SUPPLEMENTARY INFORMATION

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

Carla Fernández-Rico,[1] Robert W. Style,[1] Stefanie Heyden,[2]
Shichen Wang,[3] Peter D. Olmsted,[3] and Eric R. Dufresne[4,5]
[1]*Department of Materials, ETH Zürich, 8093 Zürich, Switzerland.*
[2]*Department of Civil, Environmental and Geomatic Engineering, ETH Zürich, 8093 Zürich, Switzerland.*
[3]*Department of Physics, and Institute for Soft Matter Synthesis and Metrology, Georgetown University, Washington DC, 20057, USA.*
[4]*Department of Materials Science & Engineering, Cornell University, Ithaca, USA*
[5]*Laboratory of Atomic and Solid State Physics, Cornell University, Ithaca, USA*
(Dated: December 1, 2025)

I. FITTING FLORY-HUGGINS THEORY TO THE PHASE DIAGRAM FOR UNCROSSLINKED POLYMER AND SOLVENT

We posit that the liquid-liquid phase separation data (in Figure 2 of the main paper) can be described by Flory-Huggins theory with a chi-parameter given by

$$\chi = \chi_0(T) + C\phi = A + \frac{B}{T} + C\phi. \tag{1}$$

This is inserted into the Flory-Huggins free energy:

$$f_{\mathrm{FH}}(\phi, T) = \phi \log \phi + \nu(1-\phi)\log(1-\phi) + \chi(\phi, T)\phi(1-\phi), \tag{2}$$

where $\nu = \frac{v_s}{v_p}$.

To fit this expression to our data, we start by obtaining a value for C. We do this by noting that the position of the critical point – the topmost point of the phase diagram – only depends on C, while being independent of the other parameters: A and B. Thus, we can directly obtain C from a measurement of the solvent concentration at the critical point, $\phi_c = 0.805$ – which we obtain by fitting a parabola to the data in Figure 2b of the main text. In particular, at the critical point, $\frac{\partial^3 f_{\mathrm{FH}}}{\partial \phi^3} = 0$. With some algebra, this yields that

$$C = \frac{1}{6}\left(\frac{\nu}{(1-\phi_c)^2} - \frac{1}{\phi_c^2}\right). \tag{3}$$

For the values in the main text, we used the value of $\nu = 6.9 \times 10^{-3}$ to obtain that $C = -0.227$.

Once we have determined C, we fit A and B by considering the shape of the experimental data. To do this, we first use the value of C to obtain a phase diagram in terms of ϕ and χ_0 – i.e. we obtain a curve $\chi_0(\phi)$. This is related to the phase boundary in T, ϕ space by

$$T(\phi) = \frac{B}{\chi_0(\phi) - A}. \tag{4}$$

As such, we can then do a least squares fitting of A and B to match the equation above to the experimental data points for $T(\phi)$. In the main text, we use this to obtain that $A = 0.2108$ and $B = 247.76$.

II. TESTING SENSITIVITY OF OUR RESULTS TO VALUES OF A, B, C, ν

The main source of uncertainty in the fitting is the value of ϕ_c, and it is important to address whether errors in this value will alter our conclusions. In fact, ϕ_c can be chosen anywhere in the range $\phi_c = 0.8 \pm 0.5$ (see Figure 2b). Then, following the process described above, we can fit values corresponding of A, B, C. These always produce binodal curves that do a good job of fitting the phase diagram for liquid-liquid phase separation. As an example, if we take $\phi_c = 0.844$, then we obtain $C = -0.1869$, and $A = -0.0661$, $B = 319.89$. The resulting fit is shown as the yellow curve in Figure S1A, and matches well with the experimental data.

Importantly, using different values of A, B, C to fit LLPS data makes very little difference to our conclusions from the main text. Figures S1A,B use the new values of A, B, C. They show, respectively, the resulting calculations of swelling equilibria and metastable binodals when we include strain stiffening elasticity (using measured elastic parameters). The results are essentially the same as those from the main text – despite the values of A, B, C being rather different. There are only small quantitative differences, Thus, the exact choice of how to fit A, B, C does not appear to be too important.

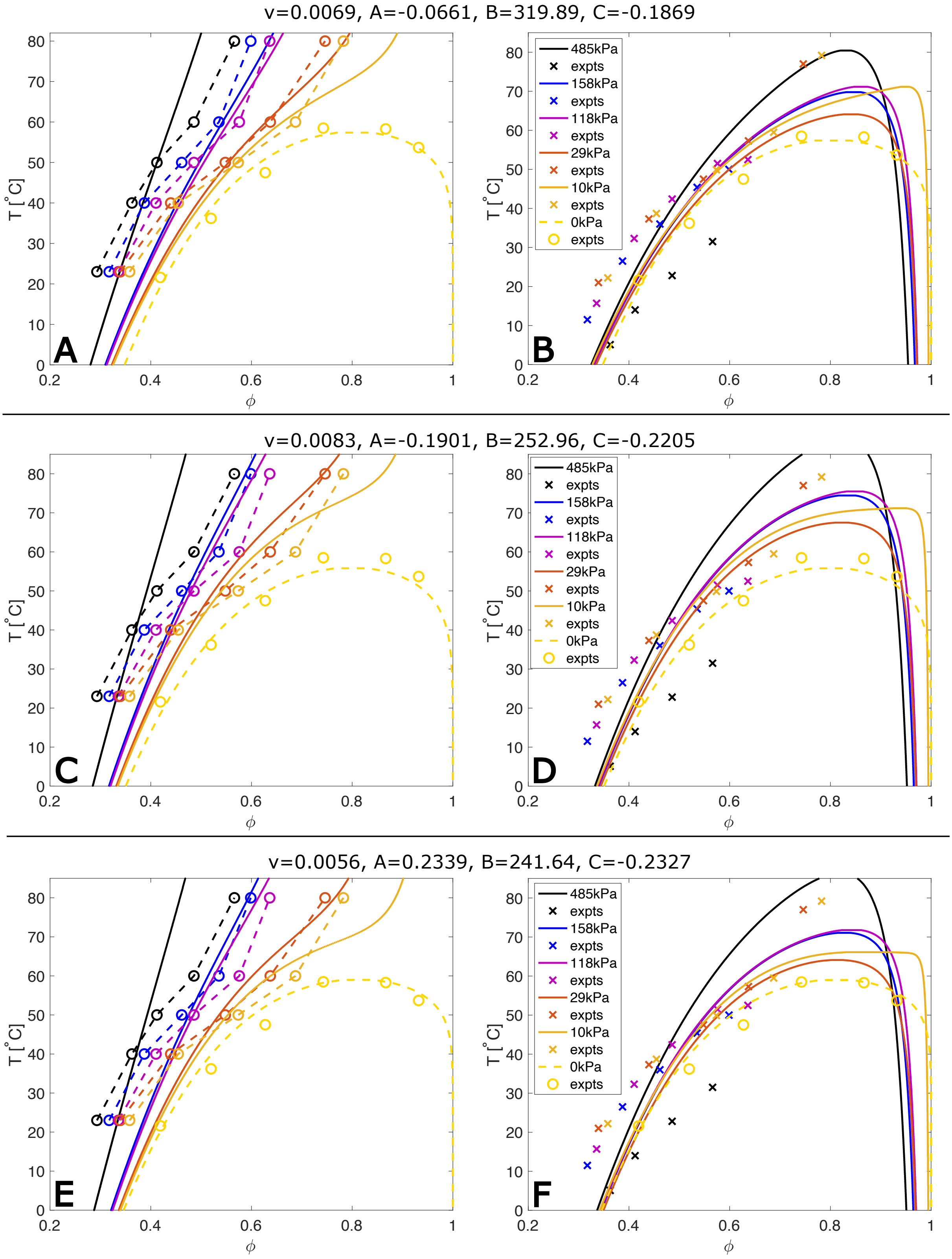

FIG. S1: Demonstration that the results are relatively insensitive to our fitting of LLPS data. The figures show calculations of swelling equilibria (A,C,E) and metastable binodals (B,C,F) for a range of different values of ν, A, B, C to those used in the main text. Here, these parameters are chosen in three different ways to fit the phase diagram for mixtures of uncrosslinked polymer precursor and solvent (see description in the text above). There are only small differences to the resulting phase diagrams. A,B) We keep $\nu = v_s/v_p$ the same as in the main text, but use different values of A, B, C that fit the LLPS data (these give a slightly shifted position of the critical point). C,D) We increase ν relative to the value in the main text and use corresponding best fit values of A, B, C. E,F) The same as in (C,D), but with a decreased value of ν.

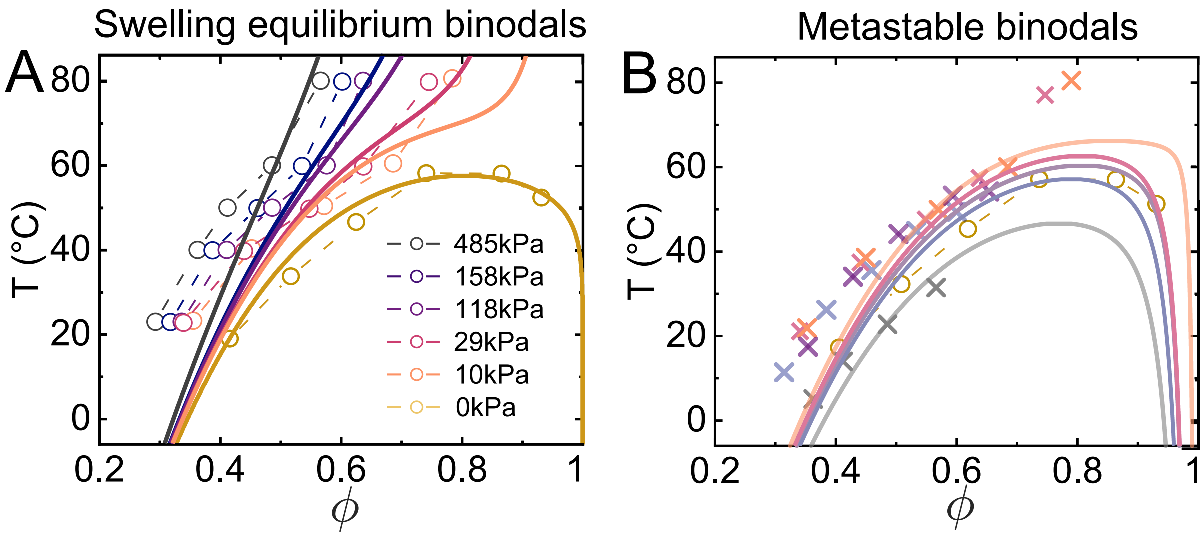

FIG. S2: Predicted phase diagrams when an additional volumetric term, $-\mu \log J$, is included in the elastic strain-energy density. A) Swelling equilibrium and B) binodals for microphase separation. All other parameters are the same as used in Figure 8 of the main text.

We can also address the question of uncertainties in the value of ν. In the paper, we use values of molecular weight, and density (as reported by the manufacturers) to calculate ν. However, we can also check whether our results would be sensitive to this number. We do this by calculating phase diagrams for a larger value: $\nu = 0.0083$ (Figures S1C,D) and a smaller value: $\nu = 0.0056$ (Figures S1E,F). Again, we see that the results do not significantly change. There are small quantitative differences, but the results still show good agreement with our experimental data. Thus, the results do not depend strongly on the precise value of ν.

III. EFFECT OF THE OSMOTIC CONTRIBUTION TO THE ELASTIC ENERGY

In deriving the phase diagrams above we made an important assumption about the dependence of the elastic energy on volume changes, given by $-\mu\alpha \ln J$. In particular, we chose $\alpha = 0$, which follows the phantom-network theory [1], as well as the microscope calculation of Panyukov and Rabin [2]. We revisit this assumption to study how the value of α influences the results.

The value of α is still debated in the literature [3]. The three most commonly-found predictions allow us to state upper and lower bounds (e.g. [4]). Firstly, the phantom-network model of James and Guth [1] predicts that $\alpha = 0$. Secondly, Flory's affine network theory predicts that $0 < \alpha \leq 1$ [3]. If one requires that the elastic network is stress-free in the as-prepared state, then $\alpha = 1$ (this is typically used for the free energy of compressible, neo-Hookean solids). Although the more recent replica calculations of Panyukov and Rabin [2] suggest that averaging over disorder restores the value $\alpha = 0$, we will explore the consequences of a non-zero value below.

We repeat the phase-boundary calculations with $\alpha = 1$ in Figure S2. The swelling equilibrium curves with $\alpha = 0, 1$ are very similar (Figures 8A main text and S2A). However, the microphase-separation binodals are qualitatively different (Figures 8B main text and S2B). Increasing μ now reduces the temperature at which microphase separation occurs (Figure S2B). As a result the prediction of the microphase-separation binodals now agrees better with the stiffest experimental sample.

IV. CONFIRMING THAT NONLINEAR ELASTICITY YIELDS PHASE BEHAVIOR

In the main text, we argue that strain-stiffening is the key factor that yields phase diagrams like that in Figure 6. *i.e.* phase diagrams with separate swelling equilibria and metastable binodals. It is important to rule out that this type of phase diagram arises from other effects. In particular, we must prove that the features of the phase diagram are not a result of our choice of a ϕ-dependent χ. We show this by repeating the calculation with a simple, temperature-dependent form of $\chi(T) = A + B/T$. In this case, we obtain results that are qualitatively the same (Figure S3). Thus, it is not our chosen form of χ that yields the form of the phase diagram, but the inclusion of strain-stiffening.

---

[1] H. M. James and E. Guth, The Journal of Chemical Physics **21**, 1039 (1953).

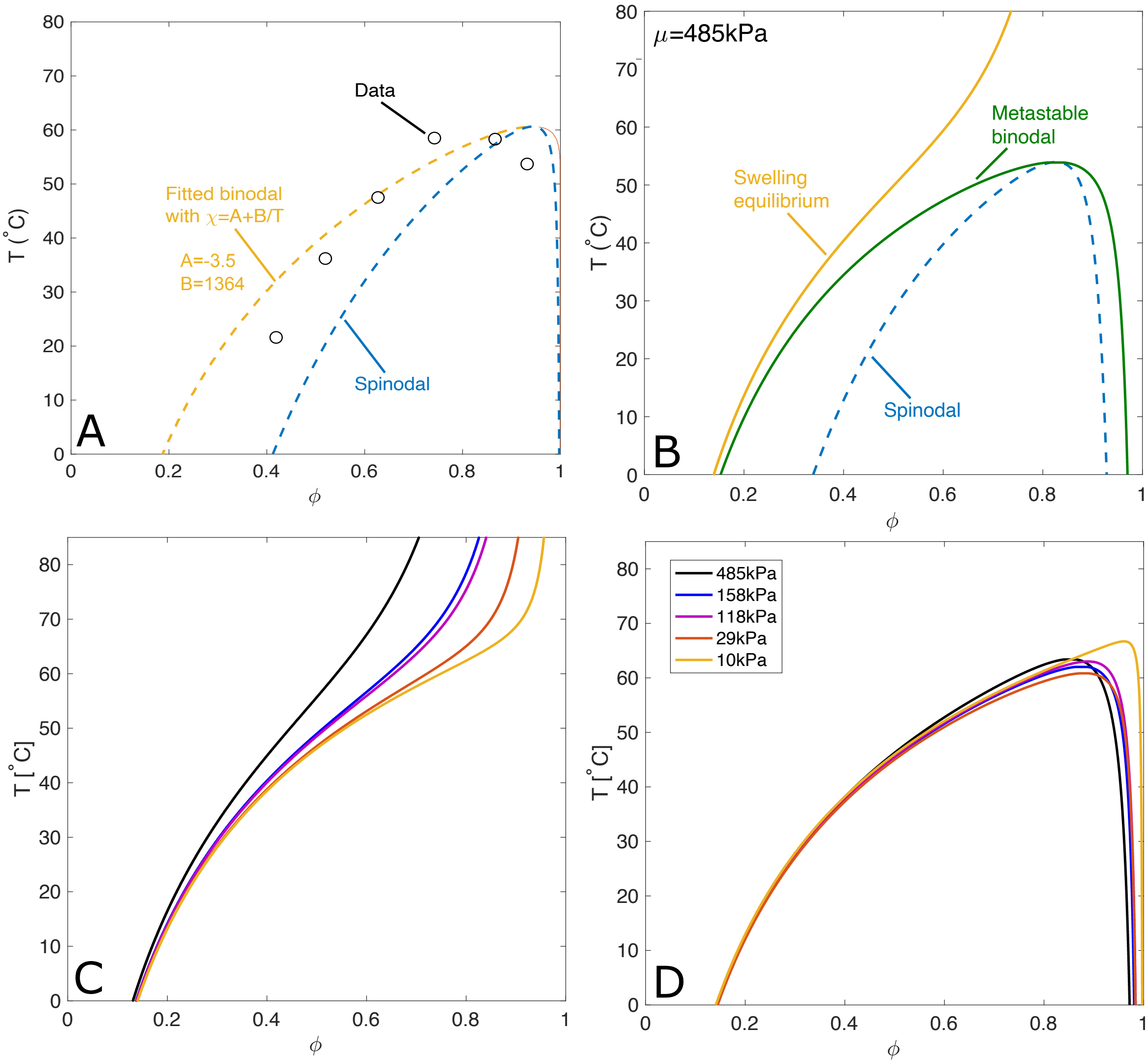

FIG. S3: Phase diagrams derived when we use $\chi = A + B/T$ to fit the LLPS data, instead of $\chi = A + B/T + C\phi$. A) Fitted binodal compared to the LLPS data. B) We use the fitted χ from (A) to calculate the predicted phase diagram for the silicone sample with $\mu = 485$kPa. C) Swelling equilibria for all the different materials in the main text. D) Metastable binodals for all the different materials. For all calculations, $\alpha = 0$, and we use the fitted Arruda-Boyce models from the main text.

[2] S. Panyukov and Y. Rabin, Physics Reports **269**, 1 (1996).
[3] P. J. Flory, Proceedings of the Royal Society of London. A. Mathematical and Physical Sciences **351**, 351 (1976).
[4] K. Binder and H. Frisch, The Journal of chemical physics **81**, 2126 (1984).