Soft Matter

“Patterning with Loops” to Dynamically Reconfigure Polymer Gels

Journal:	*Soft Matter*
Manuscript ID	SM-ART-02-2018-000270.R2
Article Type:	Paper
Date Submitted by the Author:	09-Apr-2018
Complete List of Authors:	Biswas, Santidan; University of Pittsburgh, Chemical Engineering Yashin, Victor; University of Pittsburgh, Balazs, Anna; University of Pittsburgh, Chemical Engineering

“Patterning with Loops” to Dynamically Reconfigure Polymer Gels

Santidan Biswas, Victor V. Yashin, Anna C. Balazs*

Chemical Engineering Department, University of Pittsburgh, Pittsburgh, PA 15261,

United States

* balazs@pitt.edu

Keywords: polymer gels, gel lattice spring model (gLSM)

Abstract

The structural and mechanical properties of gels can be controlled by promoting the unfolding (and refolding) of loops (stored lengths) embedded within the networks. As a loop unfolds, the released chain length can increase the extensibility and reconfigurability of the gel. Here, we develop a theoretical model that couples the elasticity of the gel to the dynamic transitions occurring in loops that lie between the crosslinks. Using this model, we show that a thermally-induced swelling of the gel generates an internal strain, which unfolds the loops and thereby further increases the degree of gel swelling. We exploit this cooperative behavior to reconfigure the gel by patterning the location of the loops within the sample. Through this approach, we convert flat, two-dimensional layers into three-dimensional forms and introduce architectural features into uniform 3D slabs. At a fixed temperature, an applied force produces analogous structural transformations. The shape-changes are reversible: the systems return to their original structure when the temperature is reset or the force is removed. The findings provide guidelines for creating materials that interconvert thermal, chemical and mechanical energy to perform work. Such systems could be useful for designing soft robotic materials that convert environmental stimuli into useful functionality.

I. Introduction

Loops are a ubiquitous and vital structural motif in biomolecules.[1] The unfolding and refolding of loops in DNA and proteins enables the structural transformations that are crucial to the functionality of these biopolymers. The unfolding process releases the length of the coiled chain and thereby increases the extensibility of the biomaterials; the reversible refolding contributes to the elasticity of the system. Loops are also pervasive in synthetic polymer networks. Fixed, immutable loops can diminish the mechanical behavior of the network.[2,3] Loops that undergo controllable unfolding and refolding would, however, increase the extensibility and elasticity of the gel. (It is noteworthy that modular polymers mimicking the unfolding and refolding of the protein titin [4] have been synthesized and were demonstrated to exhibit enhanced mechanical properties.[5,6].) Such highly stretchable, elastic gels constitute ideal materials for creating artificial muscles, actuators and soft robotic systems. One challenge in creating these materials is establishing effective means to regulate the folding and unfolding of the loops embedded in synthetic gels. A second challenge is determining how the dynamic interactions between the gels and the loops affect the structural evolution of the material; this information is vital to harnessing the loop-containing gels for useful applications.

Here, we develop theoretical and computational models that describe the synergistic interactions occurring between the polymer network and the embedded loops as these loops unfold (and refold). Using this model, we design stimuli-responsive gels that open and close the loops with variations in temperature or force. In the first case described below, we devise a thermo-responsive gel that expands with a temperature change and thereby generates the internal strain to unlock the loops. In this scenario, even an already swollen gel can be stretched beyond its initial, equilibrium degree of swelling and thus, the extensibility of the network can be dramatically increased. In the second case, we determine how an external force can be utilized to reconfigure the gel. The latter stimulus is particularly useful when the gel is in collapsed state because the applied force causes the loops to unravel and thereby swell the shrunken network. Hence, the mechanical properties of both the swollen and collapsed gels can be dynamically tailored in these loop-containing networks. Notably, the processes in both scenarios are reversible: the loops refold when the temperature is reset or the forces are removed. Through our simulations, we also design a new form of patterned gels, where the loops are localized in specific regions of the network. We show that by "patterning with loops", we augment the approaches used to reconfigure and actuate soft matter.

Our specific system consists of a thermo-responsive gel that exhibits a lower critical solubility temperature (LCST). Here, we match our simulation parameters to capture the volume phase transition behavior of poly(N-isopropylacrylamide) (pNIPAAm), which expands as the temperature is lowered below $T \approx 32^\circ\mathrm{C}$ and contracts when T is increased above this value.[7] In our model, the loops are introduced between the cross-links in the network. We first examine how the swelling gel causes the loops to unfold as T is decreased below $T \approx 32^\circ\mathrm{C}$ and determine the extent to which the network is extended through this process. As we show below, we can attain as much as a 38% increase in the lateral degree of swelling (and hence a factor of 2.5 increase in volume) even with small, embedded loop. With the loops confined to certain areas of the network, we demonstrate that uniform structures can be dynamically converted into complex architectures, which can provide the system with new functionality (e.g., asymmetric actuation). We then vary not only the placement of the loops, both also the geometry of the sample to design distinctive shape-changing materials.

We also examine the behavior of samples at $T > 32^\circ\mathrm{C}$, where the gel is collapsed and thus, cannot exert sufficient strain to extend the loops. Here, the applied force unbinds the sites that maintain the closed loop and enables the network to assume a swollen structure. Notably, this extensional deformation allows the system to be reconfigured at constant temperature. The combination of "patterning with loops" and the extensional force provides a further means of tailoring reversible changes in the shape of the gel.

We iterate that a distinctive feature of our system over other modes of patterning gels is that the loop-containing networks can be made to controllably (and repeatedly) release stored length. Consequently, by tailoring the length of the loops, we can dynamically and dramatically tailor the extensibility of the system. The changes in extensibility can be accomplished not only by varying temperature, but also at constant temperature with the application of force. Hence, the materials can be processed at a fixed temperature. This versatility and variations in extensibility are more difficult to achieve through other means of network modification. Finally, because the materials release stored length in response to internal strain or external pressure, they can be particularly useful as novel force sensors.

Below, we begin by describing our new theoretical treatment and computational approach to determine the dynamic behavior of the loop-containing gels. Notably, recent experimental advances in synthesizing foldamer- [8] and DNA- [9] containing gels makes it possible to experimentally realize the predictions discussed further below.

II. Methodology

A. Theoretical model

We consider the permanently cross-linked, swollen polymer gel schematically depicted in Fig. 1; the cross-links in the network are represented by grey solid circles and the chains between these cross-links are drawn in green. These chains contain reactive, labile bonds that are marked as the blue and red solid circles in the figure. In the undeformed state, these reactive sites bind to form a loop. When the network is mechanically deformed, the labile bonds break and cause the chain to unfold. If the deformation is released, the labile bonds can come together to reform the loop, so that the network chains reassemble the initial folded conformation. In our model, the transitions between the looped and un-looped chain conformations mimic the reversible folding and unfolding transitions in biopolymers [1,4] and biomimetic modular synthetic polymers [5,6] caused by an applied force.

A chain in the network contains $n+l$ Kuhn segments, with l being the number of segments that form the loop (see Fig. 1). We assume that the time scale for the breaking and reforming of the bond between the reactive groups is longer than the time scale associated with conformational changes of the chain. Hence, the probability of the chain being in the unfolded conformation, p_U, as a function of time t is governed by the equation for the kinetics of bond rupture and formation

$$dp_U / dt = k_r(R)(1-p_U) - k_f(R)p_U \tag{1}$$

Here, $k_r(R)$ and $k_f(R)$ are the respective rate constants of the bond rupture and formation that depend on the distance between the chain ends, R. The rate of bond rupture depends on R because the stretching of the chain increases the force acting on the bond, and the force facilitates bond breakage. We utilize the Bell model [10] to take the latter effect into account, and hence the rupture rate is calculated as

$$k_r(R) = k_r^{(0)}\exp[\gamma_0 F_n(R)/k_B T] \tag{2}$$

where $k_r^{(0)}$ is the rupture rate at zero force, $F_n(R)$ is the force needed to separate the ends of a chain of n segments to the distance R, and γ_0 is the parameter that characterizes the sensitivity of the bond to the applied force. The loop does not contribute to $F_n(R)$, which depends only on the number of segments n in the unlooped part of the chain (Fig. 1).

The force acting on the bond is calculated according to the freely-jointed chain model (FJC),[11] which accounts for the finite extensibility of the chain and yields the following expression:

$$F_n(R) = \frac{k_B T}{b} \mathcal{L}^{-1}[R(nb)^{-1}] \ , \tag{3}$$

where

$$\mathcal{L}(x) = \coth(x) - x^{-1} \tag{4}$$

Here, $\mathcal{L}(x)$ is the Langevin function. In eq. (3), k_B and T are the respective Boltzmann's constant and temperature, and b is the length of the Kuhn segment. It is convenient to re-write the dimensionless variable $x = R(nb)^{-1}$ in eq. (4) in terms of the chain extension λ as $x = \lambda n^{-1/2}$. Note that we take into account the finite chain extensibility because it has a strong effect on the rate of bond rupture, i.e., through the expression for $F_n(R)$ in eq. (2).

The rate constant for forming a labile bond, $k_f(R)$, depends on the chain end-to-end distance R because to form a bond, the reactive units in the unfolded chain of $n+l$ segments must first come into contact, and the probability of contact, P_c, depends on R. When in contact, the reactive units form a labile bond with the rate constant $k_f^{(0)}$, and hence $k_f(R) = P_c(R) k_f^{(0)}$. As in previous studies,[12–17] it is assumed that $k_f^{(0)}$ does not depend on the force acting on the bond. The probability of contact, $P_c(R)$, is calculated using the conformational statistics of the polymer chain: $P_c(R) = P_n(R) P_l(0) / P_{n+1}(R)$, where $P_n(R)$ is the probability distribution function for finding the ends of a chain of n segments at distance R apart. For the FJC model, this distribution function is [11]

$$P_n(R) = \frac{[\mathcal{L}^{-1}(x)]^2}{(2\pi n b^2)^{3/2} x \{1 - [\mathcal{L}^{-1}(x) \operatorname{csch}(x)]^2\}^{1/2}} \left[\frac{\sinh \mathcal{L}^{-1}(x)}{\mathcal{L}^{-1}(x)} \right]^n \exp[-n x \mathcal{L}^{-1}(x)] \tag{5}$$

where $x = R(nb)^{-1} = \lambda n^{-1/2}$. Through the equations for $k_f^{(0)}$ and $P_c(R)$, the rate of chain folding depends on both the total length of the chain $(n+l)$ and the length of the loop (l).

At steady-state, $dp_U / dt = 0$ so that eq. (1) results in

$$p_U(R) = \{1 + k_f^{(0)} / k_r^{(0)} P_c(R) \exp[-\gamma_0 F_n(R)/k_B T]\}^{-1} \tag{6}$$

The above equation relates the probability of unfolding the loops to the characteristics of the bond formation and rupture, the length of the chain and the force acting on the loop.

To proceed further, we must derive the necessary constitutive equation, which relates the stress and strain within the gel. The general relationship between the stress and strain for a polymer gel is described by the following equation:[18–20]

$$\hat{\boldsymbol{\sigma}} = \hat{\boldsymbol{\sigma}}_{\mathrm{el}} - \pi_{\mathrm{FH}}(\phi, T)\hat{\mathbf{I}} \ . \tag{7}$$

Here, $\hat{\boldsymbol{\sigma}}_{\mathrm{el}}$ is the contribution from the elasticity of the polymer chains, and $\pi_{\mathrm{FH}}(\phi, T)$ is the osmotic pressure in the system according to the Flory-Huggins model

$$\pi_{\mathrm{FH}}(\phi, T) = -[\phi + \log(1-\phi) + \chi(\phi, T)\phi^2] \tag{8}$$

where ϕ is the volume fraction of polymer, and the function $\chi(\phi, T)$ describes the polymer-solvent interactions, which depend on the volume fraction of polymer and temperature T. The gel elasticity contribution, $\hat{\boldsymbol{\sigma}}_{\mathrm{el}}$, is usually introduced through the neo-Hookean model

$$\hat{\boldsymbol{\sigma}}_{\mathrm{el}} = c_0 v_0 \phi_0^{-1} \phi \hat{\mathbf{B}} - c_0 v_0 \phi (2\phi_0)^{-1} \hat{\mathbf{I}} \tag{9}$$

where c_0 is the cross-link density, v_0 is the volume of a monomeric unit, $\hat{\mathbf{B}}$ is the Finger strain tensor, and ϕ_0 is the volume fraction of the polymer in the as-prepared gel. Here, stress is measured in units of $k_B T / v_0$.

Equation (9) for $\hat{\boldsymbol{\sigma}}_{\mathrm{el}}$ is based on the Gaussian model of polymer chains and does not capture the finite extensibility of the unfolded chains. Since the latter effects are crucial in our system, we must modify the above expression. To do so, we use the following generalization [21] of eq. (9) for the FJC model:

$$\hat{\boldsymbol{\sigma}}_{\mathrm{el}}(n) = c_0 v_0 \phi_0^{-1} \phi \zeta(\bar{\lambda} n^{-1/2}) \hat{\mathbf{B}} - c_0 v_0 \phi (2\phi_0)^{-1} \zeta_0(n) \hat{\mathbf{I}} \ . \tag{10}$$

Here, $\zeta(x) = (3x)^{-1}\mathcal{L}^{-1}(x)$, where $\mathcal{L}^{-1}(x)$ is the inverse Langevin function, $\zeta_0(n) = \zeta(n^{-1/2})$, and $\overline{\lambda}$ is the average strain calculated as $\overline{\lambda} = \sqrt{(\lambda_1^2 + \lambda_2^2 + \lambda_3^2)/3}$ with λ_1, λ_2, and λ_3 being the principal strains. In contrast to eq. (9), the stress tensor in eq. (10) explicitly accounts for the finite chain extensibility through the inverse Langevin function, which, in turn, depends on the number of Kuhn segments n in a network chain. Figure 2 shows that the model with finite extensibility (eq. (10)) results in a lower extension than the model that utilizes the neo-Hookean gel elasticity (eq. (9)); the parameters used for this calculation are given further below and in the figure caption.

In the systems considered here, some of the chains are in the folded state and some chains are in the open configuration. We assume that the deformation of the gel is affine, so the contributions of the folded and unfolded chains to the network elasticity are additive.[11,22] The resulting constitutive equation is

$$\hat{\boldsymbol{\sigma}} = p_U(\overline{\lambda})\hat{\boldsymbol{\sigma}}_{\mathrm{el}}(n+l) + [1 - p_U(\overline{\lambda})]\hat{\boldsymbol{\sigma}}_{\mathrm{el}}(n) - \pi_{\mathrm{FH}}(\phi, T)\hat{\mathbf{I}} \tag{11}$$

where $p_U(\overline{\lambda})$ is the probability of chain unfolding at the average degree of stretching $\overline{\lambda}$. The probability of unfolding is found from the equation for the bond kinetics, eq. (1), or from eq. (6) for the steady-state scenario. In eq. (11), it is implicitly assumed that all network chains in the gel contain the reactive groups. This restriction could be easily modified to the case when only a fraction of the network chains contains such sites.

B. Computational model

The above analytical equations are used to simulate the dynamic behavior of the loop-containing gels with the aid of our gel lattice spring model (gLSM) computational technique [18–20] briefly outlined below. The 3D gLSM combines a finite element approach and a finite difference approach and thus, allows us to numerically solve the elastodynamic equations that characterize the behavior of chemo-responsive polymer gels. We originally developed the gLSM to capture the dynamic behavior of self-oscillating polymer gels undergoing the Belousov-Zhabotinsky (BZ) reaction [18,23,24] and used this approach to examine the response of these BZ gels to an applied force,[25–28] with our predictions being validated by corresponding experiments.[28] For example, we examined the effect of applying a compressive force P to the ends of a BZ gel confined in a capillary tube. Our computer simulations revealed that the compression of the BZ gel leads to a stiffening of the sample due to an increase in the cross-link density.[27] In another study, we modified the gLSM to account for the formation of additional, reversible cross-links in response to a change in the degree of oxidation of polyacrylamide-based BZ gels; we obtained excellent agreement between our findings and the corresponding experiments.[29]

Recently, we modified the gLSM to simulate the dynamics of photo-responsive gels, which encompass chromophores that undergo a light-induced isomerization reaction.[30–32] We also adapted the model to describe the dynamic behavior of thermo-responsive gels that contain embedded posts, which undergo an exothermic chemical reaction with reagents in the surrounding solution,[33] capturing the observed behavior and predicting new properties that were validated by the experiments.[33] We now augment our 3D gLSM to take into account the finite extensibility of the chain, as described below.

The gLSM is based on the two-fluid model for polymer networks.[34–36] The dynamics of the polymer network is assumed to be purely relaxational, so that the forces acting on the swollen, deformed gel are balanced by the frictional drag due to the motion of the solvent. It is also assumed that the gel motion occurs solely due to the polymer-solvent interdiffusion. Hence, the velocity of the polymer, $\mathbf{v}^{(p)}$, can be calculated as [19]

$$\mathbf{v}^{(p)} = \Lambda_0 (\phi/\phi_0)^{-3/2} (1-\phi) \nabla \cdot \hat{\boldsymbol{\sigma}} , \tag{12}$$

where Λ_0 is the kinetic coefficient, which is inversely proportional to the polymer-solvent friction coefficient η_0. In the computer simulations, we choose some l_0 and t_0 for the respective units of length and time, and stress is measured in the units if $k_B T / v_0$, where v_0 is the volume of a monomeric unit within a polymer chain. Then, the kinetic coefficient Λ_0 is dimensionless and calculated as [19] $\Lambda_0 = k_B T (v_0 \eta_0 l_0^2 t_0^{-1})^{-1}$.

Within the framework of the gLSM, a 3D gel sample is represented by a set of general lineal hexahedral elements.[37,38] Initially, the sample is undeformed and consists of $(L_x - 1) \times (L_y - 1) \times (L_z - 1)$ identical cubic elements; here L_i is the number of nodes in the i-direction, $i = x, y, z$. In the un-deformed state, each element is characterized by the same volume fraction ϕ_0 and cross-link density c_0 . Upon deformation, the elements move together with the polymer network so that the amount of polymer and number of cross-links within each hexahedral element remain equal to their initial values. Correspondingly, the volume fraction of polymer in the element $\mathbf{m} \equiv (i, j, k)$ is determined as $\phi(\mathbf{m}) = \phi_0 \Delta^3 / V(\mathbf{m})$, where Δ and $V(\mathbf{m})$ are the un-deformed element size and volume of the deformed element, respectively.

The gel dynamics is described through motion of the nodes of the elements caused by the forces acting on these nodes. In order to determine the nodal forces, we use the finite element approximation to calculate total energy of the gel as

$$U_{tot} = \Delta^3 \sum_{\mathbf{m}} u(\mathbf{m}) \quad , \tag{13}$$

where the contribution from the element $\mathbf{m}$, $u(\mathbf{m})$, depends only on the coordinates of the nodes of this element denoted as $\mathbf{r}_n(\mathbf{m})$, $n = 1, 2, \ldots, 8$. (Note that $u(\mathbf{m})$ is the gel energy per unit volume of the un-deformed element.) As a result, the force acting on each node is given by the equation

$$\mathbf{F}_n(\mathbf{m}) = -\frac{\partial U_{tot}}{\partial \mathbf{r}_n(\mathbf{m})} \quad . \tag{14}$$

The same node can belong to several elements, so the right hand side of the above equation contains contributions from all elements adjacent to a given node. Finally, the velocity of the node is proportional to the force and is determined from an equation similar to eq. (12)

$$\frac{d\mathbf{r}_n(\mathbf{m})}{dt} = M_n(\mathbf{m})\mathbf{F}_n(\mathbf{m}) \quad , \tag{15}$$

where $M_n(\mathbf{m})$ is the mobility of the node proportional to the kinetic coefficient Λ_0. Further details on the derivation and functional forms of $\mathbf{F}_n(\mathbf{m})$ and $M_n(\mathbf{m})$ are given in ref. 20.

The stress-strain relationships discussed in the previous section are introduced into the gLSM through the appropriate choice of the gel energy per unit volume in the un-deformed state, $u(I_1, I_3)$, as a function of the first, I_1, and third, I_3, invariants of the strain tensor $\hat{\mathbf{B}}$.[18–20] The correspondence between $u(I_1, I_3)$ and the stress-strain relationship is established through the following equation: [39]

$$\hat{\boldsymbol{\sigma}} = 2I_3^{-1/2} w_1 \hat{\mathbf{B}} + 2I_3^{-1/2} w_3 I_3 \hat{\mathbf{I}} \tag{16}$$

where

$$w_i = \frac{\partial}{\partial I_i} u(I_1, I_3) \quad . \tag{17}$$

After specifying $u(I_1, I_3)$, the finite element approximation is applied to determine the element energy density $u(\mathbf{m})$ as described in ref. 20.

The stress-strain relationships given by eqs (7)-(9) correspond to the following choice of the energy density: [35,36,40]

$$u(I_1, I_3) = u_{\mathrm{G}}(I_1, I_3) + u_{\mathrm{FH}}(I_3) \quad , \tag{18}$$

where

$$u_{\mathrm{G}}(I_1, I_3) = \frac{c_0 v_0}{2}(I_1 - 3 - \ln I_3^{1/2}) \tag{19}$$

represents the neo-Hookean model for the elasticity of a polymer network that involves Gaussian chains. The second term on the right hand side of eq. (18) describes the polymer-solvent interaction according to the Flory-Huggins model:

$$u_{\mathrm{FH}}(I_3) = I_3^{1/2}\left[(1-\phi)\ln(1-\phi) + \chi_{FH}(\phi,T)\phi(1-\phi)\right] \quad . \tag{20}$$

In eq. (20), the volume fraction of polymer ϕ itself depends on I_3 as $\phi = \phi_0 I_3^{-1/2}$, where ϕ_0 is the volume fraction of polymer in the un-deformed state. The interaction parameter $\chi(\phi,T)$ in eq. (8) is related to the Flory-Huggins interaction parameter $\chi_{FH}(\phi,T)$ in eq. (20) as $\chi(\phi,T) = \chi_{FH}(\phi,T) + (1-\phi)\partial_\phi \chi_{FH}(\phi,T)$.

As noted above, we now take into account the finite extensibility of the chains by using the FJC model. The corresponding energy density is written as: [21]

$$u(I_1,I_3) = u_{\mathrm{FJC}}(I_1,I_3;n) + u_{\mathrm{FH}}(I_3) \ , \tag{21}$$

where

$$u_{\mathrm{FJC}}(I_1,I_3;n) = \frac{c_0 v_0}{2}[\zeta(\bar{\lambda} n^{-1/2}) I_1 - 3 - \zeta_0(n) \ln I_3^{1/2}] \quad . \tag{22}$$

By applying eqs (16) and (17) to eqs (21), we obtain the stress-strain relationships given by eqs (7), (8) and (10).

Equations (21) and (22) are further modified to describe the gel containing the loops, which are unfolded with the probability p_U. The resulting gel energy density is given by following equation (cf. eq. (11)):

$$u(I_1,I_3) = p_U u_{\mathrm{FJC}}(I_1,I_3;n+l) + (1-p_U) u_{\mathrm{FJC}}(I_1,I_3;n) + u_{\mathrm{FH}}(I_3) \ . \tag{23}$$

Finally, we note that the above formulation can be used to model heterogeneous gels, which encompass domains that contain loops and domains that do not. In particular, the contributions of the elements to the gel energy are additive, eq. (13), and hence, the function $u(\mathbf{m})$, which specifies the gel structure and properties, can differ from area to area.

C. Model parameters and verification of computational approach

We modeled the gel by using the parameters for poly(N-isopropylacrylamide) (pNIPAAm) from the relevant experimental values.[7] The volume fraction of polymer and the cross-linker density were calculated to be $\phi_0 = 0.129$ and $c_0 = 5.4\times10^{-4}$. The number of Kuhn segments of polymer chains between cross-links was chosen to be $n = 4$. For the gels containing loops, the volume fraction of polymer is calculated as $\phi = \phi_0(1 + l/n)$ where l is the number of Kuhn segments in the loop. The polymer-solvent interaction for pNIPAAm-water was taken to be [7] $\chi(\phi,T) = \chi_0(T) + \chi_1\phi$. The temperature dependence of the Flory-Huggins coefficient is given as: $\chi_0(T) = [h - (T_0 + T)s][k_B(T_0 + T)]^{-1}$ where $h = -1246.0$, $s = 4.717$, $T_0 = 273.15$, $k_B = 1.3807$ and $\chi_1 = 0.518$. The dimensionless kinetic coefficient was chosen to be $\Lambda_0 = 100$.[20] In our gLSM simulations, the dimensionless units of time and length correspond to ~1s and ~40 μm, respectively, for the given choice of parameters.[18–20]

For affine deformations, the degree of swelling (λ in Fig. 2) is equal to the chain extension, so the same notation is used for the both values. The degree of gel swelling λ is defined as the lateral extension of the gel sample i.e., $\lambda = l/l_0$ where l is the length of the gel sample along the specified direction and l_0 is the length of the reference gel. We simulate the equilibrium swelling of a pNIPAAm gel as a function of temperature for various numbers of Kuhn segments in the loop. We carried out gLSM simulations with $4\times4\times4$ grid elements. To verify the gLSM approach, in Figs. 3 and 4, we compare the results of the gLSM simulations with numerical solutions of the constitutive equation, eq. (11), which were obtained using *Mathematica*^{TM} . The agreement between the output from the gLSM simulations and the numerical solutions obtained from *Mathematica*^{TM} in both plots validates our computational approach. Such comparisons can be made for the limiting case of a small homogeneous sample; to model the larger, heterogeneous samples described further below, we must use the the gLSM simulations.

Figure 3 shows the dependence of the probability of unfolding, p_U, in the steady-state on the chain extension λ (see eq. 6) for various values of γ_0 , the parameter characterizing the sensitivity of the bond to the applied force. The plots exhibit agreement between the data points obtained from the gLSM simulations and the lines from numerical solutions of eq. (6). The data also reveal that the unfolding occurs at progressively lower chain extensions as the dimensionless parameter γ_0 / b is increased. (The latter parameter characterizes the sensitivity of the bond rupture to force.) Moreover, at higher values of γ_0 / b , the gels display a smoother transition from the folded to unfolded state of the loops. In following discussion, we fix the value of $\gamma_0 / b = 2.15$.

Figure 4 shows the degree of gel swelling, λ , as a function of temperature for isotropic swelling at various numbers of Kuhn segments in the loop, l . Again, the plots reveal the agreement between the data points obtained from gLSM simulation, eq. (15), and the lines obtained by solving eq. (11). For longer loops, $l = 3, 4$ and 5 , the value of λ exhibits distinctive jumps at lower temperatures. These jumps correspond to the unfolding of the loops and release of their stored length.

III. Results of 3D simulation

A. Effect of varying temperature

1. Square- and rectangular-shaped gels. We use our modified gLSM to simulate the behavior of gels of various shapes and spatial distributions of loops. To simulate inhomogeneous systems, which encompass regions with and without loops, we must use the gLSM. Initially, the polymer volume fraction ϕ in every gel element is set to the equilibrium value attained at $T = 30°\mathrm{C}$. In the absence of loops, the freely jointed chains (FJC) between each cross-link have $n = 4$ Kuhn segments in length. The loops are also composed of FJCs and are $l = 5$ Kuhn segments in length. The majority of the loops remain closed at the initial temperature of 30°C (see the line in Fig. 4 for $n = 4$ and $l = 5$).

When the temperature is decreased from $30°\mathrm{C}$ to $15°\mathrm{C}$, the swelling of the LCST gel leads to a buildup in the force acting on the loops. This increase in force, in turn, increases the rate of bond breaking (see eq. (2)) between the sites that hold the loop together and thereby causes the loop to unfold. The consequent release of stored length provides a significant difference in the swelling between gel elements with loops and without loops, as can be seen by comparing the plot in Fig. 4 for $l = 5$ and $l = 0$. Notably, that the value of λ is 38% greater for the $l = 5$ case than for $l = 0$.

Conceptually, these results are similar to recent experimental findings on polymer gels that contain a chromophoric foldamer, [8] which formed a single loop in the folded state. When placed in an organic solvent, the gel was significantly swollen and the foldamers became unfolded. The unfolding was detected by a change in the color of the sample. The chemo-mechanical interaction described in the latter system is similar to the phenomena occurring in our system: an environmentally-induced swelling of the gel leads to a mechanical breaking of the bond that held the loop together. The process in the experiments is reversible; the foldamers return to the folded configuration with a change in solvent. These experiments illustrate two important points with respect to our studies. First, the swelling of a gel can generate the internal force that is sufficient to break the chemical bonds that bind loops.[8] Second, researchers can synthesize gels with a relatively uniform distribution of loops.

Given the ability to synthesize such chemo-mechanically responsive loop-containing gels, as well as the chemically identical matrix that does not contain foldamers, it seems feasible to bind pieces of these similar gels together [41,42] to form heterogeneous networks such as those in Fig. 5. Here, specified regions of the responsive gel contain loops, while other regions do not and hence, this structure is achieved by "patterning with loops". Through the various examples below, we show that the system displays thermo-mechanical behavior that drives the gels to undergo reversible morphological transitions.

The gel sample in Fig, 5a has a bilayer structure, where all the elements in the top layer are devoid of loops, but all the elements in the lower layer do contain the loops. With a decrease in temperature, the unfolding of the loops in the bottom layer extends this region beyond the equilibrium degree of swelling attained in the top layer. Such relative differences in swelling within a given material can lead to pronounced morphological transitions.[43–45] With the patterning in Fig. 5a, the differential swelling causes the gel to bend as shown in Fig. 5b. Thus, the loops convert a flat, two-dimensional layer into a three-dimensional structure.

This mode of patterning can also be used to turn a rectangular slab into a complex form. The examples in Fig. 5c and 5e highlight different alternating arrangements of loops in a vertical bar block. Figures 5d and 5f show the morphology of the respective samples when the temperature is decreased, revealing that the loop-containing elements on the surface bulge outward from the gel. (The interior loop-containing elements are constrained from significant expansion by all the neighboring elements.) Hence, the loops can be utilized to create distinct relief patterns or preferentially actuate just certain portions of the material and thus imbue the material with new functionality. For instance, due to the localized protrusions, a single slab of gel can provide a series of valves that simultaneously shut off (and re-open) different regions of a chamber in a microfluidic device.

2. **Cutting the samples: complex shapes and holes.** The mode of actuation can be tailored further by changing the geometry of the sample. This is illustrated in Fig. 6, where we considered a gel that encompasses four pads (petals) around the central square (core). In

effect, we have cut a large bilayer into a more complex geometry. By placing the loops in the bottom layer of the pads and the top layer of the central domain, the shape can be controllably distorted so that the pads and central square form the respective convex and concave structures. Hence, the previously flat layer now resembles four flower petals that emanate from a dome-shaped core. More generally, the figure shows that we can generate geometric surfaces of different mean and principal curvatures by preferentially localizing loops into complex shapes. By increasing the aspect ratio of the pads, the sample can encompass rectangular protrusions, which could act as arm-like appendages in soft robotic systems.

Another means of accentuating the differences in local curvature is to introduce holes into the sample [46,47]. This behavior can be seen by comparing the local curvature in uncut and cut samples where the loops are confined to the bottom of the bilayer. The uncut sample in Fig. 7a is seven elements in length and width, and two elements in height. Introducing a hole between each adjacent element leads to the checkerboard arrangement in Fig. 7b.

As a measure of the local curvature, we determine the mean curvature H [48] and the vertical height (in the z-direction) at every node; the color bar in Fig. 7d indicates the magnitude of H. In the uncut sample, the elements along the edge are less constrained than the interior pieces and thus, can swell more than the interior domains. Hence, the edges exhibit the highest height from the z=0 plane and all the edge sites lie at the same height. As described further below, in the cut sample, all the edge elements are not identical. Complex interactions lead to the height variation in Fig. 7d. The blue edge pieces attain the greatest height because steric interactions between these neighboring sites mutually “push” each other upwards as the loops swell. Importantly, a comparison of Figs. 7c and 7d reveals that the presence of the holes enables the cut sample to display greater variations in height (and thus curvature).

To understand the subsequent behavior, it is best to orient the sample as shown in Fig. 8a-b. As can be seen, the center of the sample along the *x*-direction is formed from one column of elements, while the center of the sample along the *y*-direction is formed from two columns having the same number of elements. This asymmetry affects the subsequent structural development as the temperature is lowered and the loops are unfolded. In particular, each central column along the *y*-direction is sterically constrained by the equally-sized neighboring column. Hence, the elements in these two vertical columns are more hindered from swelling than the other elements.

Notably, the cut sample in Fig. 8a-c shows the salient behavior seen in prior studies of mechanically deformed elastomers and porous materials. [46,47] Namely, the shapes of the holes are altered by the deformation. This variation in hole shape throughout the sample can lead to local variations of the mechanical properties within the gel and mechanical behavior that is distinct from the uncut material. We can tailor the behavior of the gels further by designing materials that contain both the holes and localized placement of the loops. Figure 8d-f shows the effects of varying the placement of loops within these cut materials. With the loops in the top layer, the upper layer is more expanded and the pads curve downwards. Correspondingly, with the loops in the bottom layer, the pads curve upward.

B Effect of applying an external force

In this section, we consider the effect of an external force on the swelling of gels that contain loops. We first consider the idealized case, when a cube-shaped gel swells uniformly both along and perpendicular to the direction of the applied force of value F_g, so the strain tensor is diagonal:

$$\hat{\mathbf{B}} = \begin{bmatrix} \lambda^2 & 0 & 0 \\ 0 & \lambda_\perp^2 & 0 \\ 0 & 0 & \lambda_\perp^2 \end{bmatrix} . \qquad (24)$$

Here, λ and $\lambda_{\perp}$ are the degrees of swelling along the longitudinal and transverse directions, respectively. By balancing the forces in these two orthogonal directions (see eqs. (7), (8) and (10)), we obtain the following equations to determine the equilibrium values of λ and $\lambda_{\perp}$:

$$c_0 v_0 \phi_0^{-1} \phi [P(\bar{\lambda}) \lambda^2 - 2^{-1} P_0(\bar{\lambda})] + (h_0 \lambda_{\perp})^{-2} F_g = \pi_{\mathrm{FH}}(\phi) \qquad (25)$$

$$c_0 v_0 \phi_0^{-1} \phi [P(\bar{\lambda}) \lambda_{\perp}^2 - 2^{-1} P_0(\bar{\lambda})] = \pi_{\mathrm{FH}}(\phi) \qquad (26)$$

In the above equations, h_0 is the un-deformed gel size, the functions P and P_0 depend on $\bar{\lambda} = \sqrt{(\lambda^2 + 2\lambda_{\perp}^2)/3}$, and are defined as

$$P(\bar{\lambda}) = p_U(\bar{\lambda}) \zeta(\bar{\lambda}(n+l)^{-1/2}) + [1 - p_U(\bar{\lambda})] \zeta(\bar{\lambda}\, n^{-1/2}) \quad ,$$

$$P_0(\bar{\lambda}) = p_U(\bar{\lambda}) \zeta_0(n+l) + [1 - p_U(\bar{\lambda})] \zeta_0(n) \quad .$$

Here, the functions p_U, ζ, and ζ_0 are given in Section II. In eqs. (25) and (26), the volume fraction of polymer is taken as a function of λ and $\lambda_{\perp}$, i.e, , $\phi = \phi_0 \lambda^{-1} \lambda_{\perp}^{-2}$. Finally, it is convenient to introduce the dimensionless force $F = F_g / F_0$, where the unit of force is $F_0 = c_0 v_0 h_0^2$.

We solve eqs. (25) and (26) numerically, and compare the results with the results of the gLSM simulations. We find that the applied force *F* serves to increase the gel swelling. Namely, comparison of Figs. 4 and 9 reveals that the degree of gel swelling is greater when the external force is applied than when the loops unfold solely due to the internal strain (which arises from the expansion of the gel with increases in temperature).

As in the previous section, we consider a bilayer gel sample; however, we use the applied force as a tool to examine a different type of loop patterning. In particular, the bottom layer does not contain loops, but the top layer contains the pattern of loops and no loops shown in Fig. 10a. Using the gLSM, five nodes in both layers at the left most end of the gel are held fixed; a constant tensile force *F* (*F* = 80) is applied along this nodal region at the opposite end of the sample. The temperature is held fixed at 30°C. As the force starts to stretch the gel, the probability of unfolding increases and the gel elements with loops unfold. This causes a difference in swelling between elements with and without loops; consequently, the two layers show different curvatures (see Figs. 10b-c). Here again, we see that the patterning with loops can be used in conjunction with the applied force to transform a flat sheet into a curved structure.

As the above results indicate, force and temperature can be used as independent variables to swell the gels. Namely, Section III.A shows that below the volume phase transition temperature (T~32°*C*), the extensibility of even swollen gels can be increased by decreasing *T* to unfold the loops. Figure 11a shows a snapshot when a bilayer with loops in the bottom layer is held at *T*=30°*C* and the sample is subjected to a tensile deformation. Here the force is increased in increments of 0.001 every simulation time step.

On the other hand, if the system is constrained to lie above the volume phase transition temperature, then even initially collapsed gels can be swollen to some extent by the application of force. Figure 11b shows that the loop-containing bottom layer is swollen relative to the structure of the layer in the presence of force at *T*=33.5°*C*. These findings also demonstrate that even when the loop-containing gels are held at a constant temperature, the sample can be controllably reconfigured through an external force.

IV. Conclusions

We developed a theoretical model to capture the cooperative interactions that occur as stimuli-responsive gels trigger the unfolding of embedded loops (stored length) and the unfolding loops in turn stretch the overall network. To this end, we derived the kinetic expressions for the loop dynamics and formulated a constitutive equation that characterizes the elasticity and finite extensibility of the loop-containing gel. We incorporated these newly derived expressions into our 3D gel lattice spring model (gLSM) to simulate the structural changes that happen within the system in response to external stimuli. In particular, we designed thermo- and mechano-responsive materials where temperature or an applied force leads to the unfolding of the loops and significant enhancements in the extensibility of the materials. The processes are reversible: the loops refold when the temperature is reset to the initial value or the force is released.

With this gLSM approach, we showed how the equilibrium degree of swelling, λ, depends on the loop length; notably, λ increased by a factor of 38% when l was increased from $l = 0$ to $l = 5$ at $T = 15°C$, yielding a 2.5 increase in the volume of the sample. Taking advantage of this differential in the degree of swelling, we designed heterogeneous networks that encompass specific arrangements of the loop-containing domains. Using this “patterning with loops”, we devised gels that undergo distinctive shape-changes. For these LCST gels, a decrease in temperature causes the gel to expand and release the stored length in the loop-containing domains. This mode of patterning provides a new means of reconfiguring and actuating responsive gels. Consequently, square and rectangular structures can be controllably reconfigured to exhibit pronounced curvature and architectural features. With the appropriate placement of loops, the system can be actuated asymmetrically so that one face or region is more swollen than the rest of the sample. In this way, the sample can display new functionality or undergo directed motion.

In scenarios where the temperature is fixed, an applied force can be used to reconfigure and actuate gels patterned with loops. This attribute is particularly useful in cases where the operating conditions are constrained to lie above the volume phase transition temperature, where the LCST gels are in the collapsed state. The external force leads to the unfolding of the loops and the introduction of swollen domains and curved surfaces into the shrunken material, allowing the gel to be used for new applications.

The findings highlight a responsive system that can interconvert thermal, chemical and mechanical energy to perform a function. Such systems could be useful for designing soft robotic materials that translate environmental changes into useful work. Given recent advances in the synthesis of foldamer-[8] and DNA-[9] containing gels, our predictions could be tested and the model systems described here could be experimentally realized.

Conflicts of Interest

There are no conflicts of interest to declare.

Acknowledgements

ACB gratefully acknowledges financial support from the DOE.

References

1 L. Rognoni, J. Stigler, B. Pelz, J. Ylänne and M. Rief, *Proc. Natl. Acad. Sci. U. S. A.*, 2012, **109**, 19679–84.

2 Y. Gu, K. Kawamoto, M. Zhong, M. Chen, M. J. A. Hore, A. M. Jordan, L. T. J. Korley, B. D. Olsen and J. A. Johnson, *Proc. Natl. Acad. Sci. U. S. A.*, 2017, **114**, 4875–4880.

3 M. Zhong, R. Wang, K. Kawamoto, B. D. Olsen and J. A. Johnson, *Science*, 2016, **353**, 1264–8.

4 M. S. Z. Kellermayer, S. B. Smith, H. L. Granzier and C. Bustamante, *Science*, 1997, **276**, 1112–1116.

5 Z. Guan, J. T. Roland, J. Z. Bai, S. X. Ma, T. M. McIntire and M. Nguyen, *J. Am. Chem. Soc.*, 2004, **126**, 2058–2065.

6 J. Chung, A. M. Kushner, A. C. Weisman and Z. Guan, *Nat. Mater.*, 2014, **13**, 1055–62.

7 S. Hirotsu, *J. Chem. Phys.*, 1991, **94**, 3949.

8 J. Chen, A. W. Ziegler, B. Zhao, W. Wan and A. D. Q. Li, *Chem. Commun.*, 2017, **53**, 4993–4996.

9 A. Cangialosi, C. Yoon, J. Liu, Q. Huang, J. Guo, T. D. Nguyen, D. H. Gracias and R. Schulman, *Science*, 2017, **357**, 1126–1130.

10 G. I. Bell, *Science*, 1978, **200**, 618–627.

11 M. Rubinstein and R. H. Colby, *Polymer Physics*, Oxford University Press, Oxford, 2003.

12 B. V. S. Iyer, I. G. Salib, V. V. Yashin, T. Kowalewski, K. Matyjaszewski and A. C. Balazs, *Soft Matter*, 2013, **9**, 109–121.

13 B. V. S. Iyer, V. V. Yashin, T. Kowalewski, K. Matyjaszewski and A. C. Balazs, *Polym. Chem.*, 2013, **4**, 4927.

14 M. J. Hamer, B. V. S. Iyer, V. V. Yashin, T. Kowalewski, K. Matyjaszewski and A. C. Balazs, *Soft Matter*, 2014, **10**, 1374–1383.

15 M. J. Hamer, B. V. S. Iyer, V. V. Yashin and A. C. Balazs, *Nano Lett.*, 2014, **14**, 4745–4750.

16 B. V. S. Iyer, V. V. Yashin, M. J. Hamer, T. Kowalewski, K. Matyjaszewski and A. C. Balazs, *Prog. Polym. Sci.*, 2015, **40**, 121–137.

17 T. Zhang, B. L. Mbanga, V. V. Yashin and A. C. Balazs, *ACS Nano*, 2017, **11**, 3059–3066.

18 V. V. Yashin and A. C. Balazs, *Science*, 2006, **314**, 798–801.

19 V. V. Yashin and A. C. Balazs, *J. Chem. Phys.*, 2007, **126**, 124707.

20 O. Kuksenok, V. V. Yashin and A. C. Balazs, *Phys. Rev. E - Stat. Nonlinear, Soft Matter Phys.*, 2008, **78**, 41406.

21 L. Anand, *Comput. Mech.*, 1996, **18**, 339–355.

22 F. Horkay and G. B. McKenna, in *Physical Properties of Polymers Handbook*, Springer, New York, 2007, pp. 497–523.

23 V. V. Yashin, O. Kuksenok and A. C. Balazs, *Prog. Polym. Sci.*, 2010, **35**, 155–173.

24 V. V. Yashin, O. Kuksenok, P. Dayal and A. C. Balazs, *Reports Prog. Phys.*, 2012, **75**, 66601.

25 O. Kuksenok, V. V. Yashin and A. C. Balazs, *Soft Matter*, 2009, **5**, 1835.

26 V. V. Yashin, K. J. Van Vliet and A. C. Balazs, *Phys. Rev. E*, 2009, **79**, 46214.

27 V. V. Yashin, O. Kuksenok and A. C. Balazs, *J. Phys. Chem. B*, 2010, **114**, 6316–22.

28 I. C. Chen, O. Kuksenok, V. V. Yashin, A. C. Balazs and K. J. Van Vliet, *Adv. Funct. Mater.*, 2012, **22**, 2535–2541.

29 P. Yuan, O. Kuksenok, D. E. Gross, A. C. Balazs, J. S. Moore and R. G. Nuzzo, *Soft Matter*, 2013, **9**, 1231–1243.

30 O. Kuksenok and A. C. Balazs, *Adv. Funct. Mater.*, 2013, **23**, 4601–4610.

31 O. Kuksenok and A. C. Balazs, *Sci. Rep.*, 2015, **5**, 9569.

32 O. Kuksenok and A. C. Balazs, *Mater. Horiz.*, 2016, **3**, 53–62.

33 X. He, M. Aizenberg, O. Kuksenok, L. D. Zarzar, A. Shastri, A. C. Balazs and J. Aizenberg, *Nature*, 2012, **487**, 214–218.

34 B. Barrière and L. Leibler, *J. Polym. Sci. Part B Polym. Phys.*, 2003, **41**, 166–182.

35 A. Onuki, *Adv. Polym. Sci.*, 1993, **109**, 63–121.

36 M. Doi, *J. Phys. Soc. Japan*, 2009, **78**, 52001.

37 I. M. Smith, D. V. Griffiths and L. Margetts, *Programming the Finite Element Method*, John Wiley & Sons, 2013.

38 O. C. Zienkiewicz, R. L. Taylor and J. Z. Zhu, *The Finite Element Method: Its Basis and Fundamentals*, Butterworth-Heinemann, 7th edn., 2013.

39 R. J. Atkin and N. Fox, *An introduction to the theory of elasticity*, Dover, New York, 2005.

40 T. L. Hill, *An introduction to statistical thermodynamics*, Dover, New York, 1986.

41 X. Yong, A. Simakova, S. Averick, J. Gutierrez, O. Kuksenok, A. C. Balazs and K. Matyjaszewski, *Macromolecules*, 2015, **48**, 1169–1178.

42 A. Beziau, R. N. L. de Menezes, S. Biswas, A. Singh, J. Cuthbert, A. C. Balazs, T. Kowalewski and K. Matyjaszewski, *Polymers (Basel).*, 2017, **9**, 186.

43 S. Timoshenko, *J. Opt. Soc. Am.*, 1925, **11**, 233.

44 S. J. Jeon, A. W. Hauser and R. C. Hayward, *Acc. Chem. Res.*, 2017, **50**, 161–169.

45 A. S. Gladman, E. A. Matsumoto, R. G. Nuzzo, L. Mahadevan and J. A. Lewis, *Nat. Mater.*, 2016, **15**, 413–418.

46 S. Singamaneni, K. Bertoldi, S. Chang, J.-H. Jang, E. L. Thomas, M. C. Boyce and V. V. Tsukruk, *ACS Appl. Mater. Interfaces*, 2009, **1**, 42–47.

47 B. Cao, G. Wu, Y. Xia and S. Yang, *Extrem. Mech. Lett.*, 2016, **7**, 49–54.

48 N. Dyn, K. Hormann, S.-J. Kim and D. Levin, in *Mathematical Methods for Curves and Surfaces*, eds. T. Lyche and L. L. Schumaker, Vanderbilt University, Nashville, TN, USA, 2001, pp. 135–146.

Figure Captions

Fig. 1 (Top) Schematic of a polymer gel network containing loops in folded and unfolded state. Polymer network is represented in green. Grey solid circles represent crosslinks and the reactive labile bonds are shown in red when open and in blue when bonded and forms a loop. The bottom panel displays a magnified representation of the chains with n Kuhn segments containing loops with l Kuhn segments in folded (left) and unfolded state (right). R is the chain end-end distance.

Fig. 2 Lateral extension of the gel (λ) with temperature. Extensions of the gel following the linear chain elasticity (eq. (9)) is represented by black dashed lines while the red line shows the extension for gels characterized by the constitutive equation which accounted for chains with finite extensibility eq. (10). The polymer-solvent interaction for the pNIPAAm-water system was taken to be [7] $\chi(\phi,T)=\chi_0(T)+\chi_1\phi$ where $\chi_0(T)=[h-(T_0+T)s][k_B(T_0+T)]^{-1}$ and $\chi_1=0.518$. The value of the parameters [7] are $h=-1246.0$, $s=4.717$, $T_0=273.15$, and $k_B=1.3807$. Number of Kuhn segments in the chain $n=4$. The gel parameters are $\phi_0=0.129$ and $c_0=5.4\times10^{-4}$.

Fig. 3 Probability of unfolding p_u of the loop in steady-state as a function of chain extension λ for different force sensitivity parameter γ_0.The length of Kuhn segment b is assumed to be 1. The volume fraction of the gel with loop of Kuhn segment l is calculated as $\phi_0(1+l/n)$ .As γ_0 is increased, the unfolding probability increases gradually to 1 at lower extensions. We use the value of $\gamma_0=2.15$ in our gLSM simulations.

Fig. 4 Lateral extension of the gel λ as a function of temperature T at various numbers of Kuhn segments l in the loop part of the chains. Lines show numerical solutions obtained by solving eq. (11) using the *Mathematica*^{TM} software; results of the gLSM simulation are denoted by open circles. The gel dimension for the gLSM simulations is $4 \times 4 \times 4$. The plot shows excellent agreement between the two approaches. As the number of Kuhn segments in the loops increases, the gel extension becomes greater at lower temperatures. The prominent jump in the extension ($l = 3, 4$ and 5) at lower temperature corresponds to unfolding of the loops as the gel swells.

Fig. 5 Shape changes due to gel swelling in square and rectangular shaped gels with patterned placement of loops. (a, c and e) shows the initial equilibrium configuration of the gel sample at $T = 30°C$. Unless explicitly mentioned in all the figures, the light gray elements denote polymer gels without loops containing $n = 4$ Kuhn segments, the black elements represent gels with loops having $n = 4$ and $l = 5$ Kuhn segments and the volume fraction at $T = 30°C$ is 0.105. Gel dimensions are (a) $18 \times 6 \times 2$, (c) $8 \times 8 \times 14$, and (e) $8 \times 8 \times 14$. The equilibrated gel sample at $15°C$ is shown in (b, d and f). The color bar represents the volume fraction ϕ of the gel elements.

Fig. 6 Gel patterned with four pads and a central square. The initial equilibrium configuration of the gel sample at $T = 30°C$ is shown in (a). The pad dimension is $9 \times 9 \times 2$, and the central region is $12 \times 12 \times 2$ with $3 \times 3 \times 2$ elements at each corner being part of the pad. As temperature is changed to $15°C$, the gel swells upon equilibration. The swelling differential between the elements with and without loops results in a flower pattern, where the central region is concave, and the four pads representing the petals are convex.

Fig. 7 Mean curvature H for different gel patterns. The equilibrium configuration at $T = 15°C$ for a bilayer gel sample of dimension $7 \times 7 \times 2$ is shown for the patterns (a) without and (b) with holes. The mean curvature of the gel samples are shown in (c) and (d). The difference between the maximum and minimum value in the z direction for the entire sample is denoted by Δz. The curvature of sample (b) is greater as seen from the mean curvature and the Δz value.

Fig. 8 Gel patterns containing holes. Figure (a) represents a bilayer like pattern with gel elements containing loops in the bottom layer and elements without loop in the top layer, and with the alternate elements removed. The sample is equilibrated at $T = 30°C$. The gel dimension is $7 \times 7 \times 2$. The equilibrated gel sample at $T = 15°C$ is shown (b) top-view and (c) side-view. Gel sample with holes divided into four quadrants. Each alternating quadrant has loops placed in opposite layers as shown in (d). The sample in (d) shows the equilibrated configuration at $T = 30°C$. The equilibrated gel sample at $T = 15°C$ is shown (e) top-view. Side-view (f) of the sample exhibits both concave and convex regions because of the alternating loop placement.

Fig. 9 Lateral extension of the gel (along the direction of force) λ as a function of temperature for various numbers of Kuhn segments l in the loop part of the chains under the effect of a tensile force ($F = 0.7$). Numerical solutions obtained with *Mathematica*^{TM} software are represented by lines; the results of the gLSM simulation are denoted by open circles. Comparison to Fig. 4 shows that application of force enhances swelling of the gel.

Fig. 10 Effect of force on a gel sample patterned with loops. (a) Top figure shows the initial patterned gel sample of dimension $10 \times 10 \times 2$. At one end, five nodes of both layers are fixed; a constant force is applied on the five nodes (shown in red) at the opposite end. The bottom figure shows the equilibrated gel sample at $T = 30°C$. The final gel configuration under the effect of a constant force ($F = 80$) as seen from top (b) and bottom (c).

Fig. 11 Gel swelling under the application of force. Starting from an equilibrated flat bilayer gel sample of dimension $7 \times 7 \times 2$, with loops placed only in the elements of the bottom layers. One end of the samples are fixed along the x-direction but are free to move in the y-z direction. A force ramp of $\Delta F = 0.001$ is applied the other end along the x-direction. The figure shows the final configuration before rupture for bilayer gel samples at (a) $T = 30°C$ and (b) $T = 33.5°C$. The degree of swelling is very high for the sample below the critical temperature at $T = 30°C$ as seen in (a). Even above the critical temperature, at $T = 33.5°C$, the sample swells due to unfolding the loops by the applied force.

Graphical Abstract

Modeling shape changes in gels that arise from the thermally or mechanically induced unfolding (and refolding) of embedded loops.