

Non-linear photo-response of disordered elastomers.

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We model the polarisation-dependent photo-contractions of polydomain nematic elastomers. Contraction initially arises by light-induced director rotation. At higher light intensity, strain recovers because the local order parameter diminishes. Thus we predict photo-strains non-monotonic with light intensity and the induction of a negative global order parameter for the system of polydomains. Non-monotonic strains would give curvature reversal in thick samples. Our model also predicts an elongational strain response to non-polarised light.

Light can externally stimulate actuation in a variety of monodomain liquid-crystalline elastomers [LCE] containing moieties that undergo a *trans-cis* isomerisation on absorbing a photon of appropriate colour [1–3]. Conventional thermally induced contractions of nematic monodomain elastomers can be huge (up to a factor of 4 or more). Heating reduces the orientational order and hence the shape anisotropy of the chains making up the elastomeric network. Macroscopic strain follows the network molecules' shape change in a way we discuss below. Dye molecules (chromophores, for example containing azo-benzene) are often rod-like in their ground (*trans*) state. Photon excitation gives the bent *cis* state, see fig. 1(c), and nematic order is reduced, analogously to the thermal case, as the dye is bleached. It has been proposed and observed that thermal and photo effects can be exactly mapped on to each other [1]. Order parameter is recovered and hence strain reversed in the dark as bent molecules decay back to their straight form. Photo-contraction becomes photo-curling when attenuation of light is appreciable through the thickness giving rise to differential strains. We consider samples thin enough compared with absorption lengths that contraction is uniform.

Are photo-elastic effects simply a thermal response when heat is released on the back-decay from the *cis* excited to *trans* ground state? Ikeda and Yu *et. al.* [4, 5] induced a glassy polydomain network to contract (and curl) along the polarisation direction of the incident light. No bulk thermal actuation of polydomain systems is possible since no unique direction exists. If one assumes that heat is generated in domains aligned with the polarisation direction but transferred quickly to all others, the unique direction is lost. Then these polydomain experiments appear to prove that light actuation must be an optical rather than a disguised thermal effect. Domains are typically very small, often not optically resolvable, and thus heat diffusion very quick. The polarisation specificity of these polydomain samples offers much richer behaviour than monodomains – photo curling can be along any axis desired, useful for complicated actuation. Suggested applications of photo-elasticity range from microfluidic valves to artificial muscles [6].

We model the photo-response of polydomain elastomers, rather than glasses. It is complex since we find that director rotation of the domains occurs, in parallel with the usual reduction of orientational order, and is initially the dominant cause of mechanical strain. We also find that the photo-strain is non-monotonic with the intensity of the incident light and hence even the sign of curl induced in thick samples could reverse. At high intensity most domains are reduced to local orientational isotropy – the equivalent to just heating a polydomain elastomer. The original overall shape is then recovered even though the constituent domains are changed.

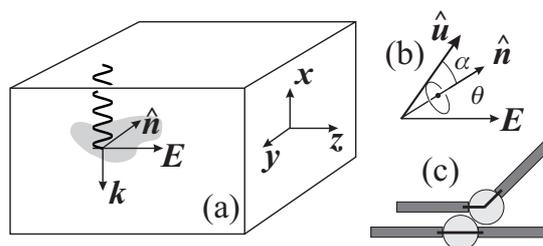


FIG. 1: (a) a polydomain elastomer illuminated by light polarised along the \underline{E} direction (b) a test rod, direction \hat{u} , in a region with director currently along \hat{n} (c) *trans* and *cis* (bent) forms of a dye rod with a central azo unit. Parallel ordering is now hindered.

The situation we seek to model is shown in fig. 1, plane polarised light propagating in the \mathbf{k} direction is incident

normally on a thin polydomain LCE. A region with current director \hat{n} is shown; we do not discuss the origin of domains or require their length scale (typically microns) in what follows. Consider a local test rod within the domain shown described by a unit vector \hat{u} . The probability of photon absorption by a rod depends on the intensity along its axis, $(\underline{E} \cdot \hat{u})^2$. The rate of the photo-induced *trans-cis* reaction is hence $\Gamma \langle (\underline{E} \cdot \hat{u})^2 \rangle n_t(t)$, where Γ is a constant, and $n_t(t)$ is the number density of *trans* nematogens at time t . The local thermodynamic average $\langle \rangle$ is taken over test rods in the region with \hat{n} . The back reaction rate, thermal or photo-induced, is $(n_p - n_t(t))/\tau$, where n_p is the total number density of photo-nematogens and τ is the *cis* state's mean lifetime. In the steady state these two rates match and the fractional *cis* population n_c is

$$\frac{n_c}{n_p} = \frac{\Gamma\tau \langle (\underline{E} \cdot \hat{u})^2 \rangle}{1 + \Gamma\tau \langle (\underline{E} \cdot \hat{u})^2 \rangle}. \quad (1)$$

If $I = E^2$ is the intensity and $Q = \langle P_2(\cos \alpha) \rangle$ the current nematic order parameter of the uniaxial domain, then

$$\langle (\underline{E} \cdot \hat{u})^2 \rangle = \frac{1}{3}I(1 + 2QP_2(\cos \theta)). \quad (2)$$

We assume linear dynamics (i.e. unaffected by mechanical strain etc.) and that the angular diffusion rate is rapid. The latter assures that Q takes the equilibrium value characteristic of the current concentration of unbent nematogen molecules, and that the biaxiality is zero, reflecting the underlying nematic free energy.

The number of *cis* molecules as a fraction of the total number density of nematogens is

$$\phi(Q, I, \theta) = A \frac{I(1 + Q(3 \cos^2 \theta - 1))}{(3I_c + I(1 + Q(3 \cos^2 \theta - 1)))}, \quad (3)$$

where A is the ratio of the number density of photo-nematogens to that of all nematogens, n_n , i.e. $A = n_p/n_n$, and $I_c = 1/\Gamma\tau$ is an equivalent intensity by which we reduce light intensities, $\tilde{I} = I/I_c$. We assume that *cis* molecules have no nematic character, and thus no longer contribute to the nematic free energy. Measurement of n_c/n_p in isotropic polymers [7] suggests \tilde{I} can be as large as 10-12, while timescales for attaining photo-equilibrium range from minutes to seconds, depending upon chemistry and stimulation of backreactions. The low illumination limit, $\tilde{I} \ll 1$, of *cis* concentration is thus $\phi \rightarrow \frac{1}{3}\tilde{I}A(1 + 2QP_2(\cos \theta))$. Note, even domains at rightangles to the polarisation, with $\theta = \pi/2$ and thus $P_2(\cos \theta) = -1/2$, have some *cis* concentration induced if $Q < 1$ because not all rods in the domain are perpendicular to \underline{E} if the order is not perfect. At high intensity, $\tilde{I} \gg 1$, $\phi \rightarrow A$ – all photo-rods are bent and the sample is bleached. Eventually, perpendicular domains are also bleached, except in the unphysical case of those with perfect underlying order, $Q = 1$. It is this capacity to approach bleaching of all regions that causes the polydomain system to lose overall mechanical response when light is intense.

The combined free energy density f in a domain is that of the ordering of the nematogens, f_{LC} , plus the nematic rubber elastic cost of deformation and director rotation with respect to the matrix f_{EL} , that is $f = f_{EL} + f_{LC}$. The wall energy, established at domain formation, may change on deformation and bleaching, but it is smaller than f_{EL} by a factor of $\xi_N/\xi_D \sim 10^{-2}$ [8] where $\xi_D \sim 10^{-6}$ m is the domain size and $\xi_N \sim 10^{-8}$ m is the nematic penetration depth in elastomers. We take local directors in what follows and do not require details of ξ_D .

We adopt a mean field model of nematics based on the canonical Maier-Saupe (MS) model [9]. The true nematic potential H is replaced by that of a mean field h . A test rod feels a mean field potential $H_0 = -hP_2(\cos \alpha)$. The mean field free energy density f_{LC} is:

$$f_{LC} = n_n(1 - \phi)(-k_B T \ln Z(h) + hQ - \frac{1}{2}J(1 - \phi)Q^2). \quad (4)$$

T is temperature, J the MS interaction parameter, and $Z(h) = \int_0^\pi \exp(hP_2(\cos \alpha)/k_B T) \sin \alpha d\alpha$ the partition function. Eqn (4) differs from the standard MS free energy density in two ways. The MS interaction parameter is reduced, $J \rightarrow J(1 - \phi)$, due to each nematogen's reduced co-ordination. Also the number density of nematogens is reduced, $n_n \rightarrow n_n(1 - \phi)$. The optimal mean field and order parameter are found by minimising f_{LC} with respect to h , and the combined f with respect to Q . Eqn (3) shows that ϕ introduces a new source of Q -dependence, the extent of which depends on illumination, \tilde{I} and the orientation, θ , of the particular domain. We sum over all domains, coupled as specified below, following their evolving orientation from their initial randomly distributed values θ_0 .

Classical Gaussian rubber elasticity generalises [8] to a nematic rubber-elastic free energy density

$$f_{EL} = \frac{1}{2}\mu \text{Tr} \left[\underline{\underline{\lambda}} \cdot \underline{\underline{l}}_0 \cdot \underline{\underline{\lambda}}^T \cdot \underline{\underline{l}}^{-1} \right] + \frac{1}{2}\mu \ln \left[\det[\underline{\underline{l}}] / \det[\underline{\underline{l}}_0] \right] \quad (5)$$

in which $\mu = n_s k_B T$ is the shear modulus, with n_s the number density of network strands and $\underline{\lambda}$ the deformation gradient tensor. The bulk modulus of elastomers is typically $\sim 10^4 \mu$, and they consequently deform at constant volume, constraining the deformation gradient tensor to have unit determinant. The remaining tensors \underline{l}_0 and \underline{l}^{-1} are the shape and inverse shape tensors defining the Gaussian distribution of uniaxial nematic polymer chains before and after illumination. They are characterised by the anisotropy direction, initially \hat{n}_0 and rotating to \hat{n} , and the degree of order, initially Q_0 and relaxing to Q which is the minimiser of f now with $\phi \neq 0$. Within the freely jointed rod model they are given by

$$\begin{aligned}\underline{l}_0 &= a \left[(1 - Q_0) \underline{\delta} + 3Q_0 \hat{n}_0 \hat{n}_0 \right], \\ \underline{l}^{-1} &= \frac{1}{a} \left[\frac{1}{1 - Q} \underline{\delta} + \left(\frac{1}{1 + 2Q} - \frac{1}{1 - Q} \right) \hat{n} \hat{n} \right],\end{aligned}$$

with a the rod length. We assume here for simplicity that the length a is itself unchanging as elements of the chain transform from *trans* to *cis*, i.e. they bend. If the chromophores are pendant to the backbone, or are guests in the matrix, this is a good assumption. If $A \ll 1$ it is also a good assumption, even when rods are integral rather than pendant.

The shape tensors set the scale for spontaneous strains. Heating a *monodomain* to the isotropic state ($Q \rightarrow 0$ in \underline{l} above), eqn (5) predicts [8] the elastomer would suffer a uniaxial contraction of $\lambda_m = ((1 - Q_0)/(1 + 2Q_0))^{1/3} \sim 0.56$ for the initial order parameter of $Q_0 = 0.615$ adopted in our illustrations. Separate measurements [10] of the order parameter $Q(T)$ (optically) and the spontaneous distortion confirm the freely-jointed rod model connection $\lambda_m(T) = (((1 + 2Q_0)/(1 - Q_0))[(1 - Q)/(1 + 2Q)])^{1/3}$. In practice even nearly ideal nematic elastomers do not suffer the M-S jump in order parameter (and hence in strain) at the transition temperature T_{ni} because of non-ideal additions to eqn (5) and internal fields. These effects are widely discussed in the literature, see a summary in [8], and briefly below in the adoption of strains. These effects do not seem to influence the connection between order parameter and spontaneous distortion.

Typically there are ~ 50 nematogens per network strand, i.e. $n_n/n_s \sim 50$. We reduce the mean field and coupling by their natural scale, $k_B T$; $\tilde{J} = J/(k_B T)$ and $\tilde{h} = h/(k_B T)$. Both f_{EL} and f_{LC} scale as $k_B T$, thus the only interesting temperature dependence is via \tilde{J} and \tilde{h} . The total free energy density is given by integrating the sum of f_{EL} and f_{LC} over all domains

$$f_{tot} = \int_0^\pi (f_{LC}(\theta_0) + f_{EL}(\theta_0)) \sin \theta_0 d\theta_0. \quad (6)$$

The effect of the network on the phase transition is thus typically small, unless we are sufficiently close to T_{ni} that the low weighting $n_s/n_n \sim 1/50$ of f_{EL} is overcome.

We assume all domains suffer the same, simple uniaxial (about \underline{E}) deformation gradient $\underline{\lambda}$ as the bulk

$$\begin{pmatrix} \frac{1}{\sqrt{\lambda}} & 0 & 0 \\ 0 & \frac{1}{\sqrt{\lambda}} & 0 \\ 0 & 0 & \lambda \end{pmatrix}, \quad (7)$$

that also conserves volume, $\det(\underline{\lambda}) = 1$. In the small strain limit this assumption gives the Taylor (upper) bound on the free energy. In reality there must be a degree of non-affineness – the approximate form (7) generates unphysical internal stresses (the variation of which can imply body forces) that we ignore. Similar approximations arise in modelling the thermal transitions of monodomain elastomers with sub-domains undergoing phase transitions at differing temperatures [11]. More general choices of $\underline{\lambda}$, differing from domain to domain depending on the initial orientation, θ_0 , can be made. For instance including simple shear opens up the possibility of soft deformations, allowing a domain to rotate away from the polarisation direction with almost no elastic penalty as the domain contracts. For small strains this would correspond to the Sachs (lower) bound on the free energy. However there are strong constraints of compatibility and volume conservation that are difficult to meet at large deformations, even in an average sense, and we retain the simple form above.

Inserting $\underline{\lambda}$ into f_{EL} , eqn (5), and adding this energy to f_{LC} gives the local free energy $f_{EL} + f_{LC}$ to be minimised in each domain over director orientation, θ , and order parameter, Q , at a fixed λ . The liquid crystal component f_{LC}

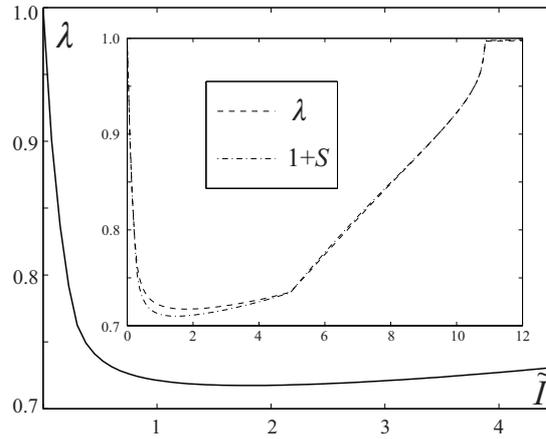


FIG. 2: The global z -contraction λ (also in inset) and mean orientational order S (inset) against reduced light intensity \tilde{I} .

depends only on the current θ (through ϕ) whereas f_{EL} depends on both θ and θ_0 ; thus $\theta(\theta_0, \lambda)$. Equally the order parameter in each domain has the dependence $Q(\theta(\theta_0, \lambda))$. Finally the integral over random initial conditions, θ_0 , gives the total free energy f_{tot} , eqn (6), to be minimised over λ to give the optimal global contraction. Since each domain suffers the same compromise $\underline{\lambda}$, they are in general at a strain unnatural for their current conditions. Such strains act as powerful external fields and eliminate jumps in the order parameter of nematic elastomers.

RESULTS: Figure 2 shows the photo-contraction $\lambda(\tilde{I})$ against reduced light intensity \tilde{I} for the ratio of network strands to rods $n_s/n_n = 1/50$, the fraction of rods that are dye $A = 1/6$, initial order parameter $Q_0 = 0.615$, and inverse reduced temperature $\tilde{J} = 1/0.20$. The transition in a non-crosslinked M-S liquid crystal is at $\tilde{J} = 1/0.22$; thus we are at a real temperature $T = (.2/.22)T_{ni}$, say 32C below a transition at 50C. The contraction at low intensity is drastic, followed by a slower recovery as \tilde{I} increases. There are two kinks in $\lambda(\tilde{I})$ as the elastomer recovers its initial shape at high intensities.

The reasons for the non-monotonic response and the kinks are revealed by figs. 3 that show the new orientation θ and new order parameter Q of the domains as a function of their initial orientation for selected intensities \tilde{I} .

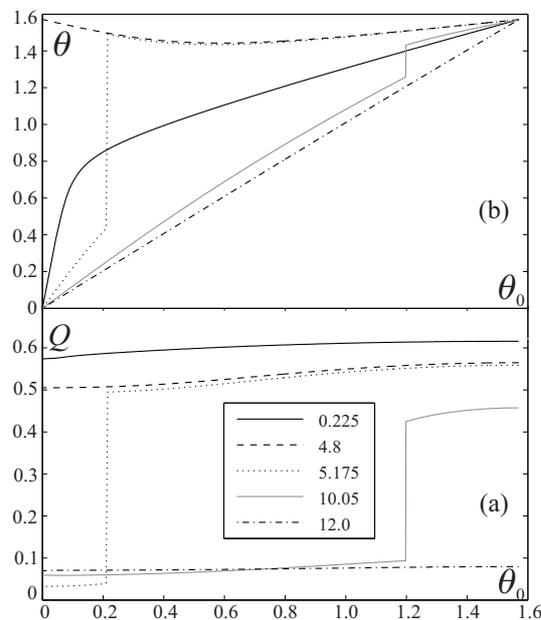


FIG. 3: Current director angle θ (a) and order parameter Q (b) against the initial director angle θ_0 of a domain for various intensities, \tilde{I} , indicated in the legend.

At $\tilde{I} = 0.225$ fig. 3(b) shows very little reduction in local order parameters but fig. 3(a) reveals large rotations of directors away from \underline{E} , most especially of those with small (but $\neq 0$) initial angles θ_0 . The free energy is lowest when the local order parameter is maintained, which is possible when $\hat{\mathbf{n}}$ is rotated away from \underline{E} to avoid dye molecules bending. The rapid overall contraction, $\lambda < 1$, partially accommodates these rotating regions. In rotating from 0 to $\pi/2$, they want to contract along \underline{E} and elongate in their chosen direction in the perpendicular plane. The overall λ is a compromise between the drive of these regions and those regions as yet unchanging. The average order parameter, $S = \int_0^{\pi/2} Q(\theta, \lambda) P_2(\cos \theta) \sin \theta d\theta$, is plotted in the inset of fig 2 as $1 + S$ since $S \leq 0$. It is no longer zero since the domains are no longer randomly distributed but are biased towards $\theta = \pi/2$; thus the negativity of S . Since the local order parameters Q are little reduced at low \tilde{I} , then $S \sim Q_0 \langle P_2(\cos \theta) \rangle$ initially, reaching a minimum of $S \sim -0.3$. Throughout, S remains close to $\lambda - 1$, that is $\lambda \simeq 1 + S$.

By $\tilde{I} = 4.8$ the domains initially around $\theta_0 = 0$ have jumped to $\theta \sim \pi/2$ to which, by now, all domains have tended. Contraction due to rotation is thus complete and relaxation back towards $\lambda = 1$ now starts because the local order parameters $Q(\theta_0)$ are becoming depressed. There is a broad minimum of $\lambda(\tilde{I})$. As λ rises again, domains initially near \underline{E} but currently around $\theta = \pi/2$ rotate back towards a cone closer to \underline{E} . They are now bleached by \underline{E} , that is, most of their rods that are dye molecules are in their bent, excited states. In such regions the local order parameter is very low. The bleached regions now want a lesser contraction along \underline{E} , and overall the compromise λ starts increasing more rapidly. The kink in $\lambda(\tilde{I})$ near $\tilde{I} = 5$ is where this reversion to $\theta \sim \theta_0 \sim 0$ starts. Figs. 3 show in $\theta(\theta_0)$ and $Q(\theta_0)$ the cone of reorientation and bleaching at $\tilde{I} = 5.175$, just above the kink. S now becomes less negative because contributors to it are losing their local order parameter and fewer are rotated towards the perpendicular plane.

The cone widens and λ recovers as \tilde{I} climbs, see $\tilde{I} = 10.05$. The regions, initially at high angles, that are now bleached and therefore isotropic want to contract along their initial directions and elongate therefore along the preferred direction. They thus accelerate the drive of λ back to 1. Bleaching extends to all angles by $\tilde{I} \sim 11$. Beyond this second kink $\lambda \sim 1$ and $S \sim 0$, see $\tilde{I} \sim 12$. The individual $Q(\theta_0)$ are now all small, though curiously those near $Q(\theta_0) \sim 0$ have increased slightly, a consequence of elongation toward $\lambda \sim 1$.

Non-monotonicity in strain and in the macroscopic birefringence, $S(\tilde{I})$, are both predictions to be tested in the next generation of experiments on these delicate, responsive materials. Polarisation-dependent curvature experiments, when performed on polydomain elastomers rather than glasses, could give curling of the opposite sense if the intensity of the minimum of $\lambda(\tilde{I})$ is exceeded in thick samples - the front surface may contract less than the rear surface.

For *unpolarised* normally incident light, our model predicts uniaxial extensions along the beam direction \mathbf{k} , fig 1, and corresponding contractions in the plane of the film. Now the regions with director in the plane of the sample rotate towards the beam. Such strains turn out to be large in our model, i.e. comparable to those suffered by cooling monodomains.

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