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Thermodynamics of microphase separation in a swollen, strain-stiffening polymer network

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Elastic MicroPhase separation (EMPS) provides a simple route to create soft materials with homogeneous microstructures by leveraging the supersaturation of crosslinked polymer networks with liquids. At low supersaturation, network elasticity stabilizes a uniform mixture, but beyond a critical threshold, metastable microphase-separated domains emerge. While previous theories have focused on describing qualitative features about the size and morphology of these domains, they do not make quantitative predictions about EMPS phase diagrams. In this work, we extend Flory–Huggins theory to quantitatively capture EMPS phase diagrams by incorporating strain-stiffening effects. This model requires no fitting parameters and relies solely on independently measured solubility parameters and large-deformation mechanical responses. Our results confirm that strain-stiffening enables metastable microphase separation within the swelling equilibrium state and reveal why the microstructures can range from discrete droplets to bicontinuous networks. This work highlights the critical role of nonlinear elasticity in controlling phase-separated morphologies in polymer gels.

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1 Introduction

Phase separation is a ubiquitous process that can be harnessed to create structured materials.^{1,2} In this process, two or more components demix, typically triggered by changes in temperature, composition, or degree of polymerization.^{3–5} Demixing creates microstructures with discrete domains or bicontinuous channels. For classical phase-separation processes, like liquid–liquid phase separation, domains gradually coarsen due to the influence of surface tension.^{6,7} When this coarsening is arrested (for example by solidification, or going through a glass transition^{8–10}), solid materials with intricate and stable microstructures can be created.^{11,12} Synthetic examples include metal alloys,¹³ membranes,¹⁴ and cell tissue scaffolds,^{15,16} while natural examples include structurally-colored materials produced by many different animals,^{17,18} and phase-separated domains inside cytoplasm and lipid membranes.^{19–22}

Recently, elastic microphase separation (EMPS) has emerged as an alternative, convenient route to create phase-separated

microstructures that do not coarsen.^{11,23,24} In essence, EMPS exploits mechanical forces imposed by a polymer network to counteract interfacial tension. In typical EMPS experiments, an elastomer is equilibrated with solvent at high temperatures (see Fig. 1A). Then, cooling triggers phase separation of the solvent within the elastomer. Phase separation occurs rapidly and locally, within a few seconds. Microstructures with either

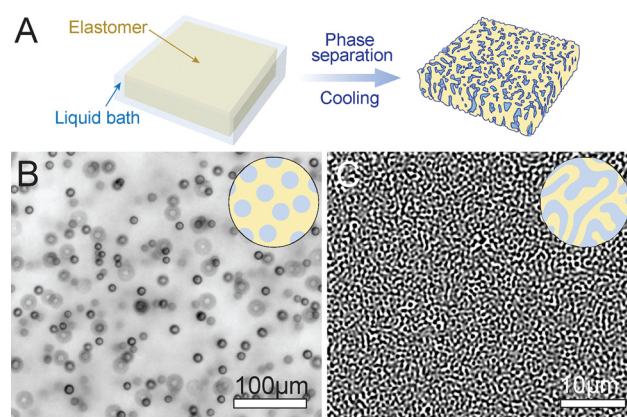


Fig. 1 Schematic of EMPS. (A) First, an elastomer is swollen in a liquid bath at elevated temperatures. After swelling equilibrium is reached, cooling induces phase separation. Different phase separated morphologies and sizes are obtained as a function of the matrix's composition and stiffness: (B) droplet²³ and (C) bicontinuous morphologies.²⁴

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discrete droplets or bicontinuous channels form, depending on the elastomer's degree of swelling and stiffness (see Fig. 1B and C). This process is simple and robust enough to easily produce large pieces of material with precisely controlled microstructures. While these microphase-separated structures are stable to coarsening, they are unstable to the loss of solvent to the surrounding bath on a timescale that is $O(10\text{ h})$.²⁵ The onset of elastic microphase separation is characterized by a novel phase boundary inside the super-saturated regime of the network-solvent swelling equilibrium, as described in ref. 23 and 24.

EMPS is closely connected to liquid-liquid phase separation. At the monomer scale, both the elastomer and solvent are liquid-like. Thus, we expect the earliest stages of phase separation to be insensitive to the relatively sparse elastic constraints imposed by the cross-links between the polymer chains. However, at later stages of phase separation, we expect the elasticity of the polymer phase to become important – in a similar fashion to how elasticity controls swelling and volume phase transitions in gels.^{26–35} Indeed experiments suggest that the elastomer's Young's modulus plays an essential role in defining morphology and thermodynamics.^{23–25,36} Importantly though, theoretical studies agree that linear elasticity is insufficient to capture key aspects of the experiments. For example, previous works have investigated the role of mesh size,^{37,38} viscoelasticity,³⁹ damage,^{40,41} and heterogeneous or non-local elasticity^{42–46} and non-linear elasticity.^{37,47,48}

Out of all these topics, several recent theoretical studies have emphasized that strain stiffening of the polymer network should be a key feature controlling EMPS. For example, strain-stiffening has been shown to play a role in setting the scale of microphase-separated structures,^{48–51} in determining whether separated domains can grow larger than the mesh size of an elastomer,³⁷ and in cavitation: where solvent-filled droplets form in quenched elastomers.⁵² Finally, Hennessy *et al.*⁴⁷ showed that 1D gels with non-linear elasticity have similar phase diagrams to EMPS with two distinct phase boundaries. While all of the above theories qualitatively capture different aspects of EMPS, there have been no quantitative comparisons of theory and experiments.

Here, we explore the impact of strain-stiffening on the phase separation of liquids within elastic matrices by extending Flory–Huggins' (FH) theory of macromolecular liquid-liquid phase separation, incorporating energy stored in large elastic deformations. We show that strain-stiffening enables metastable microphase separation in a subset of the super-saturated region of the swelling phase diagram – indeed, this type of phase separation does not occur without strain stiffening. Using this model, we can quantitatively predict EMPS phase diagrams from measurements of the (i) stress-strain relationship of the neat elastomer and (ii) solubility of uncrosslinked polymer in the solvent. These predictions are in reasonable agreement with measured phase diagrams of fluorinated oil in a silicone elastomer. Finally, we discuss the role of cavitation instabilities in selecting the microphase-separated morphology.

2 Liquid-liquid phase separation

In order to understand how elasticity affects phase separation, we start by characterizing liquid-liquid phase separation of the elastomer's uncrosslinked polymer precursors in the solvent of interest. Here, this consists of 28 kDa vinyl-terminated PDMS chains in heptafluorobutyl methacrylate (HFBMA, 268.1 Da) (see Fig. 2A). As reported previously,²⁴ we determine the phase diagram of this system by recording the temperature at which phase separation initiates during simultaneous cooling and observation under a light microscope (see Materials & methods). The resulting phase diagram takes the classical LLPS form shown in Fig. 2B (see black circles). Above a critical temperature

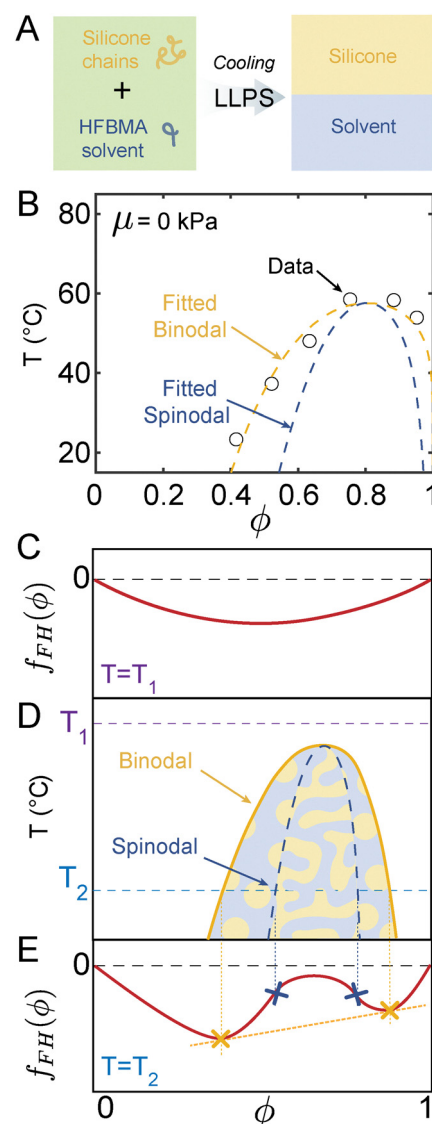


Fig. 2 Liquid-liquid phase separation behavior of uncrosslinked silicone polymer mixed with HFBMA solvent. (A) Schematic of macroscopic phase separation. (B) Experimental phase diagram of the LLPS silicone-HFBMA (see black circles) fitted with classical FH theory (see dashed yellow line). Here, ϕ is the solvent volume fraction. (C) and (E) Schematic of the total free energy of mixing at different temperatures, T_1 and T_2 . (D) Schematic LLPS diagram corresponding to (C) and (E).



$T_c \approx 60$ °C, the two fluids are always miscible. At lower temperatures, demixing occurs for a range of HFBMA volume fractions, ϕ , in the mixture.

LLPS phenomena can be described using Flory–Huggins (FH) theory,⁵³ which expresses the stability of solvent–polymer mixtures based on an expression for the dimensionless Helmholtz free energy per unit volume of a mixture of the form:⁵⁴

$$f_{\text{FH}}(\phi, T) = \phi \log \phi + \frac{v_s}{v_p}(1 - \phi) \log(1 - \phi) + \chi(\phi, T)\phi(1 - \phi), \quad (1)$$

where ϕ is the volume fraction of the solvent, v_s and v_p are the molecular volumes of solvent and polymer, respectively, and $\chi(\phi, T)$ is the Flory–Huggins polymer–solvent interaction parameter.^{55,56} Often, χ is assumed to only depend on T . However, extensive studies have shown that χ must also depend on ϕ in order to capture experimental observations.⁵⁵ Note that this model assumes that there is no polymer chain polydispersity.⁵⁷ The free energy density f_{FH} is normalized by $k_B T/v_s$, where k_B is Boltzmann's constant and T is the absolute temperature. The first two terms in this equation represent the entropy of mixing of the two components, which favours a single mixed phase. The last term represents the enthalpy of mixing, which favours separation into polymer-rich and solvent-rich phases.

To convert an expression for free energy, like that above, into a phase diagram, we use the classical approach illustrated in Fig. 2C and D.⁵⁴ Fig. 2C and E show schematic representations of f_{FH} at different temperatures (Fig. 2C and E). Above T_c , $f_{\text{FH}}(\phi)$ is globally convex downward, due to the dominance of the entropic terms (see Fig. 2C). The free energy of the mixture can not be lowered by separating into two phases. Thus, the system remains completely mixed. Below T_c , the enthalpy of mixing becomes more important, and f_{FH} develops concavity (see Fig. 2E). In this case, phase separation can occur because the system's free energy can be reduced by splitting into two different phases. The range of ϕ where phase separation occurs can be found by applying the double-tangent construction (see full derivation in Appendix A), which essentially consists of a tangent line (see yellow line in Fig. 2E) that connects the bottom sides of the two convex regions. This double-tangent line ensures that the chemical potentials of the solvent and the polymer are equal in both phases, fulfilling the condition for phase equilibrium. Furthermore, the points of tangency (yellow crosses in Fig. 2E) then represent the equilibrium composition of the two phases and are known as the binodal points.

The range of ϕ over which the system undergoes phase separation can be further subdivided, based on the curvature of f_{FH} . When $\partial^2 f_{\text{FH}}/\partial \phi^2 > 0$ (outside the blue crosses), the mixture is metastable and phase separation occurs by localized nucleation and growth (see droplet morphologies in Fig. 2D). When $\partial^2 f_{\text{FH}}/\partial \phi^2 < 0$, (between the blue crosses, Fig. 2E), the mixture is unstable, and system separates continuously through spinodal decomposition (see interconnected structures in Fig. 2D).⁵⁴ By performing this calculation across a range of different

temperatures, we construct the binodal and spinodal curves of the phase diagram shown in Fig. 2D.

To fit our LLPS data using Flory–Huggins theory, we need to determine v_s/v_p and $\chi(\phi, T)$. While v_s/v_p is easily calculated from molar volumes of the two components ($v_s/v_p = 6.90 \times 10^{-3}$), we fit the experimental binodal (black circles in Fig. 2A) with $\chi(\phi, T)$ ⁵⁸ using the simplest ϕ -dependent form:^{59–61}

$$\chi(\phi, T) = A + B/T + C\phi. \quad (2)$$

We find best-fit values of $A = 0.2108$, $B = 247.76$ K and $C = -0.227$ (see fitted binodal and spinodal dashed lines in Fig. 2B).

Although it may seem excessive to use three fitting parameters to fit 6 data points, it is not possible to fit the data with less, as each parameter has a separate effect on the phase diagram: A essentially moves the phase diagram up and down, B changes the width of the peak, while C is the only parameter that moves the peak laterally. See the supplement for a description of the fitting process, and a demonstration that the results presented here are insensitive to changes in these fitting parameters and to the specific form chosen for χ .

In Section 3.4, we will use these parameters to predict EMPS phase diagrams. This assumes that $\chi(\phi, T)$ does not change when the silicone chains cross-link into an elastic network.

3 Phase separation in an elastic network

In this section, we briefly review the essential features of phase diagrams in elastic microphase separating systems before extending Flory–Huggins theory to account for large-deformation elasticity of polymer matrices upon swelling and phase separation.

Compared to LLPS, crosslinking silicone chains into elastic networks qualitatively changes phase separation of HFBMA in silicone. This is shown in the experimental phase diagrams for polymer networks with shear moduli $\mu = 485$ kPa and 118 kPa shown in Fig. 3A and B respectively. The higher boundary (circles) represents macroscopic swelling equilibrium of the silicone swollen in pure HFMBMA (see sketch Fig. 3C(i)). Below this boundary (shallow quench), the system is supersaturated, but no microscopic phase separation is observable (see Fig. 3C(ii)). Instead, the solvent inside the matrix diffuses to the bath until it reaches a new swelling equilibrium (see Fig. 3C(iv)). This deswelling process takes a time $\tau_{\text{deswell}} = O(10$ h) for a cm-scale sample. The lower boundary (crosses) marks the onset of microphase separation. When cooled below this line (deep quench), the system undergoes microscopic phase separation as shown in Fig. 3C(iii). This microscopic process occurs within a much shorter time, $\tau_{\mu\text{PS}} = O(1$ min), and involves no exchange of material out of the gel. The micro-scale structures are metastable and after a long time, τ_{deswell} , the solvent inside the microstructures diffuses to the bath and reaches a new swelling equilibrium (see dashed arrows). The microphase-separation boundary does not behave like classical spinodal and binodal curves. Like a spinodal, we observe a



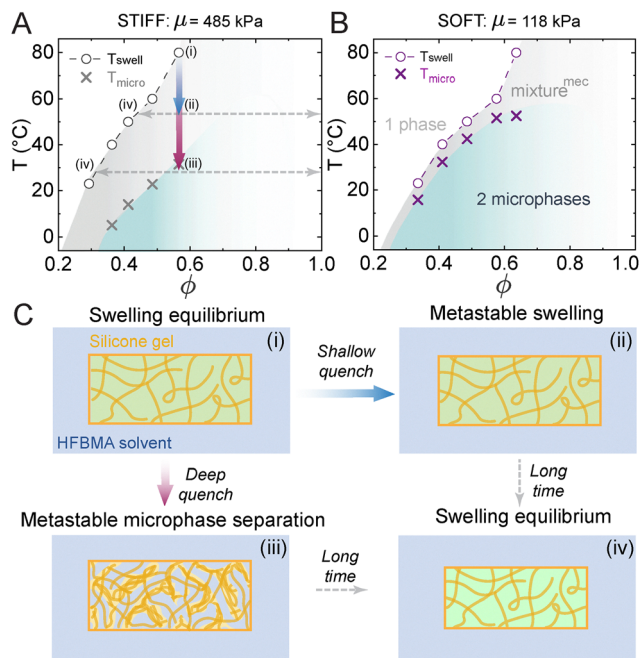


Fig. 3 EMPS of HFBMA solvent in silicone polymer matrices. Experimental phase diagrams of the HFBMA–PDMS system for (A) 485 kPa (stiff) and (B) 118 kPa (soft) samples. The boundaries at T_{swell} , T_{micro} are shown by empty circles and \times 's respectively. The gray area shows the part of the phase diagram where the mixture is stabilized mechanically (mixture^{mec}) and the turquoise area where microphase separation is observed (2 microphases). The mixture^{mec} region size increases with μ . (C) Schematics of the different states of the system depending on the temperature: (i) swelling equilibrium, (ii) metastable swelling, (iii) metastable microphase separation, (iv) new swelling equilibrium.

continuous phase transformation when the boundary is crossed. Like a binodal, phase-separated domains dissolve at the same temperature they form.²⁴

Importantly, the size of the gap between the swelling equilibrium and microphase boundaries depends on the stiffness of the unswollen silicone, with the stiffer silicone having a much larger gap than the softer one.²⁴ The gap, or ‘mechanically-stabilized regime’, vanishes as stiffness decreases, and the two phase boundaries merge into one that approaches the LLPS phase boundary in Fig. 2B.

There are two further key differences between the phase diagram for a solvent in an elastic network and the phase diagram for liquid mixtures. First, there are no phase boundaries at high temperature (above the critical point) in liquid mixtures. However, swollen elastic networks always have at least one phase boundary at any temperature – the swelling equilibrium curve. Second, while phase-separated domains in LLPS always coarsen (due to coalescence and Ostwald ripening),^{39,44} this coarsening is completely suppressed in the microphase separation in EMPS.^{23–25}

3.1 Thermodynamics of phase separation in an elastic network

To model these phenomena, we update the free-energy density shown in eqn (1) to include the effects of crosslinking of the

silicone chains into an elastic network. Crosslinking removes the translational entropy of the polymer (*i.e.*, the second term in eqn (1)) as $\nu_p/\nu_s \rightarrow \infty$.[‡] We account for elasticity of the polymer network by simply adding an additional elastic free-energy density f_{el} to f_{FH} .^{26,47,50,62,63} Then, the resulting free-energy density is

$$f_{\text{tot}}(\phi, T) = \phi \log \phi + \chi(\phi, T)\phi(1 - \phi) + f_{\text{el}}(\phi). \quad (3)$$

For comparison with data, we will assume that crosslinking does not alter the form of $\chi(\phi, T)$ (eqn (2)). Here, f_{el} is related to the standard strain-energy density, W_{el} , from elasticity theory, as:

$$f_{\text{el}} = (1 - \phi) \frac{W_{\text{el}}}{k_{\text{B}}T/\nu_s}. \quad (4)$$

Here, the factor of $k_{\text{B}}T/\nu_s$ non-dimensionalizes W_{el} , while the factor of $(1 - \phi)$ converts from a free energy per volume of dry polymer to a free energy per unit volume in the swollen state. In general, W_{el} is a function of the principal stretches in the polymer network: $\lambda_1, \lambda_2, \lambda_3$. For many simple polymer networks,⁶⁴

$$W_{\text{el}} = \bar{W}_{\text{el}}(I_1) - \alpha \mu \log J, \quad (5)$$

where $I_1 = \lambda_1^2 + \lambda_2^2 + \lambda_3^2$ is the mean-squared stretch in the polymer network, $J = \lambda_1\lambda_2\lambda_3$ is the change in volume of the network relative to the dry state, μ is the shear modulus, and α is a positive dimensionless number. The second term on the right-hand side is meant to describe the increased entropy of the crosslinking points during swelling.^{26,65} However, it has been shown to vanish in a careful calculation that averages over the disorder of a crosslinked network.⁶⁶ Thus, we take $\alpha = 0$ (see the supplement for a further discussion). We also assume isotropic swelling, $\lambda_i = (1 - \phi)^{-1/3}$, so that $I_1 = 3(1 - \phi)^{-2/3}$ and $J = (1 - \phi)^{-1}$.

3.2 Characterizing polymer network elasticity

We obtain expressions for $\bar{W}_{\text{el}}(I_1)$ for our polymer networks by performing large extension tensile tests on unswollen samples ($\phi = 0, J = 1$) of the five different types of silicone elastomers used in our EMPS experiments (see Materials and methods). Example plots of engineering stress, σ^{eng} , versus stretch, λ , are shown in Fig. 4 for several different stiffness silicone networks.

At small stretch ($\lambda \lesssim 2$), all the polymer networks can be well-described by classical (non strain-stiffening) neo-Hookean solids (see fits as green dashed lines in Fig. 4), with

$$\bar{W}_{\text{el}}^{\text{nh}}(I_1) = \frac{\mu}{2}(I_1 - 3), \quad (6)$$

where μ is the small-strain shear modulus. For uniaxial tension, the relation between engineering stress and stretch

[‡] Note that some previous works do not remove the translational entropy term, and it qualitatively changes predicted phase behavior.^{48,50,51}



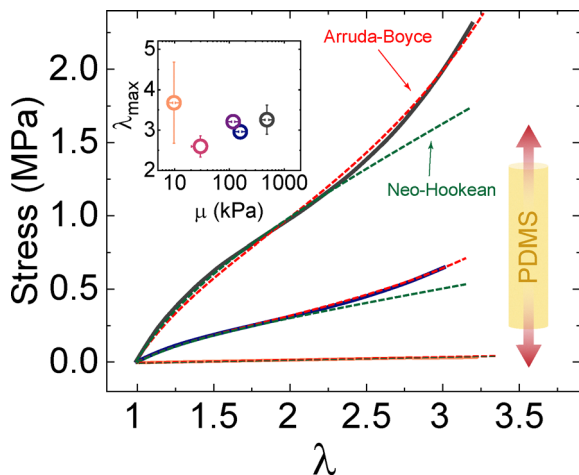


Fig. 4 Mechanical characterization of the silicone polymer networks prior to swelling with the HFMA solvent. Examples of engineering stress versus stretch λ for an incompressible uniaxial extension, with neo-Hookean curves fitted up to $\lambda = 2$ and then Arruda-Boyce curves fit over the whole range of λ . The inset shows the Arruda-Boyce fit parameters for all the materials used here (see Table 1 in Materials and methods). Error bars show standard deviations of the measured values.

is calculated from \tilde{W}_{el} as:⁶⁷

$$\sigma^{\text{eng}} = 2 \left(\lambda - \frac{1}{\lambda^2} \right) \frac{d\tilde{W}_{el}}{dI_1} \Big|_{I_1 = \lambda^2 + 2/\lambda}, \quad (7)$$

where λ is the uniaxial stretch, and we assume that the dry polymer network is incompressible.

For $\lambda > 2$, all our silicone elastomers strain stiffen, diverging from the neo-Hookean model predictions (see fits as green dashed lines in Fig. 4). To capture this behavior, we fit the results with the strain-stiffening Arruda-Boyce model.⁶⁸ This continuum model is based on the physics of the underlying polymer chains, accounting for the limiting stretch of each chain. The Arruda-Boyce model can be approximated by

$$\tilde{W}_{el}^{\text{ab}} = \frac{\mu}{2} \frac{\sum_{i=1}^5 \frac{\alpha_i}{\lambda_m^{2i-2}} (I_1^i - 3^i)}{\sum_{i=1}^5 \frac{i\alpha_i}{\lambda_m^{2i-2}} 3^{i-1}}, \quad (8)$$

where $\alpha_1 = 1/2$, $\alpha_2 = 1/20$, $\alpha_3 = 11/1050$, $\alpha_4 = 19/7000$ and $\alpha_5 = 519/673750$. Again, μ is the small-strain shear modulus, while λ_m is the maximum ‘‘locking’’ stretch of individual polymer chains relative to their end-to-end distance in the as-prepared elastomers. The stress–stretch relationship is again found by inserting the strain-energy density into eqn (7). The resulting fits are shown in Fig. 4 as the red dashed lines, showing a good agreement between the data and the model over the whole range of λ . We extract values of μ and λ_m for five different polymer networks containing different amounts of crosslinker, and obtain values of μ ranging from 10 to ~ 490 kPa and λ_m values ranging from 4 and 3 (see Table 1, Materials and methods), as shown in the inset in Fig. 4. Note that, in uniaxial tension, samples can reach stretches $\lambda > \lambda_m$. This is counterintuitive, but permitted, as individual chains stretch

Table 1 Arruda-Boyce fitted values of the shear modulus μ_{AB} and maximum microscopic polymer elongation $\lambda_{m\mu}$ for pure, unswollen silicone networks as a function of crosslinker density

Crosslinker density (mol%)	μ_{AB} (kPa)	λ_m (—)
12.9	485.3	3.2
10.3	158.4	3.0
7.4	117.7	3.2
6.4	29.8	2.6
5.2	9.8	3.7

significantly less than the applied macroscopic stretch λ applied to a sample. *E.g.*, in the Arruda-Boyce model, individual chain stretch during a uniaxial test is $\sqrt{(\lambda^2 + 2/\lambda)}/3$.⁶⁹ Thus, chain locking (which causes stress divergence) will only occur when this reaches λ_m . *I.e.* for a material with $\lambda_m = 3$, the maximum possible uniaxial sample stretch is $\lambda = 5.2$.

Note that in previous works^{23,24} we characterized the same silicone samples using indentation with a flat punch. Here, we characterize the materials using uniaxial tension testing, as this allows us to probe the large-strain material response, and provides more accurate measurements. We also use μ instead of the Young’s modulus E (which we reported previously), as this is a more natural parameter for working with swollen materials.⁷⁰

With the mechanical fits, we now have expressions for f_{el} that we can use in the total free energy (3). This allows us to compare the predicted phase diagrams for the neo-Hookean and Arruda-Boyce models, and examine the role of strain-stiffening in EMPS.

3.3 Phase separation in a neo-Hookean matrix

We first examine the stability of swollen neo-Hookean networks. This is the simplest hyperelastic model, and does not feature any strain stiffening. To do this, we insert eqn (6) into eqn (4) to obtain

$$f_{el}^{\text{nh}} = 3\bar{\mu}[(1 - \phi)^{1/3} - (1 - \phi)], \quad (9)$$

where $\bar{\mu} = \mu/(2k_B T/v_s)$ is the dimensionless, small-strain shear modulus. The form of $f_{el}^{\text{nh}}(\phi)$ is shown in Fig. 5A. Interestingly, it does not monotonically increase as the network swells. This is because the network volume increases faster than the total stored elastic energy in the system. Thus, the elastic energy density (measured with respect to the current state) decreases at high swelling.

To calculate the phase diagram for EMPS, where we ignore the slow exchange of solvent with the surroundings, we must include $f_{el}^{\text{nh}}(\phi)$ in the free energy, eqn (3) (see full expression in Appendix B). Then, $f_{\text{tot}}(\phi)$ takes the form shown schematically in Fig. 5C, where the curve is convex for small ϕ , and concave for large ϕ (where elasticity dominates). This concave section indicates the presence of phase separation, but there is no stabilizing convexity at large ϕ , which is needed to perform the double-tangent construction. Hence, thermodynamic phase separation between networks at different levels of swelling



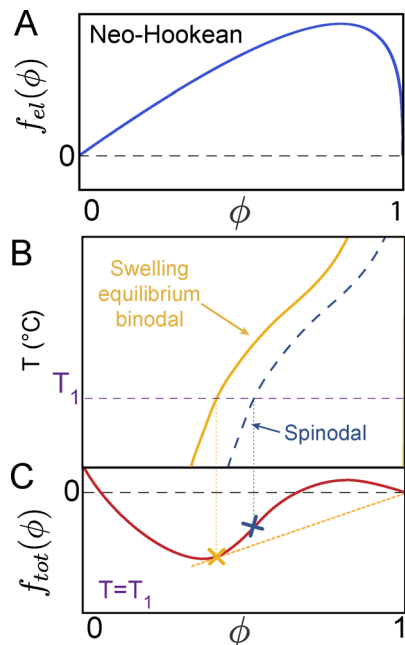


Fig. 5 Effect of neo-Hookean elastic energy on the classical FH free energy of mixing. (A) Schematic of the elastic contribution to the free-energy density for the neo-Hookean model as a function of solvent volume fraction, ϕ . (B) Schematic phase diagram. (C) Schematic of the total energy of mixing for a neo-Hookean system.

(*i.e.* EMPS) is not possible using neo-Hookean elasticity and the measured $\chi(\phi, T)$.

However, there is a macroscopic swelling equilibrium between pure HFMBBA and a swollen network, which occurs at long times. Geometrically, this is found with a single-tangent construction that passes through the point where ($f_{tot} = 0$, $\phi = 1$) (see dotted line in the figure, and derivation in Appendix A). The tangent point (yellow cross) then represents swelling equilibrium in pure solvent, while spinodal decomposition still happens when $\partial^2 f_{tot}/\partial \phi^2 < 0$ (to the right of the blue cross). The resulting schematic form of the phase diagram is shown in Fig. 5B. Note that the swelling equilibrium curve is essentially the same as the predictions of Flory–Rehner theory.²⁶

Overall, the resulting phase diagram does not fully capture the EMPS behavior seen in Fig. 3. While this model is capable of describing the swelling equilibrium boundary (long-time equilibrium at fixed chemical potential, with solvent exchange between the gel and the surroundings) it cannot predict EMPS (short-time phase separation at fixed volume). Note that the spinodal boundary (see dashed boundary in Fig. 5B) cannot explain the onset of EMPS. If phase separation were to occur at the spinodal, the resulting phase-separated domains would only dissolve when heated up to the separate binodal curve. However, when observing EMPS in experiments, we see the formation and dissolution of microphase separated domains at the same temperature.²⁴

3.4 Phase separation in a strain-stiffening matrix

When we introduce strain-stiffening into the elastic network, we obtain a phase diagram (see Fig. 6) which much more

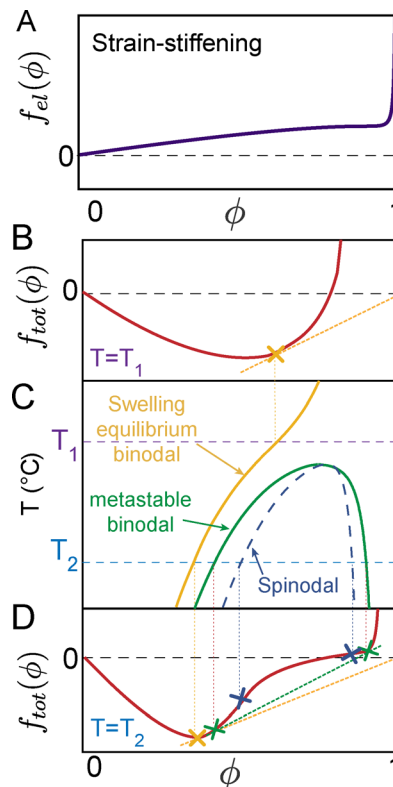


Fig. 6 Effect of strain-stiffening on the classical FH free energy of mixing. (A) Schematic of the free energy for the Arruda–Boyce model. (B) and (D) Schematic of the total free energy of mixing for strain-stiffening at different temperatures, T_1 and T_2 . (C) Schematic of phase diagram that results from (A) and (D).

closely resembles the EMPS phase diagram (Fig. 3A and B). Now, we use the Arruda–Boyce strain-energy density, eqn (8) to obtain the elastic free energy-density, $f_{el}^{ab}(\phi)$:⁷¹

$$f_{el}^{ab} = \bar{\mu}(1 - \phi) \frac{\sum_{i=1}^5 \frac{3^i \alpha_i}{\lambda_m^{2i-2}} ((1 - \phi)^{-2i/3} - 1)}{\sum_{i=1}^5 \frac{i \alpha_i}{\lambda_m^{2i-2}} 3^{i-1}}, \quad (10)$$

where $\bar{\mu} = \mu/(2k_B T/v_s)$, as before.

The typical form of f_{el}^{ab} is shown in Fig. 6A. While the free energy density decreased monotonically in the neo-Hookean case, there is now a divergence in the elastic energy density as the chains reach their locking stretch: $\sqrt{I_1/3} \rightarrow \lambda_m$. This occurs when $\phi \rightarrow (\lambda_m^3 - 1)/\lambda_m^3$.

At high temperature (Fig. 6B), f_{tot} is convex. A single-tangent construction (dashed yellow line) reveals the macroscopic swelling equilibrium of a swollen network with pure solvent (yellow cross). At lower temperatures (Fig. 6D), f_{tot} becomes partially concave. As before, a single-tangent construction yields the macroscopic swelling equilibrium (yellow cross). However, now a double-tangent construction (green dotted line) also reveals the coexistence of two partially-swollen phases (green crosses). These states have a higher energy than the macroscopic swelling equilibrium (the green line is above



the yellow line). Thus, the partially-swollen phases are metastable with respect to deswelling to the macroscopic swelling equilibrium.[§] However, when the system is thermally quenched, the microphase separation into partially-swollen states is kinetically favored, since it can be achieved through rapid exchange of solvent between microscopic domains on a timescale $\tau_{\mu\text{PS}} \approx R^2/D$, where D is a diffusion coefficient and $R \approx \mu\text{m}$ is the characteristic domain size. To reach the macroscopic swelling equilibrium, solvent must be transported across the whole sample, which takes a time $\tau_{\text{ds}} \approx L^2/D$, where $L \approx \text{mm-cm}$ is the sample size. The ratio of timescales $\tau_{\text{ds}}/\tau_{\mu\text{PS}} \sim 10^6\text{--}10^8$ can be enormous, leading to the persistent EMPS phase. Note that such behavior follows Ostwald's step rule by proceeding through phases with successively lower free energies.⁷²

The form of the phase diagram for a swollen strain-stiffening network is shown schematically in Fig. 6C. It displays the essential features of the data in Fig. 3. In particular, we obtain the two phase boundaries, representing where macroscopic swelling equilibrium (yellow curve) and metastable microphase separation (green curve) occur. Thus, strain-stiffening behavior appears to be a key ingredient in capturing the phase behavior of EMPS.

Using this strain-stiffening model of elasticity, we obtain reasonable agreement between calculated phase diagrams and our experimental data, as shown in Fig. 7. There, we have used $\chi(\phi, T)$ from the fit of LLPS of HFBMA and silicone and μ and λ_{B} from the stress-strain curves of neat ($\phi = 0$) silicone elastomers. Thus, there are no fitting parameters specific to EMPS (see the full expression for f_{tot} in Appendix B). There is surprisingly good agreement between theory and experiments for both the macroscopic swelling equilibria, and microphase separation boundaries (Fig. 7). Deviations between predictions and experiments are largest at high stiffnesses. In that limit, however, the predictions still capture essential trends.

Elasticity has different effects on the two phase boundaries in EMPS. We highlight this by separating the predicted macroscopic swelling equilibrium curves and microphase separation curves into two panels (see Fig. 8A and B – yellow curves show LLPS results). The predicted macroscopic swelling equilibrium is quite strongly affected by increasing network stiffness (Fig. 8A): the stiffer the network, the less it swells, especially at higher temperatures. By contrast, the predicted microphase phase boundary is relatively insensitive to changes in network stiffness (Fig. 8B) – leading to an increasing ‘mechanically-stabilized regime’ between the two boundaries as stiffness increases. We note, that there is a small overall movement of this microphase phase boundary to higher temperatures with increasing stiffness.

The elastic properties μ and λ_{m} have different effects on phase equilibria. Results for varying μ at fixed λ_{m} are shown in Fig. 8C and D, and for varying λ_{m} at fixed μ are shown in Fig. 8E

[§] In principle, it is possible for the partially-swollen phases to have a lower energy than the macroscopic swelling equilibrium, so that a gel would spontaneously phase separate into coexisting swollen phases. However, this only occurs for unusual functional forms of $\chi(\phi)$.^{59,60}

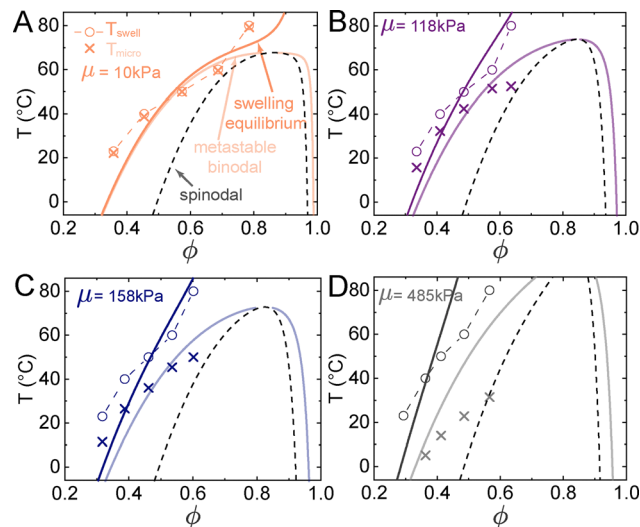


Fig. 7 Experimental phase diagrams fitted with the modified Flory–Huggins theory with strain-stiffening. We used values of (A) $\mu = 10$ kPa and $\lambda_{\text{m}} = 3.7$, (B) $\mu_{\text{m}} = 118$ kPa and $\lambda_{\text{m}} = 3.2$, (C) $\mu = 158$ kPa and $\lambda_{\text{m}} = 3.0$ and (D) $\mu = 485$ kPa and $\lambda_{\text{m}} = 3.2$. Circles and crosses are the experiments and curves are the theoretical swelling equilibrium boundaries (dark color, continuous), microphase-separation binodals (light color, continuous), and spinodal boundaries (black, dashed).

and F. The results show that the polymer network's stiffness has a significantly larger impact than λ_{m} in the position of the swelling equilibrium curve (see Fig. 8C and E), suggesting that macroscopic swelling equilibrium is relatively insensitive to strain-stiffening. On the other hand, the microphase-separation binodals seem to be similarly sensitive to both stiffness and strain-stiffening with a shift towards higher temperatures and slightly lower solvent-rich composition with increasing μ and λ_{m} .

3.5 Structure: channels vs. cavitation

In EMPS experiments, we generally observe the formation of bicontinuous structures at the onset of microphase separation (see Fig. 1B). The domains are swollen polymer networks, with different concentrations of solvent. This bicontinuous structure is stable in stiff networks ($\mu > 200$ kPa). In soft networks, the bicontinuous morphology is unstable, and we observe the nucleation and growth of droplets of pure solvent, embedded in swollen networks.²⁴ The composition of the droplets can be quantified with stimulated Raman spectroscopy (SRS), see Fig. 9A, which shows the presence of holes in the silicone network (see right Fig. 9A), filled in with pure HFBMA solvent (see left image Fig. 9A). The latter state can only occur when the phase separation is able to cavitate the silicone networks – *i.e.* to push open macroscopic, liquid-filled holes in the polymer networks.^{23,37,40,49,73} Our theoretical model can be further extended to capture the onset of this cavitation behavior.

For cavitation to occur, the excess pressure of solvent that fills any microscopic flaws in the material has to reach a critical value $P_{\text{c}} \sim \mu$ (*e.g.* $P_{\text{c}} = 5\mu/2$ for incompressible neo-Hookean elastomers⁷⁴). At this point, the liquid can push open the flaws



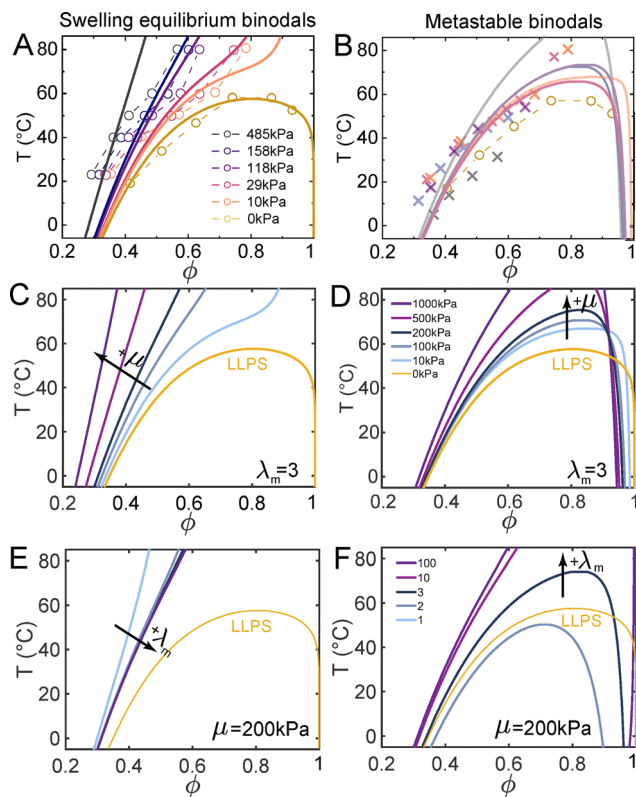


Fig. 8 Effect of network mechanics (λ_m and μ) on the swelling equilibrium and microphase separation boundaries. (A) Experimental swelling equilibrium data (circles) with theory (continuous curves) and (B) experimental measurements of the onset of metastable microphase separation (crosses) with theory (curves). (C)–(F) Theoretical effect of μ and λ_m on phase diagrams. (C) and (D) $\lambda_m = 3$ and μ varies from 10 to 1000 kPa. (E) and (F) Shear modulus is $\mu = 200$ kPa and λ_m varies from 1 to 100. In all figures, yellow circles/curves show the experimental/fitted LLPS phase boundary. Note that for all these calculations, we assume $\alpha = 0$.

without a further increase in pressure.²³ Thus, the criterion for observation of droplets is when the solvent in the EMPS system is in equilibrium with pure solvent in the cavities with an excess pressure, P_c . As shown in Appendix A, this condition can be found graphically with an additional single-tangent construction: cavitation can occur at any concentration, ϕ , when the tangent line to f_{tot} at that concentration (*e.g.* dashed lines, Fig. 9B) meets the right-hand vertical axis above the point [$\phi = 1, f_{tot} = P_c v_s / (k_B T)$]. This last point represents pure solvent at an excess pressure, P_c . For example, in Fig. 9B, we show the three concentrations where the cavitation condition is exactly met (yellow crosses). In this case, cavitation can only occur in the marked ranges in the figure.

With this, we can predict quite accurately when cavitation occurs. Fig. 9C shows observed microphase separated morphologies in our experimental system. We saturate polymer networks in the HFBMA solvent at 60 °C and cool them down, and observe when phase separation/cavitation occurs. For small amounts of cooling there is no phase separation (see green area Fig. 9C). For intermediate cooling, we observe microphase separation with a bicontinuous morphology (see blue area

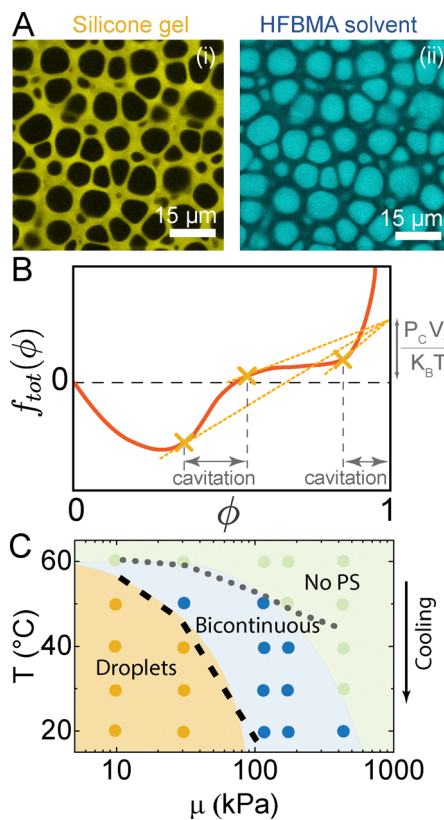


Fig. 9 Cavitation in EMPS. (A) Raman microscopy images of a cavitated samples where droplets of pure solvent are found surrounded by a matrix. (B) Tangent construction for determining the cavitation threshold. (C) Experimental data (dots) compared with theory: dashed lines correspond to cavitation threshold (black dashed line) and microphase phase separation boundary (grey dotted line). In this phase diagram samples have been incubated at 60 °C.

Fig. 9C). For deep cooling, or the softest materials, the bicontinuous morphology abruptly changes to droplets (see orange area Fig. 9C). We next apply the two tangent constructions (see Fig. 6D and 9B) to predict the phase separation boundary (dotted curve in Fig. 9C) and cavitation threshold (dashed curve in Fig. 9C). For the cavitation boundary, we assume that the cavitation threshold in our swollen strain-stiffening material is the same as for an incompressible neo-Hookean network ($P_c = 5\mu/2$). Even with this drastically simplifying assumption we find a remarkably good quantitative agreement between the observed experimental regimes and the predicted ones.

4 Discussion and conclusions

We have demonstrated good agreement between experimental phase diagrams and a simple extension of Flory–Huggins theory, incorporating non-linear elasticity. We have confirmed that strain-stiffening is an essential ingredient for microphase phase separation in elastic matrices. By integrating this with models for elastic cavitation, we can rationalize the selection of bicontinuous and droplet morphologies.



5.4 Uniaxial tensile tests and fitting parameters

To measure the non-linear behavior of the pure, unswollen silicone networks, we prepare cylindrical silicone samples by using Teflon tubes with an internal diameter of 1.5 mm as molds. After pouring the mixture of PDMS chains and cross-linker into the tubes, we transfer them into a 60 °C oven for a week. After fully curing the materials, we carefully peel off the Teflon tubing, and cut the resulting PDMS cylinders into lengths of 5 cm long pieces. We then glue the end of the tubes into rectangular pieces of PDMS of the same stiffness, using a drop of the PDMS mixture as a glue. The rectangular ends enable an easier clamping for the mechanical test. We cure the whole construct over two days at 60 °C.

We next perform uniaxial tests on our samples using a tensile testing machine (stable micro systems), where we record the engineering strain–stress curves until failure. All mechanical tests were performed in air, at room temperature, and at elongation speeds of 0.05 mm per second.

Using the Arruda–Boyce model,⁶⁸ we fit the strain–stress curves for multiple samples with five different crosslinking densities and obtain the fitted values shown in Table 1. Each value reports average results for three replicates – except the samples with 7.4 mol% crosslinker, where two specimens were measured. All values of μ deviated from the mean by less than ~15%, and values of λ_m by less than ~20%.

5.5 Calculating phase diagrams

We use the convex-hull technique described by⁷⁷ to calculate phase diagrams. In brief, this finds concave sections of a free-energy curve by comparing the curve with its convex hull. Example code is given as a supplement to this paper.

Author contributions

Conceptualisation: CF-R, RWS, ERD, formal analysis: CF-R, RWS, SH, SW, PDO, ERD investigation: CF-R, methodology: CF-R, SH, RWS, resources: ERD, software: RWS, SH, supervision: RWS, ERD, validation: SW, PDO, visualisation: CF-R, RWS, writing – original draft: CF-R, RWS, writing – review & editing: CF-R, RWS, PDO, ERD.

Conflicts of interest

There are no conflicts to declare.

Data availability

The data supporting this article have been included as part of the supplementary information (SI). Supplementary information is available. See DOI: <https://doi.org/10.1039/d5sm00594a>.

Data for this article, including data for the mechanical characterization and code to generate phase diagrams are

available at the Figshare repository at <https://doi.org/10.6084/m9.figshare.29153642>.

Appendices

Appendix A: conditions for phase equilibrium

In our experiments, phase separation takes place at constant pressure and temperature, and with the total number of solvent and polymer molecules fixed. Thus, phase equilibrium is found by minimizing the Gibbs free energy, G , of the whole sample. Following Doi,⁵⁴ we can write the Gibbs free energy of a two component, solvent/polymer system as

$$G = PV + \frac{k_B T}{v_s} f(\phi, T) V, \quad (12)$$

where P is the (constant) bulk pressure, V is the volume, and f is the non-dimensional Helmholtz free energy per unit volume – the same as f_{tot} from the manuscript. The key assumption in deriving this result is that the volume of the solvent and polymer do not change upon mixing.

We note that many works assume that phase separation occurs at constant (V, T) instead of constant (P, T) . In the former case, it is appropriate to work with the Helmholtz free energy, F , instead of G (e.g. ref. 47 and 48). To avoid confusion, we note that both approaches are equivalent. In particular, because the solvent and polymer do not change volume upon mixing, V is fixed. Hence, G and F only differ by a constant, PV , and minimizing G to determine phase equilibria gives identical results to minimizing F .

To minimize G , we require that the chemical potentials of solvent, μ^* , in equilibrated phases are the same. The chemical potential is defined as:

$$\mu^* = \left(\frac{\partial G}{\partial N_s} \right)_{V_p, T} = v_s P + k_B T \left(f + (1 - \phi) \frac{\partial f}{\partial \phi} \right), \quad (13)$$

where we have used that $V = v_s N_s + V_p$, and $\phi = v_s N_s / V$, where N_s is the number of solvent molecules in the system, and V_p is the volume of polymer.

Minimizing G also requires the exchange chemical potential, μ_{ex}^* , to be the same in any phases that contain polymer.⁷⁸ μ_{ex}^* is the energy change caused by adding a solvent molecule, and removing the same volume of polymer from a phase:

$$\mu_{\text{ex}}^* = \left(\frac{\partial G}{\partial N_s} \right)_{V, T} = k_B T \frac{\partial f}{\partial \phi}. \quad (14)$$

Phase equilibrium in LLPS and EMPS. In both LLPS and EMPS, we obtain two separate phases that contain solvent and polymer. Thus, both μ^* and μ_{ex}^* must take the same value in the two phases. Having the same value of μ_{ex}^* means that the two equilibrium phases (ϕ_1, ϕ_2) must be at points with the same



tangent slope: $\left. \frac{\partial f}{\partial \phi} \right|_{\phi_1} = \left. \frac{\partial f}{\partial \phi} \right|_{\phi_2}$. Enforcing equivalency of μ^* in the two phases then yields that

$$\frac{f(\phi_2) - f(\phi_1)}{\phi_2 - \phi_1} = \left. \frac{\partial f}{\partial \phi} \right|_{\phi_1}. \quad (15)$$

Geometrically, these conditions are then satisfied by the double tangent construction.

Equilibrium gel swelling. When a polymer network is in equilibrium with pure solvent, we can no longer exchange polymer between the two phases. So we lose the requirement of having the same μ_{ex}^* in the two phases. Instead we only require that the chemical potential of pure solvent, at a pressure P : *i.e.* $\mu_s^* = P\nu_s$ is equal to the chemical potential of the solvent in the swollen polymer network. This gives that

$$f + (1 - \phi) \frac{\partial f}{\partial \phi} = 0. \quad (16)$$

This condition is satisfied by a single-tangent construction with a tangent line that passes through the point $(\phi = 1, f = 0)$.

Note that, in the literature, equilibrium gel swelling is often calculated by considering equilibrium of a system consisting of just the swollen polymer gel phase. There, the gel is assumed to be in equilibrium with a bath of solvent at fixed chemical potential μ_s^* (*e.g.* ref. 63). This approach is entirely consistent with our derivation above. We see this by minimizing the relevant free energy for a gel at constant (P, T, μ^*) : $\Omega^* = G - \mu^* N_s$. Taking $\partial \Omega^* / \partial N_s = 0$ and setting $\mu^* = P\nu_s$ yields eqn (16).

The onset of cavitation. Finally, to find the onset of cavitation in a swollen gel, we use the condition for equilibrium between a swollen polymer network and an embedded droplet containing pure solvent with excess pressure ΔP (*i.e.* with total pressure $P + \Delta P$). In this case, we again only require equality of μ^* between the two phases. The chemical potential of the solvent is $\mu_s^* = P\nu_s + \Delta P\nu_s$. Thus, the droplet and swollen polymer network are in equilibrium when

$$f + (1 - \phi) \frac{\partial f}{\partial \phi} = \frac{\nu_s \Delta P}{k_B T}. \quad (17)$$

For cavitation to occur, the excess pressure in the droplet must exceed the critical pressure: $\Delta P > P_c$. Thus the cavitation condition is

$$f + (1 - \phi) \frac{\partial f}{\partial \phi} > \frac{\nu_s P_c}{k_B T}. \quad (18)$$

This is satisfied when a tangent to the f curve meets the vertical axis at the right side of the phase diagram ($\phi = 1$) above the point $(\phi = 1, f = \nu_s P_c / k_B T)$.

Appendix B: full expressions for EMPS free energies

The total dimensionless free-energy density in a swollen neo-Hookean gel is

$$\begin{aligned} f_{\text{tot}}(\phi, T) &= \phi \log \phi + \left[A + \frac{B}{T} + C\phi \right] \phi(1 - \phi) \\ &+ 3\bar{\mu} \left[(1 - \phi)^{1/3} - (1 - \phi) \right] \\ &+ 2\alpha\bar{\mu}(1 - \phi) \log(1 - \phi). \end{aligned} \quad (19)$$

The total dimensionless free-energy density in a swollen Arruda-Boyce gel is

$$\begin{aligned} f_{\text{tot}}(\phi, T) &= \phi \log \phi + \left[A + \frac{B}{T} + C\phi \right] \phi(1 - \phi) \\ &+ \bar{\mu}(1 - \phi) \frac{\sum_{i=1}^5 \frac{3^i \alpha_i}{\lambda_m^{2i-2}} ((1 - \phi)^{-2i/3} - 1)}{\sum_{i=1}^5 \frac{i \alpha_i}{\lambda_m^{2i-2}} 3^{i-1}} \\ &+ 2\alpha\bar{\mu}(1 - \phi) \log(1 - \phi). \end{aligned} \quad (20)$$

All constants are given in the main text.

Note, that the translational entropy term in Flory-Huggins theory ($(\nu_s \nu_p)(1 - \phi) \log(1 - \phi)$) does not appear in these expressions. This term is generally assumed to disappear in a polymer gel, where $\nu_s / \nu_p \rightarrow \infty$. However, the last term in f_{tot} has the same $(1 - \phi) \log(1 - \phi)$ form, but a different prefactor – now arising from the elastic energy of the gel. The presence of this latter term (if $\alpha \neq 0$, despite calculations suggesting that it vanishes⁶⁶) may partially justify the argument of some previous works that a free energy term that resembles the standard translational entropy term should be maintained in modeling gel behavior.^{42,48,50}

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