal possible slope. With further increasing thickness, d/R decreases, and eventually a neutral surface migrates to the front face and is lost. The cantilever continues to have only 2 neutral surfaces thereafter. Figure 5 shows how the neutral surfaces change with increasing thickness at fixed illumination $\alpha = 5$. With two regions of compression and two of elongation, one expects subtle behavior when considering strain-induced director rotation in such cantilevers, to which we return elsewhere.

Conclusions: we have shown that nonlinear absorption (that is, nonexponential 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 would be insignificant compared with the cantilever's thickness. The nonlinear response in the high dye-loaded limit is possibly of the greatest experimental relevance. We discuss two experiments on highly-loaded systems with extremely rich behavior.

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