

SUPPLEMENTARY INFORMATION

Developing 3D Computational Models to Capture the Spatial, Temporal and Thermal Behavior as Laser Beams Propagate through Photo-thermally Responsive Gels

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SOLUTION OF THE EQUATION FOR COMPLEX AMPLITUDE

The equation for complex amplitude, eq. (11) in the main text, could be written as

$$2ik \left(\frac{\partial A}{\partial z} + (\alpha_{eq} + \delta\alpha)A \right) = \Delta_{\perp} A + 2k^2 \frac{\delta n}{n_0} A \quad (\text{S1})$$

where α_{eq} and $\delta\alpha$ are the respective constant and space-dependent contributions to the coefficient of light absorption (see the main text for notations)

$$\alpha_{eq} = \alpha_w + \alpha_0 \phi_{eq} \phi_{ref}^{-1}$$

$$\delta\alpha = \alpha_0 \phi_{ref}^{-1} \delta\phi + (\alpha_1 - \alpha_0) \phi_{ref}^{-1} \phi p_{sp}$$

After dimensionalization $A \rightarrow A/A_0$, $\mathbf{x} \equiv (x, y) \rightarrow \mathbf{x}/R_0$, $z \rightarrow z/z_d$, eq. (S1) takes the following form:

$$2i \left(\frac{\partial A}{\partial z} + \alpha_{eq} z_d A \right) = \Delta_{\perp} A + S_{int} A \quad (\text{S2})$$

where

$$S_{int} = 2(kR_0)^2 \frac{\delta n}{n_0} - 2i \delta\alpha z_d$$

describes the non-linear effects of medium on propagation of beam. The value of S_{int} is a function of spatial coordinates \mathbf{x} and z because it depends on local values of the volume fraction of polymer ϕ and the degree of isomerization of SP units p_{sp} .

Equation (S2) is solved numerically on the static grid covering the entire simulation cell – see the main text. The 2D Laplacian operator in \mathbf{x} , Δ_{\perp} , is approximated through the 9-stencil finite difference scheme. The numerical solution of the equation for A , eq. (S2), is obtained using the 2D complex fast Fourier transform (CFFT) in \mathbf{x} . Starting from eq. (14) for $A(\mathbf{x}, 0)$, stepping in the Z direction could be represented as

$$A(\mathbf{x}, z + h_z) = \hat{F}^{-1} [G_{\mathbf{q}}^{(0)}(h_z) \hat{F} [e^{-i S_{int}(\mathbf{x}, z) h_z / 2} A(\mathbf{x}, z)]]$$

Here, $h_z = 1/6$ is the dimensionless mesh size in Z direction, \hat{F} and \hat{F}^{-1} are the respective operators of direct and inverse 2D CFFT, and $G_{\mathbf{q}}^{(0)}(z) = \exp[-(\alpha_{eq} z_d + i \lambda_{\mathbf{q}} / 2) z]$ is the Green's function of the equation of beam propagation at $S_{int} = 0$. Finally,

$$\lambda_{\mathbf{q}} = \frac{2}{3h^2} (2 \cos q_x \cos q_y + \cos q_x + \cos q_y - 4)$$

where $h = 1/4$ is the dimensionless size of square XY mesh.

SOLUTION OF THE EQUATION OF THERMAL CONDUCTIVITY

Equation (12) is transformed to the following dimensionless form through substituting $t \rightarrow t/\tau_0$, $A \rightarrow A/A_0$, $\mathbf{x} \equiv (x, y) \rightarrow \mathbf{x}/R_0$, $z \rightarrow z/z_d$

$$\partial \delta T / \partial t = D_T (\Delta_{\perp} + L_z^{-2} \partial_z^2) \delta T + \dot{Q}(|A|^2, \phi, p_{\text{sp}}) \quad (\text{S3})$$

Here, Δ_{\perp} is the 2D Laplacian in \mathbf{x} , $D_T = \kappa \tau_0 R_0^{-2}$ is the dimensionless thermal diffusivity, $L_z = z_d / R_0$ is the ratio of characteristic length scales in the Z and XY directions, and \dot{Q} is the dimensionless heat source

$$\dot{Q}(|A|^2, \phi, p_{\text{sp}}) = \frac{2\tau_0 I_{\text{ref}}}{\rho C_p} \alpha(\phi, p_{\text{sp}}) |A|^2 \quad (\text{S4})$$

Note that the heat source, eq. (S4) does not explicitly depend on δT and is an effective function on the spatial location (\mathbf{x}, z) and time t .

Equation (S3) is solved under the boundary condition $\delta T = 0$ at the bottom and top of the simulation cell that are located at $z_{\text{min}} = -0.125H$ and $z_{\text{max}} = 1.125H$, respectively, where H is the equilibrium thickness of the gel sample in the units of z_d . In order to formulate the boundary conditions in \mathbf{x} , we take into account that the characteristic lateral size of the gel, where the maximal heat is generated, is of the order of beam diameter. We also take into account that in experiments, a gel sample has a lateral size of several centimeters, whereas the lateral size of our simulation cell is much smaller than that. Therefore, we solve eq. (S3) under the boundary condition $\delta T = 0$ at $|\mathbf{x}| \rightarrow \infty$.

In order to accommodate the boundary conditions to the finite size of our simulation box in \mathbf{x} , we use the following approximate approach. At each time step of simulations, we approximate the distributed heat generation, eq. (S4), by a line heat source located at the box center $\mathbf{x} = 0$

$$\dot{Q}_{\text{eff}}(\mathbf{x}, z, t) = \delta(\mathbf{x}) \int \dot{Q}(\mathbf{x}', z, t) d\mathbf{x}' \quad (\text{S5})$$

Then, we apply the Green's function approach for the equation of thermal conductivity with a line source, eq. (5), under the boundary conditions $\delta T = 0$ at $z_{\text{min}}, z_{\text{max}}, |\mathbf{x}| \rightarrow \infty$ to approximately calculate the values of δT at the lateral boundaries of the simulation box. Finally, we utilize the sine fast Fourier transform method (SFFT) to numerically solve eq. (S3) under the found boundary values in order to update δT in the simulation box for the next time step.

MODIFICATION OF THE gLSM FORMULATION

Equations (6)-(8) from the main text for the relationship between stress and strain are obtained from the equation for the energy U of a deformed gel as a functional of the first, I_1 , and the third, I_3 , invariants of the Finger strain tensor $\hat{\mathbf{B}}$ as described in ref. [16] from the main text. Specifically, the energy of the deformed gel (in the units of $k_B T / \nu_0$) is taken in the form

$$U = \int u_{\text{el}}(I_1, I_3) dV_0 + \int u_{\text{FH}}(\phi_0 I_3^{-1/2}, p_{\text{sp}}, T) I_3^{1/2} dV_0 \quad (\text{S6})$$

The first term on the right hand side (r.h.s.) of eq (S6) describes the energy of elastic deformations, where

$$u_{\text{el}}(I_1, I_3) = \frac{c_0}{2} (I_1 - 3 - \log I_3^{1/2}) \quad (\text{S7})$$

is the energy density for the neo-Hookean model of rubber elasticity. The second term on the r.h.s. of eq. (S6) is the energy of polymer-solvent interaction according to the Flory-Huggins model with

$$u_{\text{FH}}(\phi, p_{\text{sp}}, T) = (1 - \phi) \log(1 - \phi) + [\chi_{\text{FH}}(\phi, T) + \chi_{\text{sp}}(T) f_{\text{sp}} p_{\text{sp}}] \phi (1 - \phi) \quad (\text{S8})$$

Here, we take into account that $\phi = \phi_0 I_3^{-1/2}$. Note that integration in eq. (S6) is performed over the volume of undeformed gel V_0 .

In order to formulate the gLSM, we utilize the finite element approximation for the time-dependent deformation, $\mathbf{x}(\mathbf{X}, t)$, where \mathbf{x} and \mathbf{X} are the respective coordinates of a material point in the deformed and un-deformed bodies. We use the approximation based on a tri-linear hexahedral element

$$\mathbf{x}(\mathbf{X}, t) = \sum_{n=1}^8 N_n(\mathbf{X}) \mathbf{x}_n(t) \quad (\text{S9})$$

where $N_n(\mathbf{X})$, $n = 1, 2, \dots, 8$, are the element (local) shape functions having the property

$$\sum_{n=1}^8 N_n(\mathbf{X}) = 1 \quad .$$

In our previous studies, the shape of an element in the un-deformed state of gel was taken cubic – see ref. [17] from the main text. In order to describe a non-cubic shape of element in the un-deformed state, we introduce the reference unit cube element with the shape functions $\mathbf{N}_n(\mathbf{x})$, where $\mathbf{x} = (x_1, x_2, x_3)$ with $0 \leq x_i \leq 1$ for $i = 1, 2, 3$. Then, the approximation (S9) for a non-cubic element can be represented as

$$\mathbf{x}(\mathbf{X}, t) = \sum_{n=1}^8 \mathbf{N}_n(\{X_i / L_i\}) \mathbf{x}_n(t) \quad (\text{S10})$$

Here, $\{X_i / L_i\}$ is the shorthand notation for $\mathbf{x} = (X_1 / L_1, X_2 / L_2, X_3 / L_3)$, and L_i is the size of un-deformed element along the axis $i = 1, 2, 3$.

In the present study, we use $L_1 = L_2 \equiv L_0 = 1.01 h_x / \lambda_{\text{eq}}(0)$ and $L_3 = 1.01 h_z / \lambda_{\text{eq}}(0)$, where $h_x = h_y = R_0 / 4$ and $h_z = z_d / 6$ are the respective mesh sizes of the static grid in the XY and Z directions, and $\lambda_{\text{eq}}(0)$ is the degree of gel swelling at a given temperature in dark. Note that $L_3 / L_0 \approx 27$ in the simulations.

Using the finite element approximation, eq. (S10), we calculate the strain tensor invariants I_1 and I_3 as described in ref. [16] from the main text. First, we introduce the base vectors:

$$\mathbf{g}_i(t) = \frac{\partial \mathbf{x}(\mathbf{X}, t)}{\partial X_i} = L_i^{-1} \sum_{n=1}^8 \frac{\partial \mathbf{N}_n(\{X_i / L_i\})}{\partial X_i} \mathbf{x}_n(t), \quad i = 1, 2, 3$$

The strain tensor invariants I_1 and $J = I_3^{1/2}$ are calculated through the base vectors as

$$I_1 = \sum_{i=1}^3 \mathbf{g}_i^2$$

$$J = \mathbf{g}_1 \cdot (\mathbf{g}_2 \times \mathbf{g}_3)$$

Then, the force acting on the node $n = 1, 2, \dots, 8$ from within a given element is calculated as

$$\mathbf{F}_n = -\frac{\partial U_{elem}}{\partial \mathbf{x}_n} \quad (\text{S11})$$

where U_{elem} is the energy, eq. (S6), calculated for this single element. The result of differentiation can be written as

$$\mathbf{F}_n = -L_1 L_2 L_3 \frac{c_0}{2} \int \frac{\partial I_1}{\partial \mathbf{x}_n} d\mathbf{x} + L_1 L_2 L_3 \int [\pi_{osm}(\phi_0 J^{-1}, p_{sp}, T) + c_0 (2J)^{-1}] \frac{\partial J}{\partial \mathbf{x}_n} d\mathbf{x} \quad (\text{S12})$$

where the integration is performed over the volume of reference unit cube.

The first term on the r.h.s. of eq. (S12) describes the spring-like forces between the elemental nodes, and it is calculated analytically. Due to the non-cubic shape of an un-deformed gel element, the resulting expression cannot be represented in a simple form as in ref. [17] from the main text. The second term on the r.h.s. of eq. (S12) provides the contribution of the osmotic forces, and π_{osm} is given by eq. (8) in the main text. The osmotic contribution to the nodal forces is calculated approximately through the eight-point Gaussian numerical integration.

Finally, the force \mathbf{F}_N in eq. (15) in the main text, where N is a global node number in contrast to local to an element node number $n = 1, 2, 3, \dots, 8$ in eqs. (S11) and (S12), is obtained by summation of elemental contributions, eq. (S12), from all elements adjacent to node N .

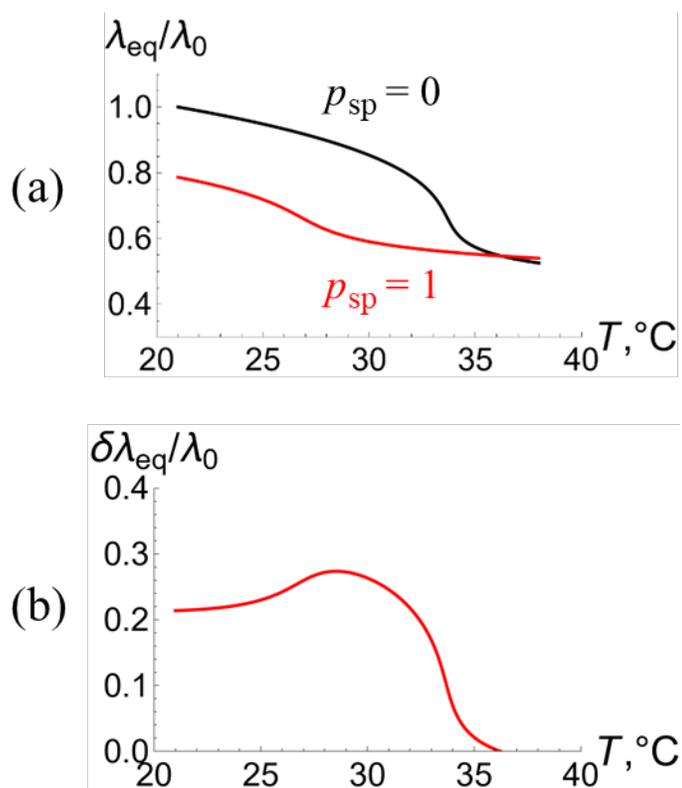


Figure S1.

The effect of illumination on the equilibrium behavior of the SP-functionalized NIPAAm gel calculated for the gel parameters $c_0 = 1.35 \times 10^{-3}$, $\phi_0 = 7.96 \times 10^{-2}$, $f_{sp} = 0.01$ as in ref. [8] in the main text. a) The relative degree of swelling of the illuminated (red) and non-illuminated (black) SP-modified pNIPAAm gel as functions of temperature, where $\lambda_0 = \lambda_{eq}(20^\circ\text{C})$ under no illumination. b) The relative change in gel size as a function of temperature. Figures a) and b) are in a good agreement with the experimental data shown in Fig. 2a and Fig. 2b, respectively, in ref. [8] in the main text.

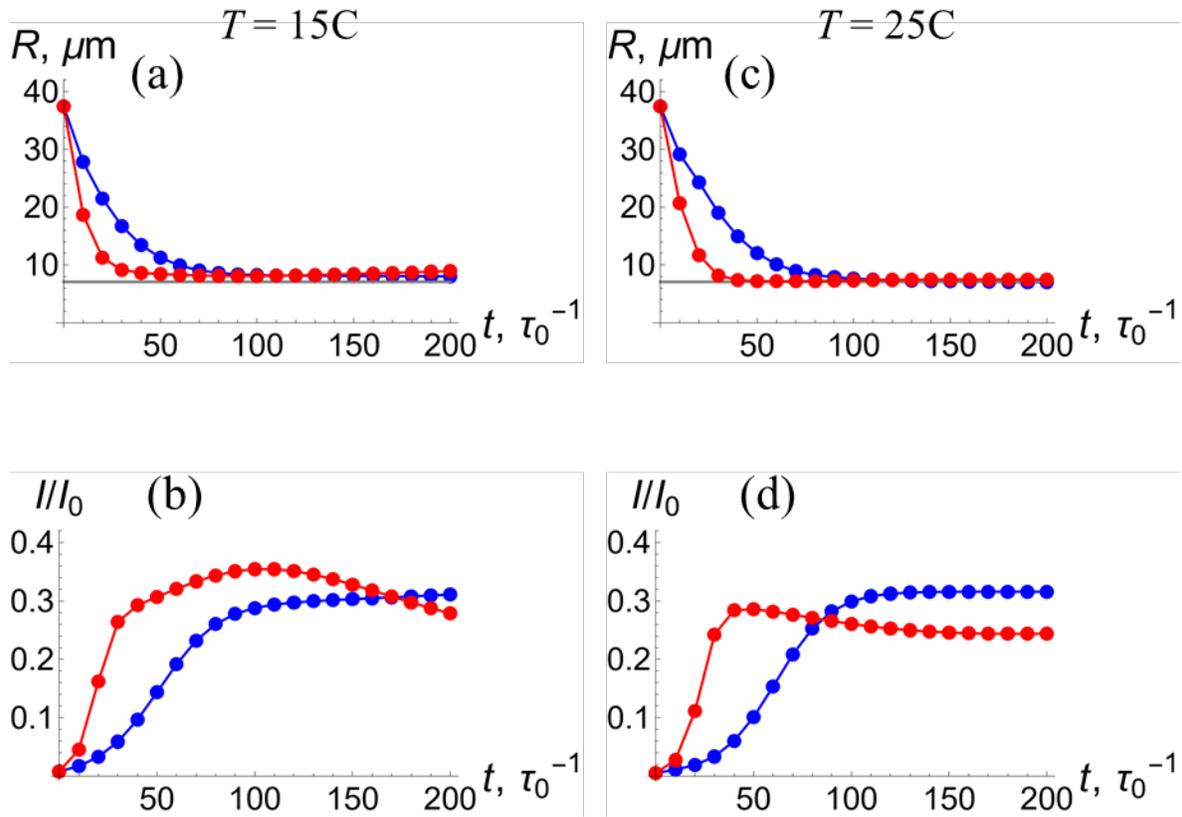


Figure S2.

The linear plots showing the kinetics of the self-trapping of a single laser beam as registered at the exit from a gel sample at $z = 3 \text{ mm}$ in the interval of time $0 \leq t \leq 200 \tau_0 \approx 130 \text{ s}$. The plots display: (a) the radius of beam R and (b) the maximal relative intensity of beam I/I_0 at the ambient temperature of $T = 15^\circ\text{C}$ and the intensities of the incoming laser beam of $I_0 = 1/4 I_{\text{ref}}$ (blue) and I_{ref} (red). Correspondingly, (c) and (d) show the kinetics of the radius and maximal intensity of the exiting laser beam, respectively, at the ambient temperature of $T = 25^\circ\text{C}$. In (a) and (c), the horizontal gray colored line corresponds to the radius $R_0 = 5\sqrt{2} \mu\text{m}$ of the incident Gaussian beam.

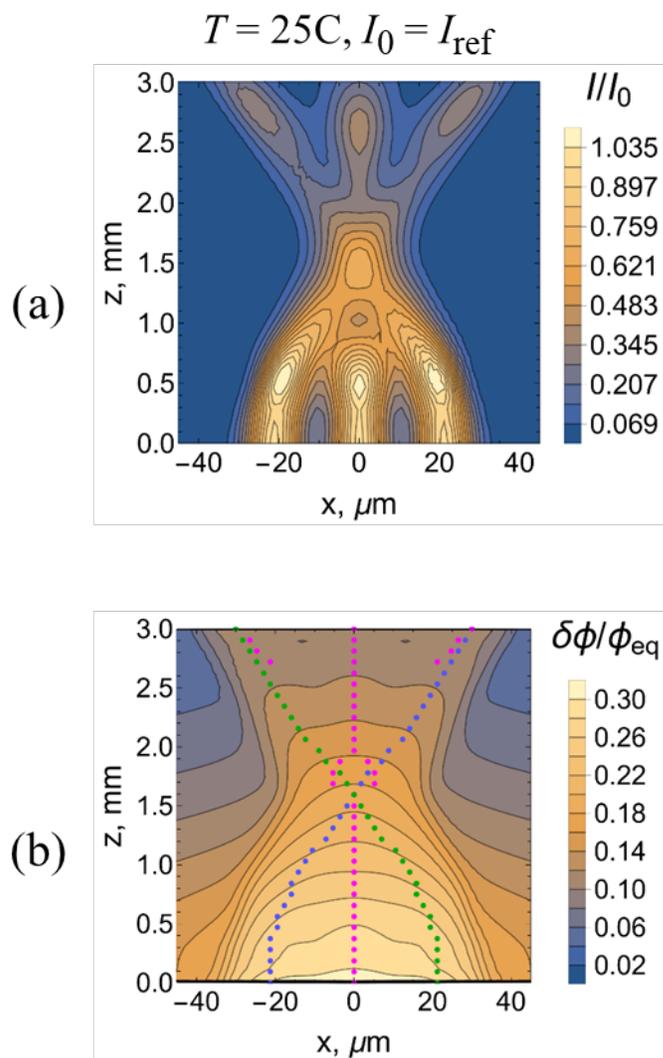


Figure S3.

Strong interaction between three incoherent laser beams of intensity $I_0 = I_{\text{ref}}$ separated by the distance of $\Delta x = 3R_0$ and propagating in the gel at the ambient temperature of $T = 25^\circ\text{C}$. (a) The spatial distribution of intensity of light I / I_0 . (b) The spatial distribution of the relative variation of the volume fraction of polymer in gel $\delta\phi / \phi_{\text{eq}}$ together with the positions of local maxima of the intensity of light in each beam presented by the red-, blue- and green-colored dots. The incident laser beams propagate in the Z direction and are focused at $z = 0$.

Movie M1.

The evolution of the spatial distribution of the light intensity in the middle cross-section during propagation of a single laser beam.

$I_0 = 1/4 I_{\text{ref}}$, $T = 15^\circ\text{C}$, $0 \leq t \leq 200 \tau_0 \approx 130\text{s}$. See Fig. 3a in the main text for $t = 2000 \tau_0 \approx 22\text{min}$.

Movie M2.

The behavior of the light intensity of exiting beam.

The red-colored line shows the evolution of light intensity of exiting beam in Movie M1 as a function of x at $z = 3\text{mm}$. For comparison, the green-colored line shows the intensity of incident Gaussian beam at $z = 0$.