Molecular model for light-driven spiral mass transport in azopolymer films - Supplemental Material

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This paper contains a more detailed derivation of the main results of our molecular model, which supplements the sketched derivation of the main Letter.

We describe each azo molecule (or azo moiety) by its position $\mathbf{r}$ and by a unit vector $\hat{\boldsymbol{\mu}}$ representing the orientation of its main axis. Let us denote with $n(\mathbf{r}, \hat{\boldsymbol{\mu}})$ the number density of azo molecules (both excited and nonexcited) per unit volume and solid angle. At equilibrium, before the irradiation starts, this density n may be written as follows:

$$n(\mathbf{r}, \hat{\boldsymbol{\mu}}) = N(\mathbf{r}) f(\hat{\boldsymbol{\mu}}) \tag{1}$$

where $N(\mathbf{r})$ is the molecule number density per unit volume (irrespective of orientation) and $f(\hat{\boldsymbol{\mu}})$ is the orientational distribution. Assuming a uniform distribution of azo molecules across the polymer film, the first is then written as follows:

$$N(\mathbf{r}) = N_0 \theta(z) \theta(L - z) \tag{2}$$

where N_0 is the (uniform) bulk number density and $\theta(z)$ is the Heaviside step function [i.e., $\theta(z) = 0$ for $z < 0$ and $\theta(z) = 1$ for $z > 0$], here used to describe, in an abrupt approximation, the polymer surface located at $z = L$ and the interface with the substrate located at $z = 0$. The equilibrium molecule orientational distribution is taken to be isotropic, that is $f(\hat{\boldsymbol{\mu}}) = 1/(4\pi)$. Putting these two factors together, we obtain the following expression for the equilibrium density:

$$n(\mathbf{r}, \hat{\boldsymbol{\mu}}) = \frac{N_0}{4\pi} \theta(z) \theta(L - z) \tag{3}$$

Now the molecule distribution will be clearly perturbed by the optical irradiation. During the irradiation, the molecules will reorient randomly and after many excitations will tend to become orthogonal to the electric field, so they become anisotropically distributed. Moreover, they will move owing to the mass migration phenomenon, so that also the spatial distribution will be altered. However, all these effects lead to higher-order terms in the optical field, as we shall see further on. Hence, in a first-order approach (that is, linearized in the field intensity) valid for sufficiently short and/or weak irradiations, we may retain the equilibrium distribution n as given by Eq. (3) also during the irradiation.

The excitation probability per unit time of a molecule is written as follows:

$$p(\mathbf{r}, \hat{\boldsymbol{\mu}}) = \alpha |\hat{\boldsymbol{\mu}} \cdot \mathbf{E}(\mathbf{r})|^2 \tag{4}$$

where $\mathbf{E}(\mathbf{r})$ is the (complex) optical electric field, α is a constant proportional to the absorption coefficient at the irradiation wavelength, and we have assumed that the absorption dipole moment is parallel to $\hat{\boldsymbol{\mu}}$. We now assume that at each excitation event a molecule moves only a small distance, relative to the characteristic lenghts defined by the optical gradients, and changes its orientation only slightly (i.e., the reorientation angle is small if expressed in radians). With this assumption, we may write the following rate equation for the number-density of excited molecules n_e at a given location and orientation:

$$\frac{dn_e}{dt} = p(n - n_e) - \frac{n_e}{\tau_e} \tag{5}$$

where $n - n_e$ corresponds to the number of non-excited molecules (for the same position and orientation) and τ_e is the excited state lifetime. In our first-order approximation we may neglect n_e compared with n. At steady-state (for which $dn_e/dt = 0$), we then obtain the following expression for the number-density of excited molecules per unit volume and solid angle:

$$n_e(\mathbf{r}, \hat{\boldsymbol{\mu}}) = p(\mathbf{r}, \hat{\boldsymbol{\mu}}) \tau_e n(\mathbf{r}, \hat{\boldsymbol{\mu}}) \tag{6}$$

From this expression it is clear that any non-equilibrium term in n depending on the irradiation field, after multiplication by the optical field factors already contained in p, will give rise to higher-order powers in the field, hence negligible in a lowest-order approximation. Inserting Eqs. (3)-(4) into Eq. (6), we obtain the following first-order expression for the excited molecule distribution:

$$n_e(\mathbf{r}, \hat{\boldsymbol{\mu}}) = \frac{\alpha \tau_e N_0}{4\pi} |\hat{\boldsymbol{\mu}} \cdot \mathbf{E}(\mathbf{r})|^2 \theta(z) \theta(L - z) \tag{7}$$

Now, the one-dimensional (1D) mass current (per unit volume and solid angle) resulting from the random walk of all excited molecules having a given orientation $\hat{\boldsymbol{\mu}}$ can be written as follows:

$$J(\mathbf{r}, \hat{\boldsymbol{\mu}}) = -D(z) \frac{dn_e}{dx_\mu} = -D(z) \hat{\boldsymbol{\mu}} \cdot \boldsymbol{\nabla} n_e(\mathbf{r}, \hat{\boldsymbol{\mu}}) \tag{8}$$

where $D(z)$ is the excited-molecule diffusion constant, for which we assume the following idealized dependence:

$$\begin{aligned} D(0) &= 0 \\ D(z) &= D_B \quad \text{for} \quad 0 < z < L \\ D(L) &= D_S \end{aligned} \tag{9}$$

Of course, the random walk described by Eq. (8) cannot push the molecule away from the polymer film, owing to the strong cohesion forces acting at the film surface. This effect could be included in the model by adding a boundary constraint-force (and hence mass current) normal to the interface planes. However, we do not actually need an explicit expression for this additional constraint force, because we are only interested in the lateral currents that are not affected by it. We simply assume that the resulting effect of this force is that of imposing $J_z(L) = 0$ for the total current resulting from the combined action of the photoinduced random walk and the constraint force (see [1]).

Inserting Eq. (7) into Eq. (8), we obtain

$$J(\mathbf{r}, \hat{\boldsymbol{\mu}}) = -\frac{\alpha\tau_e N_0}{4\pi} D(z) \left\{ \theta(z)\theta(L-z)\hat{\boldsymbol{\mu}} \cdot \boldsymbol{\nabla} \left[|\hat{\boldsymbol{\mu}} \cdot \mathbf{E}(\mathbf{r})|^2 \right] \right.$$
$$\left. + [\delta(z-L) - \delta(z)](\hat{\boldsymbol{\mu}} \cdot \hat{\mathbf{z}})|\hat{\boldsymbol{\mu}} \cdot \mathbf{E}(\mathbf{r})|^2 \right\} \quad (10)$$

where we have introduced the surface normal unit vector $\hat{\mathbf{z}}$ and Dirac's delta function $\delta(z)$. The first term appearing within curly brackets in this expression of the current is a bulk term, in which the gradients leading to the current are due to the non-uniform light illumination only. The second term, with the δ functions, can be interpreted as interfacial terms with currents driven by the rapid variation of molecule concentration. Since we have assumed $D(z) = 0$ for $z = 0$, we can drop the second of these interfacial terms (relative to the interface with the substrate) and retain only the surface term, for $z = L$.

The total current-density vector $\mathbf{J}$ is then obtained by integrating Eq. (10) over the entire solid angle:

$$\mathbf{J}(\mathbf{r}) = \int J(\hat{\boldsymbol{\mu}})\hat{\boldsymbol{\mu}} d\Omega$$
$$= -\frac{\alpha\tau_e N_0 D_B}{4\pi}\theta(z)\theta(L-z)\int \hat{\boldsymbol{\mu}}\hat{\boldsymbol{\mu}} \cdot \boldsymbol{\nabla}\left[|\hat{\boldsymbol{\mu}}\cdot\mathbf{E}(\mathbf{r})|^2\right] d\Omega$$
$$+ \frac{\alpha\tau_e N_0 D_S}{4\pi}\delta(z-L)\int \hat{\boldsymbol{\mu}}(\hat{\boldsymbol{\mu}}\cdot\hat{\mathbf{z}})|\hat{\boldsymbol{\mu}}\cdot\mathbf{E}(\mathbf{r})|^2 d\Omega \quad (11)$$

Averaging this current along z across the film thickness (assuming z-independent optical fields), we obtain the following expression for the average lateral current:

$$\bar{J}_k = \alpha\tau_e N_0\left(-D_B M_{klij}\partial_l(E_i^* E_j) + \frac{D_S}{L}M_{kzij}E_i^* E_j\right) \quad (12)$$

where $k, l = x, y$, $i, j = x, y, z$, and we set

$$M_{klij} = \frac{1}{4\pi}\int \hat{\mu}_k\hat{\mu}_l\hat{\mu}_i\hat{\mu}_j d\Omega = \frac{1}{15}(\delta_{kl}\delta_{ij}+\delta_{ki}\delta_{lj}+\delta_{kj}\delta_{il}), \quad (13)$$

δ_{ij} being the Kronecker symbol. After reinserting the latter expression into Eq. (12), we obtain our final expression for the mass transverse current:

$$\bar{J}_k = C_1\partial_k(E_l^* E_l) + C_2\partial_l(E_l^* E_k + E_k^* E_l) + C_3\partial_k|E_z|^2$$
$$+ \frac{C_S}{L}(E_z^* E_k + E_z E_k^*) \quad \text{with} \quad k,l = x,y \quad (14)$$

with

$$C_1 = C_2 = C_3 = -\frac{\alpha\tau_e N_0 D_B}{15}$$
$$C_S = \frac{\alpha\tau_e N_0 D_S}{15} \quad (15)$$

From the current, we derive the relief pattern $\Delta h(x,y)$ by using the following equation, derived from the continuity equation using the hypothesis of approximate incompressibility of the polymer and assuming that the film thickness is small as compared with the optical field characteristic transverse lengths (see [1] for details):

$$\Delta h(x,y) = -\frac{L\Delta t}{\rho}\partial_k \bar{J}_k \quad \text{with} \quad k = x,y \quad (16)$$

where Δt is the irradiation time and ρ is the polymer mass density. Inserting Eq. (14) into the latter, we obtain

$$\Delta h(x,y) = c_1\partial_k\partial_k(E_l^* E_l) + c_2\partial_k\partial_l(E_l^* E_k) + c_3\partial_k\partial_k|E_z|^2$$
$$+2c_S\partial_k\text{Re}(E_z^* E_k) \quad \text{with} \quad k,l = x,y \quad (17)$$

with

$$c_1 = c_3 = -\frac{L\Delta t C_1}{\rho} = \frac{L\Delta t\alpha\tau_e N_0 D_B}{15\rho}$$
$$c_2 = -\frac{2L\Delta t C_2}{\rho} = 2c_1$$
$$c_S = -\frac{\Delta t C_S}{\rho} = -\frac{\Delta t\alpha\tau_e N_0 D_S}{15\rho} \quad (18)$$

We note that the coefficient c_S introduced here is defined so that $c_S = c_B = c_B'/2$, where c_B and c_B' are those defined in the Supplemetary Information of Ref. [1], while the symbol c_B appearing in the main article of Ref. [1] includes an additional factor 2.

After making the sums over the transverse Cartesian coordinates explicit, Eq. (17) can be rewritten in the following final form, suitable for a direct calculation for any given irradiation field pattern:

$$\Delta h(x,y) = (c_1 + c_2)\left[\partial_x^2|E_x|^2 + \partial_y^2|E_y|^2\right]$$
$$+c_1\left(\partial_x^2|E_y|^2 + \partial_y^2|E_x|^2\right)$$
$$+2c_2\partial_x\partial_y\text{Re}\left(E_y^* E_x\right)$$
$$+c_3\left(\partial_x^2|E_z|^2 + \partial_y^2|E_z|^2\right)$$
$$+2c_S\left[\partial_x\text{Re}(E_z^* E_x) + \partial_y\text{Re}(E_z^* E_y)\right] \quad (19)$$

[1] A. Ambrosio, L. Marrucci, F. Borbone, A. Roviello, and P. Maddalena, Nat. Commun. **3**, 989 (2012)