# Supplementary Information for "Elastic ripening and inhibition of liquid-liquid phase separation"

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# I. GEL MECHANICAL PROPERTIES

Shear rheology for soft (around 2 kPa) samples show that the Gelest gel is a true solid, visible as a plateau in G' as  $\omega$  approaches zero (Figure S1). Stiff Gelest samples (around 800 kPa) were subjected to repeated elongational stretching to test for yield. On a stress vs. strain curve it is clear that relaxing samples return along the same curve as strained samples (Figure S2). This shows that even up to large strains of 45 percent, these gels remain elastic.



FIG. S1. Gelest gels are true solids, as shown by a finite value of G' as frequency  $\rightarrow 0$ . Rheology of soft Gelest samples, of Young modulus around 2kPa. G' shown in blue squares, G" in red triangles.

## II. MEASUREMENT OF $\phi_{sat}$

We made samples of silicone in petri dishes and measured the exact weight of silicone in each (approximately 3g). We then poured fluorinated oil into the petri dishes to cover the silicone, and incubated them at fixed temperature until the silicone fully saturated. After incubation, we quickly removed the covering fluorinated oil from the samples, and measured the increase in the mass with a microbalance. This extra mass corresponds to the dissolved fluorinated oil. We calculate the saturation volume fraction,  $\phi_{sat}$  as the volume of dissolved fluorinated oil divided by the sum of dry volume of the silicone and the volume of dissolved fluorinated oil.



FIG. S2. Gelest gels remain elastic after large deformations. Stiff gels of Young modulus around 800 kPa were stretched repeatedly to increasingly large strains (left panel). The measured stress during relaxation follows the stress curve of during strain (right panel). Color codes in the two panels correspond.

We measured the solubility of fluorinated oil using the procedure described above at the same temperature,  $40^{\circ}C$ , of 4 different stiffnesses: 13 kPa, 65 kPa, 290 kPa and 700 kPa (Figure S3). The solubility is independent on the stiffness.



FIG. S3. The saturation volume fraction of fluorinated oil in silicone gels of four different stiffnesses at  $40^{\circ}C$ .

We previously measured the solubility of fluorinated oil in silicone gels using the same procedure at various temperatures, between 23°C and 55°C (see [1]). Here we recalculate the volume fraction as the volume of dissolved fluorinated oil, divided by the total volume of the sample. In this range, the saturation is not dependent on the Young modulus of the gel, within experimental uncertainty. The saturation fraction increases linearly with temperature, with the line of best fit given by the relation,  $\phi_{sat}$  [%] = 0.0467*T*[°C] + 1.728. This is shown in Figure S4.



FIG. S4. The saturation volume fraction of fluorinated oil in silicone gels of two different stiffnesses, as volume percentage. The saturation is a function of temperature but does not depend on the stiffness. Blue/red points correspond to soft/stiff silicone gels respectively. The black line is the line of best fit through all six points.

## III. QUENCH RATE DEPENDENCE OF NUCLEATION TEMPERATURE

Samples with the same same stiffness (680 kPa) were cooled down at  $0.05^{\circ}$ C/min,  $0.2^{\circ}$ C/min,  $1^{\circ}$ C/min and  $5^{\circ}$ C/min. At quench rates below  $1^{\circ}$ C/min, the nucleation temperature has no significant dependence on the quench rate (Figure S5).



FIG. S5. The nucleation temperature of samples with the same stiffnesss (680 kPa) and different quench rates.

Indentation experiments were performed on a typical side-by-side gel to measure the elastic moduli profile across a gradient (Figure S6). A 2mm diameter cylinder was indented into the sample at different positions across the surface. The soft side is consistently 22 kPa far from the interface, while the stiff side is consistently around 700 kPa far from the interface, and towards the interface the measured modulus starts reaching a middle point. The spatial resolution is limited by the size of the indentation probe. For each distance away from the interface, indentation measurements were taken at two separate points, show here as separate data points.



FIG. S6. Elastic modulus of gradient sample across the interface.

#### V. POLYDISPERSE DROPLET SIZES

Figure S7 shows an estimated size distribution of the droplets in the sample shown in Figure 2d. For a total of 60 droplets, this bimodal distribution indicates there are two peaks of droplet radius: one around  $9.5\mu m$  and one at  $12\mu m$ . Supplemental Movie 4 shows that these sizes are stable for at least 170 min.



FIG. S7. Kernel density estimation of the size distribution from 60 droplets, showing a bimodal distribution.

# VI. CHEMICAL POTENTIAL BEYOND THE DILUTE LIMIT

Following Flory-Rehner theory, the free energy,  $\Delta G$ , for mixing a partially crosslinked polymer gel with a solvent is:

$$\frac{\Delta G}{k_B T} = N_s \ln \phi + N_{el} \ln(\phi_{el}) + N_c \ln(\phi_c) + N_s (1-\phi)\chi + \frac{\Delta G_{el}}{k_B T}$$
(1)

Here  $\phi$ ,  $\phi_{el}$  and  $\phi_c$  are the volume fractions of solvent, crosslinked polymer network, and uncrosslinked polymer chains respectively.  $N_s$ ,  $N_{el}$  and  $N_c$  are the number of molecules of solvent, elastic network, and free chains respectively.  $\chi$  is the interaction parameter, T is temperature, and  $k_B$  is Boltzmann's constant. In our system, the solvent is the fluorinated oil, and the polymer is the silicone gel.

We notice that the solubility of fluorinated oil is effectively independent of the network elasticity (Figure S3). Thus  $\Delta G_{el}$  must be small in comparison to the other terms in equation (1) and can be neglected.

Furthermore,  $N_s \gg N_{el}, N_c$ , so the second and third terms in equation (1) are small in comparison to the first term, and can also be neglected. We see this because the polymer network only consists of one molecule, so that  $N_{el} = 1 \ll N_s$ . For the polymer chains, a very conservative estimate gives that  $N_c \leq 0.15N_s$ . We obtain this by using the fact that

$$\frac{N_s}{N_c} = \frac{\phi}{\phi_c} \frac{\Omega_c}{\Omega_s},\tag{2}$$

where  $\Omega_s = 3.7 \times 10^{-28} \text{m}^3$  is the volume of a solvent molecule, and  $\Omega_c = 4.8 \times 10^{-26} \text{m}^3$  is the volume of an uncrosslinked polymer chain. We approximate  $\phi \sim 3\%$  (see Figure S4), and note that  $\phi_c \leq 60\%$  for the silicone gels used here [2].

With these approximations, the free energy change upon mixing reduces to

$$\frac{\Delta G}{k_B T} \approx N_s \ln \phi + N_s \chi (1 - \phi). \tag{3}$$

If  $V_s$  and  $V_p$  are the volume of solute and polymer, respectively:

$$\phi = \frac{V_s}{V_p + V_s} = \frac{N_s \Omega_s}{V_p + N_s \Omega_s}.$$
 (4)

The chemical potential,  $\mu$ , is then defined as

$$\mu = \frac{\partial G}{\partial N_s} = k_B T (\ln \phi + \chi (1 - \phi)^2 + (1 - \phi)).$$
 (5)

For a fully saturated gel in equilibrium with a bath of solvent,  $\mu = 0$ . Thus from Equation 7:

$$\chi = -\frac{(1 - \phi_{sat} + \ln \phi_{sat})}{(1 - \phi_{sat})^2}.$$
 (6)

The chemical potential of solvent inside a droplet at pressure P is

$$\mu = \frac{PM}{\rho N_A},\tag{7}$$

where M and  $\rho$  are the molar mass and the solute density respectively, and  $N_A$  is Avogadro's number.

Thus, combining Equation 9 with Equation 7, we find an expression for the volume fraction of solvent that, at equilibrium, would be dissolved in the gel network surrounding a droplet at pressure P:

$$P = \frac{\rho R_g T}{M} (\ln \phi + \chi (1 - \phi)^2 + (1 - \phi)), \qquad (8)$$

where  $R_g = k_B N_A$  is the gas constant and T is the temperature in Kelvin.

Combining Equation 8 and Equation 10, we obtain

$$P = \frac{\rho R_g T}{M} \times \left( \ln \phi - \frac{(1-\phi)^2}{(1-\phi_{sat})^2} (1-\phi_{sat} + \ln \phi_{sat}) + (1-\phi) \right).$$
(9)

This is used to plot  $\phi_{cond}$  as a function of E, as plotted in Figure 1D. To do this, we replace P with 5E/6, and solve for  $\phi = \phi_{cond}$ .

# VII. MEASUREMENT OF SOLUTE DIFFUSION COEFFICIENT

Silicone gels of three different stiffnesses were prepared in 50mm diameter glass-bottom petri-dishes (MatTek). The initial mass of these gels were recorded. A pool of fluorinated oil was deposited on top, which diffused in over time. Over the course of 10 hours, periodically the excess fluorinated oil was poured off and at each time point the mass of the oil dissolved in the gel was recorded.

We used Fick's law to calculate the time-dependent concentration profile of oil, c(z,t) (weight by volume). Since the width of the sample is much bigger than the thickness, we use a one dimensional model. The top of the gel is in contact with the pool at z = 0, and assumed to be at the equilibrium saturation concentration,  $c = c_{eq}$ . The bottom of the gel, which is touching the dish, is taken to be as infinitely far away and at zero concentration. With these boundary conditions, the concentration is:

$$c(z,t) = c_{eq} \operatorname{erfc}\left(\frac{z}{2(Dt)^{1/2}}\right).$$
(10)

Here, erfc is the complementary error function, and D is the diffusion coefficient.

We integrate this concentration over z to find the total mass of oil per unit area, and then multiply by the area of the dish. Thus, for each timepoint, t, the total mass of oil in the sample is:

$$m_{oil}(t) = (2(D\pi)^{1/2} r_{\rm dish}^2 c_{eq}) t^{1/2}$$
(11)

where  $r_{dish}$  is the radius of the petri dish. Data from three different gels is plotted in Figure S8, showing mass of oil in the gel as a function of time. Fitting to Equation 2, we find diffusion coefficients of fluorinated oil in silicone, D, of about  $5 \times 10^{-11} m^2/s$ .



FIG. S8. Calculation of diffusion coefficient, D, for gels of three different stiffnesses: 670kPa, 140kPa and 15 kPa. The dotted black line shows a slope of 1/2.

### VIII. SUPPLEMENTAL IMAGES AND MOVIES

#### A. Movie S1

This bright-field movie shows the soft side of the gradient sample after cooling. The time is shown in the upper-left hand corner, with 0 minutes being the time which droplets on the stiff side stop growing.

#### B. Movie S2

This bright-field movie shows the stiff side of the gradient sample after cooling. The time is shown in the upper-left hand corner, with 0 minutes being the time which droplets on the stiff side stop growing.

# C. Movie S3

This bright-field movie shows the interface of the gradient sample after cooling. The time is shown in the upper-left hand corner, with 0 minutes being the time which droplets on the stiff side stop growing.



FIG. S9. Droplets away from the interface are stable. For the same samples shown in Figure 2b, far field images are shown away from the interface. After cooling, small liquid droplets form on the stiff side (shown here, 4.6mm away from the interface), and larger droplets form on the soft side (shown here, 4mm away from the interface). These droplets are stable throughout the time that the droplets at the interface are changing. For movies, see Movies S1-S3

# D. Movie S4

This bright-field movie shows two droplets of different sizes formed in a homogeneous gel of 80 kPa. Over the period of 170 minutes, there is no observable ripening between the two.

#### E. Movie S5

This movie shows the average droplet profile over time for both experiments and simulations at  $E_{\rm stiff} = 750$  kPa. Other simulation parameters are  $\gamma = 4.4$  nN/m and  $\delta = 40 \ \mu$ m.

## IX. NUMERICAL SIMULATION OF RIPENING

In simulations,  $\delta$  is our only fitting parameter. Fig. S10 shows that changing  $\delta$  affects the onset of the dissolution front, but does not alter its speed at later times. A direct comparison of simulation and experiment is shown for each stiffness difference in Fig. S11. While there is excellent agreement for the large stiffness gradients, the simulations underestimate the timing of the onset for smaller stiffness differences. In Fig. SS12 we compare experiment and simulation while using  $P_C = 5E/6$ .

With a small reduction in the diffusivity, D, this value of  $P_C$  still qualitatively captures the rate of ripening. We also quantified the effect of surface tension by repeating the simulation for 750 kPa without surface tension contributing to the pressure inside the droplet. Fig. S13 shows that the effect of surface tension is negligible compared to elastic ripening.



FIG. S10. Effect of the transition length  $\delta$  at the interface between the two elastic materials. At sharper transitions the dissolution front appears sooner and closer to the interface. Simulations are for  $E_{\rm stiff} = 750$  kPa and  $E_{\rm soft} = 7$  kPa.

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FIG. S11. Comparison of kymographs between experiments and numerical simulations for different Young moduli  $E_{\text{stiff}}$  of the stiff side (values indicated in the panels), using  $P_C = E/2$  and  $D = 5 \ge 10^{-11} m^2/s$ . Additional parameters are  $E_{\text{soft}} = 7$  kPa and  $\delta = 40 \ \mu\text{m}$ .



FIG. S12. Comparison of kymographs between experiments and numerical simulations for different Young moduli  $E_{\text{stiff}}$  of the stiff side (values indicated in the panels), using  $P_C = 5E/6$ ,  $D = 4 \ge 10^{-11} m^2/s$  for the E = 750 kPa sample, and  $D = 5 \ge 10^{-11} m^2/s$  for the others. Additional parameters are  $E_{\text{soft}} = 7$  kPa and  $\delta = 40 \ \mu\text{m}$ .



FIG. S13. Comparison of the experimental profile with numerical data for ripening driven by elasticity only, surface tension only, and by both effects. Additional parameter are  $E_{\rm stiff}=750$  kPa,  $E_{\rm soft}=7$  kPa, and  $\delta=40~\mu{\rm m}.$