Electronic Supplementary Material (ESI) for Soft Matter.

Fibers on the Surface of Thermo-responsive Gels Induce 3D Shape Changes

SUPPORTING INFORMATION

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1. Formulation of the 3D gel lattice spring model (gLSM) model

To model the dynamic behavior of the gel, we use our previously developed 3D "gel lattice spring model" or gLSM[1]. Predictions that emerged from our prior gLSM modeling studies have yielded good agreement with the corresponding experimental results.[2–6] The details of the derivation of the 3D gLSM and the validation of the approach can be found in ref. [1,3,4,7–10] Here, we use the gLSM to simulate thermo-sensitive gels that encompass elastic fibers.

We represent a 3D element of the gel by a general linear hexahedral element. The whole gel sample consists of $(L_x-1)(L_y-1)(L_z-1)$ elements, where L_i is the number of nodes in the $i-$th direction, i=x,y,z. Within each element $\mathbf{m}\equiv(i,j,k)$, the volume fraction of polymer $\phi(\mathbf{m})$ is taken to be spatially uniform and calculated as

$$\phi(\mathbf{m})=\frac{\phi_0\Delta^3}{V(\mathbf{m})}\qquad, \tag{S1}$$

where $V(\mathbf{m})$ is the volume of the element in the deformed state, and Δ is the linear size of the element in the undeformed state. If the value of $\phi(\mathbf{m})$ is known within each element $\mathbf{m}$, we can use the energy density to calculate the forces acting on each node. The total force acting on the node n of the element $\mathbf{m}$ consists of two contributions: the spring-like force $\mathbf{F}_{1,n}(\mathbf{m})$, which originates from the second term on the right-hand side (RHS) of Eq. (10), and the isotropic pressure force $\mathbf{F}_{2,n}(\mathbf{m})$, which originates from the first term on the RHS of Eq. (10).

The first contribution can be shown[1] to have the following form:

$$\mathbf{F}_{1,n}(\mathbf{m})=\frac{c_0\upsilon_0\Delta}{12}\left(\sum_{NN(\mathbf{m}')}w(n',n)[\mathbf{r}_{n'}(\mathbf{m}')-\mathbf{r}_n(\mathbf{m})]+\sum_{NNN(\mathbf{m}')}[\mathbf{r}_{n'}(\mathbf{m}')-\mathbf{r}_n(\mathbf{m})]\right) \tag{S2}$$

Here $\Sigma_{NN(\mathbf{m}')}$ and $\Sigma_{NNN(\mathbf{m}')}$ represent the respective summations over all the next-nearest neighbor nodal pairs and next-next-nearest neighbor nodal pairs belonging to all the neighboring elements $\mathbf{m}'$ adjacent to the node n of the element $\mathbf{m}$. Note that $w(n',n)=2$ if n and n' belong to an internal face and $w(n',n)=1$ if n and n' belong to a boundary face.

The second contribution can be expressed in the following form: [1]

$$\mathbf{F}_{2,n}(\mathbf{m})=\frac{1}{4}\sum_{\mathbf{m}'}P[\phi(\mathbf{m}')][\mathbf{n}_1(\mathbf{m}')S_1(\mathbf{m}')+\mathbf{n}_2(\mathbf{m}')S_2(\mathbf{m}')+\mathbf{n}_3(\mathbf{m}')S_3(\mathbf{m}')] \tag{S3}$$

Here the summation is over all the neighboring elements $\mathbf{m}'$ that contain the node n of the element $\mathbf{m}$. The unit vector $\mathbf{n}_i(\mathbf{m}')$ is the outward normal to the face i of the element $\mathbf{m}'$, and $S_i(\mathbf{m}')$ is the area of this face.

Using the first term on the RHS of Eq. (12), we can derive the spring-like elastic force $\mathbf{F}_s(\mathbf{m})$ that acts between the nearest neighbor nodes within the fiber. From the second term on the RHS of Eq. (12), we can obtain the force $\mathbf{F}_b(\mathbf{m})$ that accounts for the bending stiffness of the fiber.

After obtaining the forces acting on the node n of the element $\mathbf{m}$, we can then calculate the velocity of the node in the overdamped regime as:

$$\frac{d\mathbf{r}_n(\mathbf{m})}{dt} = M_n(\mathbf{m})[\mathbf{F}_{1,n}(\mathbf{m}) + \mathbf{F}_{2,n}(\mathbf{m}) + \mathbf{F}_{s,n}(\mathbf{m}) + \mathbf{F}_{b,n}(\mathbf{m})] \tag{S4}$$

where $M_n(\mathbf{m})$ is the mobility of the node. To calculate $M_n(\mathbf{m})$, we integrate Eq. (3) over the volume of the element $\mathbf{m}$, estimate the integral on the RHS of this equation by evaluating the values of the integrand on all the nodes of the element $\mathbf{m}$, and consequently estimate the mobility in the following form: [1]

$$M_n(\mathbf{m}) = 8\frac{\Lambda_0 \phi_0^{1/2}}{\Delta^3} \frac{(1 - \langle \phi(\mathbf{m}) \rangle_n)}{\langle \phi(\mathbf{m}) \rangle_n^{1/2}} \tag{S5}$$

where $\langle \phi(\mathbf{m}) \rangle_n$ is the approximate value of the polymer volume fraction at the node n of the element $\mathbf{m}$. The average value of the $\phi(\mathbf{m}')$ is taken over all the elements $\mathbf{m}'$ adjacent to the node n of the element $\mathbf{m}$.

2. Discrete curvature analysis

We focus on the central layer of the sample and determine the Gaussian curvature of the surface of this single layer using the approach developed in ref. 11. On a square lattice of this single layer, we only calculate the Gaussian curvature K attributed to the internal nodes, which have four nearest-neighbors. For a given internal node n, the four nearest-neighbors are labeled as $n_i, i = 1,2,3,4$. We also define the edges $\mathbf{e}_i = \mathbf{n}_i - \mathbf{n}, i = 1,2,3,4$ and the angles between two successive edges $\alpha_i = \angle(\mathbf{e}_i, \mathbf{e}_{i+1}), i = 1,2,3,4$, with $\mathbf{e}_5 \equiv \mathbf{e}_1$.

We define the integral Gaussian curvature $\overline{K}_n$ with respect to the area S_n attributed to node n using the following equation: [11]

$$\overline{K}_n \equiv \int_{S_n} K_n \, ds = 2\pi - \sum_{i=1}^{4} \alpha_i \tag{S6}$$

We assume the curvatures to be uniformly distributed around the node, and normalize $\overline{K}_n$ by the area S_n to obtain K_n: [11]

$$K_n = \frac{\overline{K}_n}{S_n} \tag{S7}$$

To calculate S_n attributed to a node n, we use the barycentric area S^B, which is one third of the area of the triangles (each triangle is constructed with a pair of edges $\mathbf{e}_i$ and $\mathbf{e}_{i+1}$ of node n) adjacent to n.

Finally, we calculate the Gaussian curvature of a square element m as

$$K_m = \frac{1}{4}\sum_{i=1}^{4} K_{m_i} \quad , \tag{S8}$$

where K_{m_i} is the Gaussian curvature of the $i-$th node of the square element m, $i = 1,2,3,4$.

3. Chair and boat shapes attained by adding another layer of two short fibers above or below the existing ones in Figs. 5a,b

Greater deformations can be induced by adding another layer of two short fibers above or below the existing ones in Figs. 5a,b as shown in Fig. S1.

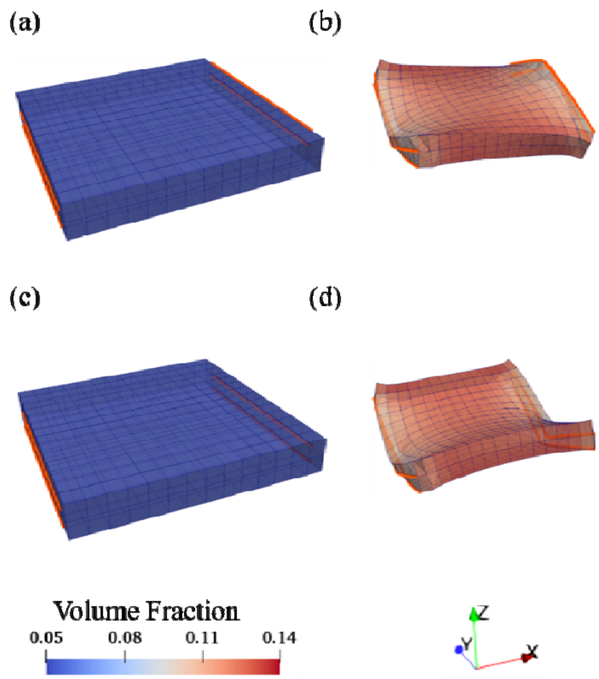

Figure S1. The chair (b) and boat (d) shapes attained by the gel samples shown in (a) and (c) after changing temperature from 20°C to 32°C, respectively. The left side of (a) is decorated with two short fibers on the bottom edge and two short fibers on the central layer; the right side of (a) is decorated with two short fibers on the top edge and two short fibers on the central layer. In (c), both the left and right sides are decorated with two short fibers on the bottom edge and two short fibers on the central layers. The sample size is $14 \times 14 \times 2$ elements. The length of a short fiber is $6L_f$, where $L_f = 1.31 L_0$ is the size of elements in the equilibrium state at 20°C. At $t = 0$, the equilibrium positions of the nodal points were perturbed by applying a random displacement of magnitude $10^{-2} L_f$. The typical final morphologies are obtained from four independent runs. The color bar indicates the local volume fraction of polymer in the sample.

References

(1) Kuksenok, O.; Yashin, V. V.; Balazs, A. C. Three-Dimensional Model for Chemoresponsive Polymer Gels Undergoing the Belousov-Zhabotinsky Reaction. *Phys. Rev. E* **2008**, *78* (4), 41406.

(2) He, X.; Aizenberg, M.; Kuksenok, O.; Zarzar, L. D.; Shastri, A.; Balazs, A. C.; Aizenberg, J. Synthetic Homeostatic Materials with Chemo-Mechano-Chemical Self-Regulation. *Nature* **2012**, *487* (7406), 214–218.
(3) Yashin, V. V.; Kuksenok, O.; Balazs, A. C. Modeling Autonomously Oscillating Chemo-Responsive Gels. *Prog. Polym. Sci.* **2010**, *35* (1–2), 155–173.
(4) Kuksenok, O.; Balazs, A. C. Modeling the Photoinduced Reconfiguration and Directed Motion of Polymer Gels. *Adv. Funct. Mater.* **2013**, *23* (36), 4601–4610.
(5) Kuksenok, O.; Yashin, V. V.; Kinoshita, M.; Sakai, T.; Yoshida, R.; Balazs, A. C. Exploiting Gradients in Cross-Link Density to Control the Bending and Self-Propelled Motion of Active Gels. *J. Mater. Chem.* **2011**, *21* (23), 8360.
(6) Chen, I. C.; Kuksenok, O.; Yashin, V. V.; Moslin, R. M.; Balazs, A. C.; Van Vliet, K. J. Shape- and Size-Dependent Patterns in Self-Oscillating Polymer Gels. *Soft Matter* **2011**, *7* (7), 3141.
(7) Kuksenok, O.; Balazs, A. C. Stimuli-Responsive Behavior of Composites Integrating Thermo-Responsive Gels with Photo-Responsive Fibers. *Mater. Horiz.* **2016**, *3* (1), 53–62.
(8) Yashin, V. V; Balazs, A. C. Pattern Formation and Shape Changes in Self-Oscillating Polymer Gels. *Science* **2006**, *314* (5800), 798–801.
(9) Yashin, V. V.; Balazs, A. C. Theoretical and Computational Modeling of Self-Oscillating Polymer Gels. *J. Chem. Phys.* **2007**, *126* (12), 124707.
(10) Kuksenok, O.; Yashin, V. V.; Balazs, A. C. Mechanically Induced Chemical Oscillations and Motion in Responsive Gels. *Soft Matter* **2007**, *3* (9), 1138.
(11) Dyn, N.; Hormann, K.; Kim, S.; Levin, D. *Optimizing 3D Triangulations Using Discrete Curvature Analysis*; Vanderbilt University: Nashville, TN, USA, 2001.