Effect of NIPAAm concentration ($C_{\text{NIPAAm}}$) on topography of gel surface in the slow heating regime.

**S1. A.** Fabrication procedure for hybrid surface. **B.** Effect of NIPAAm concentration in hydrogel ($C_{\text{NIPAAm}}$) on equilibrium morphologies formed by the surface at different temperatures. Scale bar: 125 µm.
Setup of finite element simulation

In the framework of the gel lattice spring model (gLSM), the structural evolution of the local volume fraction of polymer, \( \phi \), is governed by the following continuity equation\(^1,2\):

\[
\frac{\partial \phi}{\partial t} = -\nabla \cdot (\phi \mathbf{v}^{(p)}),
\]

(1)

where \( \mathbf{v}^{(p)} \) is the polymer velocity. All equations are presented in the dimensionless form, assuming that length and time are measured in the respective units of \( L_0 \) and \( T_0 \) (see below). We assume that it is solely the inter-diffusion of the polymer and solvent that contributes to the gel dynamics and neglect the net velocity of the polymer-solvent system.\(^1\) The latter assumption is specified through the following equation:

\[
\phi \mathbf{v}^{(p)} + (1 - \phi) \mathbf{v}^{(s)} = 0,
\]

(2)

where \( \mathbf{v}^{(s)} \) is the velocity of the solvent. The dynamics of the polymer network is taken to be purely relaxational;\(^1,2\) consequently, the forces acting on the deformed gel are balanced by the frictional drag due to the motion of the solvent. This force balance is expressed as\(^1\):

\[
\nabla \cdot \mathbf{\hat{\sigma}} = \nu_0 (k_B T)^{-1} L_0^2 / T_0 \zeta(\phi)(\mathbf{v}^{(p)} - \mathbf{v}^{(s)}),
\]

(3)

where \( \mathbf{\hat{\sigma}} \) is the dimensionless stress tensor (measured in units of \( \nu_0^{-1} k_B T \)), \( \nu_0 \) is the volume of a monomeric unit, and \( T \) is temperature. The prefactor \( \nu_0 (k_B T)^{-1} L_0^2 / T_0 \) in eq. (3) is used to express this equation in dimensionless form. The polymer-solvent friction coefficient, \( \zeta(\phi) \), is approximated as\(^3\):

\[
\zeta(\phi) = \zeta(\phi_0)(\phi / \phi_0)^{3/2}
\]

(4)

where \( \phi_0 \) is the local volume fraction of the polymer in the undeformed gel. This approximation is valid in the semi-dilute and intermediate regimes (i.e., \( \phi < 0.5 \), which is
always satisfied in the following calculations. If the stress tensor $\sigma$ is known, then Eqs. (2)-(4) give:

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

(5)

where $\Lambda_0 = k_B T (\nu_0 \zeta(\phi_0) I_0^2 / T_0)^{-1}$ is the dimensionless kinetic coefficient.

The stress tensor $\sigma$ is obtained from the energy density of the deformed gel, $u(I_1, I_2, I_3)$, and is given as

$$\sigma = 2I_3^{-1/2} (w_2 I_2 + w_3 I_3) \hat{\mathbf{i}} + 2I_3^{-1/2} w_1 \hat{\mathbf{B}} - 2I_3^{1/2} w_2 \hat{\mathbf{B}}^{-1}$$

(6)

Here, $\hat{\mathbf{i}}$ is the unit tensor and $\hat{\mathbf{B}}$ is the left Cauchy-Green strain tensor. The invariants of this strain tensor, $I_i$, $i=1,2,3$, are specified as:

$$I_1 = \text{tr} \hat{\mathbf{B}}, \quad I_2 = \frac{1}{2} [(\text{tr} \hat{\mathbf{B}})^2 - \text{tr}(\hat{\mathbf{B}}^2)], \quad I_3 = \det \hat{\mathbf{B}}.$$

Additionally, $w_i = \frac{\partial}{\partial I_i} u(I_1, I_2, I_3)$.

The energy density $u(I_1, I_2, I_3)$ consists of the elastic energy density associated with the deformation of the gel, $u_{el}$, and the polymer-solvent interaction energy density, $u_{FH}$:

$$u = u_{el}(I_1, I_3) + u_{FH}(I_3)$$

(7)

The elastic energy $u_{el}$ describes the rubber elasticity of the crosslinked polymer network $^5,6$ and is proportional to the crosslink density in the undeformed polymer network $c_0$:

$$u_{el} = \frac{c_0 U_\phi}{2} (I_1 - 3 - \ln I_3^{1/2})$$

(8)

The expression for $u_{FH}$ takes the following Flory-Huggins form: $^5$

$$u_{FH} = I_3^{1/2} [ (1 - \phi) \ln(1 - \phi) + \chi_{FH}(\phi, T) \phi(1 - \phi) ]$$

(9)
Here, $\chi_{FH}(\phi, T)$ is the polymer-solvent interaction parameter. The term $I_2^{1/2} = \phi / \phi_0$ appears in the equation because the energy density is defined by a unit volume in the undeformed state.$^1$

Substituting Eqs. (7)-(9) into Eq. (6) yields the following relationship between the stress ($\hat{\sigma}$) and strain ($\hat{\mathbf{B}}$) tensors:

$$\hat{\sigma} = -P(\phi)\hat{\mathbf{I}} + c_0\nu_0 \frac{\phi}{\phi_0} \hat{\mathbf{B}}$$

(10)

The pressure $P(\phi)$ is defined as

$$P(\phi) = -[\phi + \ln(1 - \phi) + \chi(\phi)\phi^2] + c_0\nu_0\phi(2\phi_0)^{-1}$$

(11)

where $\chi(\phi) = \chi_0 + \chi_1\phi$. Here, $\chi_0(T) = (\delta h - T\delta s) / k_B T$, with $\delta h$ and $\delta s$ being the respective changes in the enthalpy and entropy per monomeric unit of the gel.$^7$ The stress tensor can be decomposed as the sum of the hydrostatic and deviatoric stress tensors; the latter terms correspond, respectively, to the volume change and shape distortion of the gel element. Since the motion in the system is due solely to the inter-diffusion of the solvent and polymer, the hydrostatic pressure acting on the solvent is related to the hydrostatic stress on the gel element as

$$P_h = \frac{1}{3} \text{tr}(\hat{\sigma})$$

(12)

The above equations are solved numerically using our gLSM (as detailed in reference 5). In this approach, a 3D deformable gel is represented by a set of general linear hexahedral elements. Initially, the sample is undeformed and consists of $(L_x - 1) \times (L_y - 1) \times (L_z - 1)$ identical cubic elements, where $L_i$ is the number of nodes in
the $i$-direction, $i = x, y, z$; the linear size of the elements in the undistorted state with
$\varphi_0 = 0.1286$ is set to $L_0 = 1$.

The gel is attached to the solid bump, which is modeled by frozen gel nodes where
the node velocities are set to zero and the polymer volume fraction is fixed at $\varphi_{bump} = 1$.

The profile of the bump is a truncated circle and is discretized in the simulation as
illustrated in Fig. 3D, where the color bar represents the polymer volume fraction.

We utilize parameter values that are based on the experimental data for poly(N-
isopropylacrylamide) (PNIPAAm), which displays a LCST.\textsuperscript{7} The polymer volume fraction
in the undeformed gel is set to $\varphi_0 = 0.1286$ and the crosslink density in the undeformed
polymer network is $c_0 = 5.76 \times 10^{-4}$. For the gel-solvent interaction parameters, we set
$\chi_1 = 0.518$, and $\chi_0(T) = \frac{\delta h - T \delta s}{k_B T}$, where $\delta h = -12.4 \times 10^{-14}$, and $\delta s = -4.7 \times 10^{-16}$. In Eq. (5),
we use the dimensionless kinetic coefficient $\chi_0 = 100$.\textsuperscript{8,9} We set our units of length and
time to be $L_0 = 5 \mu m$ and $T_0 = 1.25 s$, respectively, to ensure that the value of the diffusion
coefficient is $L_0^2 / T_0 = 2 \times 10^{-11} \text{cm}^2 \text{s}^{-1}$.\textsuperscript{10} The physical size of the system with $101 \times 11 \times 32$
elements at $31^\circ C$ is $500 \mu m \times 50 \mu m \times 155 \mu m$. The length of a solid bump is $W_0 = 500 \mu m$
and the height $h_0 = 145 \mu m$. The thickness of the gel on the top of the bump is $10 \mu m$. 
Effect of setpoint temperature on the morphology of transient states in the fast heating regime.

**Fig S2. A.** Sideview confocal z-stack images show that at a temperature setpoint of 34°C, the gel transitions passes through a double peak state and continues to transition smoothly from non-inverted to inverted. By contrast, at a temperature setpoint of 36°C or 38°C, the surface undergoes a transition through morphology with multiple peak points before full inversion. Scale bar: 125µm.

**Fig S2. B.** Top view images show that a well-defined region of bubbles appear on the surface at 3.5 mins from the start of the temperature ramp during the inversion process for temperature setpoints of 36°C or 38°C. Scale bar: 300µm.
Effect of temperature ramp direction on the surface inversion trajectory.

**Fig S3.** A. Comparison between gel surface deformation process during heating and cooling at slow heating rate of \( R = 0.2^\circ \text{C}/\text{min} \). Small differences in the surface morphology are observed between 31 and 36°C, indicating hysteresis (e.g. see arrow). B. Comparison in the surface morphology change as a result of heating vs cooling at 5°C/min. While both processes cause the surface to undergo a double-peak transition, the peak points are offset by half a bump-to-bump periodicity. Height profiles extracted from confocal images (right) provide quantification of this difference. B. Raw confocal data showing the shape change process at critical timepoints. Scale: 125µm. C. The effect of the shape change on the movement of particles. Scale: 200µm.
Effect of preswollen gel at bump sites ($h_{\text{bump}}$) on the formation of bubble instabilities at bump sites.

Fig S4. Effect of preswollen gel height $h_{\text{bump}}$ on the formation of bubble instabilities at the bump sites upon heating to $T_{sp}=36^\circ\text{C}$ at ramp rate of $R=5^\circ\text{C}/\text{min}$. (A) Fabrication of sample with linear gradient in preswollen gel height $h_{\text{bump}}$ across the length of the sample. (B) Bubbles begin to form at the bump site as $h_{\text{bump}}$ increases (see black arrows). Scale: 750µm. (C) The number of bubbles increases with $h_{\text{bump}}$ and reaches a plateau at $h_{\text{bump}}\sim50µm$. (D) Visualization of the top surface of the gel during the contraction process reveals the formation of an ordered array of bumps at the bump sites. Scale: 500µm.

References: