Polymer-Solvent Phase Separation and Criticality in the Formation of Porous Polymeric Solids: A Modeling Study

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This manuscript describes a model for simulating the properties of polymer-solvent mixtures and the nonequilibrium processes that lead to their demixing and gel formation. In this model, the description of the system is based on a coarse grained lattice model of the polymer density field whose parameters can be chosen to reflect the microscopic characteristics of specific chemical systems. By using a lattice model, we are able to perform block renormalization and thereby access study the critical behavior of these systems upon demixing. We relate this critical behavior to the hierarchical structure of the resulting extended gel-like polymer network.

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Polymer-solvent phase separation and criticality in the formation of porous polymeric solids: a modeling study

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Abstract

The demixing of a polymer solution can lead to the formation of a porous solid with complex hierarchical structure. In this manuscript, we study the emergence of this structure and how it depends on the molecular scale properties of the polymer-solvent mixture from which it originates. We present a theoretical model of a polymer-solvent mixture that incorporates the effects of solvent fluctuations and intermolecular correlations into the kinetics and thermodynamics of demixing and polymer densification. We use this model to simulate the formation of extended network structure under a variety of different conditions. We apply iterative renormalization of our model to identify scale invariant network structure and demonstrate that sys-

tematic changes in solvent quality can be used to tune between second- and first-order phase separation.

Introduction.

One way to create a self-assembled polymeric solid is to destabilize a polymer-solvent mixture in such a way that polymer chains demix and aggregate to form an extended cross-linked network.¹⁻⁴ Many methods for promoting this destabilization, such as cooling, solvent evaporation, or the addition of co-solvents, leverage the physics of phase separation and can thus produce hierarchical network structures that exhibit scaling signatures similar to that of a multicomponent liquid near criticality.⁵⁻¹⁸ In this manuscript we demonstrate that this similarity can be leveraged to understand the relationship between the macroscopic thermal and structural properties of these polymeric solids and the microscopic interactions of their molecular constituents. We introduce a theoretical model in which a polymer-solvent mixture is described in terms of a time-dependent coarse-grained density field and show that upon phase separation the scale invariant properties of this density field can be computed through iterative renormalization. This general modeling approach can thus be applied to guide material design, for example by identifying optimal conditions for the formation of mechanically stable porous polymer gels.

Self-assembled polymeric solids have been extensively studied due to their desirable material properties and their wide range of potential applications.¹⁻⁴ The mechanical properties of these materials are determined in large part by the details of their network structure. Quantities such as the effective branch functionality of network cross-links, the density of cross-links, and the distribution of void space throughout the polymer network can, in principle, be tuned to control mechanical properties.^{16,19-21} Unfortunately, these network quantities involve collective phenomena, often out of equilibrium, that bridge a wide range of characteristic time and length scales, and are therefore difficult to predict or control.

The range of time and length scales that are necessary to accurately determine mechanical prop-

erties of polymeric solids are difficult to capture with traditional theoretical models. Approaches based on molecular dynamics simulation – even those that utilize efficient coarse-grained force fields – are generally too computationally expensive to fully characterize mechanical properties. At the same time, continuum based approaches lack the chemical specificity needed to model the molecular interactions that determine emergent thermal properties. Theoretical advances that bridge the hierarchy of scales that are inherent to these systems have the potential to reveal molecular design principles that reduce the need for costly and time consuming trial-and-error approaches to material development.

Our approach to bridging this hierarchy is the development of a model that can be adapted to describe systems across arbitrary length scales via iterative renormalization. In the following section we present the theoretical framework for this model, describe our method for simulating phase separation dynamics, and describe a real-space renormalization scheme that can be used to assess its scale invariant properties. Then, in the Results and Discussion section, we study a representative system that exhibits solvent dependent phase separation behavior. We present results showing how the dynamics of phase separation depend on solvent properties, and we apply iterative renormalization to distinguish between first- and second-order transitions and to estimate the value of the critical exponents.

Theoretical Models and Methods

The demixing of a polymer solution to form a polymeric solid is known as a sol-gel transition. Near the sol-gel point in phase-space, a polymer-solvent mixture will tend to exhibit spatial heterogeneity due to large compositional fluctuations of the polymer-solvent mixture. The emergence of this heterogeneity is incompatible with the assumptions that underlie traditional self-consistent field theories,^{22,23} yet it has important thermodynamic consequences that cannot be described with network percolation models.^{18,24,25} Here, we present a model for describing polymer-solvent demixing starting from a finite-element representation of the fluctuating microscopic polymer density

field.^{26,27} In the vicinity of criticality this model can be iteratively renormalized to determine the mesoscale interactions that govern material structure and viscoelastic properties.

We begin by assuming that the system contains a mixture of polymer and solvent with a constant overall density of polymer, given by $\phi_0 = N_{\text{poly}}/V_{\text{sys}}$, where N_{poly} is the average number of polymer segments in a volume, V_{sys} . We assume that gelation proceeds via the demixing-induced formation of polymer-rich domains that are stabilized and enriched by the formation and growth of polymer-poor solvent domains. We represent the state of the system in terms of a coarse-grained polymer density field, $\phi(\mathbf{r})$, which specifies the local polymer density at any position $\mathbf{r}$ within the system. We adopt a framework from the study of binary liquids and express the energy of the system with the Hamiltonian,

$$H = H_\phi + H_v, \quad (1)$$

where H_ϕ describes the microscopic interactions of the polymer solution and H_v describes the demixing interactions associated with the reorganization of polymer around solvent-rich domains. In the following three subsections we first describe a lattice model for H_ϕ , then we incorporate a physical description of polymer phase separation for H_v , and finally we formulate a procedure for performing iterative renormalization of the model.

A Lattice Model for Polymer-Solvent Mixtures.

We decompose the polymer density field into a sum of a slowly varying long-range component, which describes the demixing of polymer-rich and polymer-poor domains, and a rapidly varying short-range component, which describes the sub-nanometer thermal fluctuations. We model the slowly varying component of the density field as a binary lattice gas by partitioning the system into a three-dimensional cubic lattice of microscopic subvolumes that are each assigned a binary occupation number, n_i , indicating the state of the polymer density within that subvolume. Specifically, we assume $n_i = 1$ if site i contains a mixture of solvent and polymer and $n_i = 0$ if the site is demixed and contains mostly solvent. Binary liquid models of polymer solutions date back

to Staverman, Flory, and Huggins in the 1940's.^{9–14} More recent progress has been made to account for microscopic liquid density fluctuations for homogeneous systems lacking intermolecular correlation.^{28,29}

Once the polymer density field is separated into long- and short-range components, it can be expressed as,

$$\phi(\mathbf{r}) = \phi_0 n_i + \delta\phi(\mathbf{r}), \quad (2)$$

where n_i specifies the state of binary lattice in the site that contains position $\mathbf{r}$, and $\delta\phi(\mathbf{r})$ is the rapidly varying component of the local density field. Following the theoretical developments of Lum, Chandler, and Weeks,^{25,30–34} we assume that the long-range density field is governed by nearest-neighbor (Ising-like) interactions and the fluctuations in the short-range density field obey Gaussian statistics. The energy of a given configuration of the density field is expressed in terms of the Hamiltonian,

$$H_\phi = H_L[\{n_k\}] + H_S[\delta\phi(\mathbf{r}); \{n_k\}] + H_{\text{int}}[\{n_k\}, \delta\phi(\mathbf{r})], \quad (3)$$

where H_L and H_S denote the energies of the long- and short-range components of $\phi(\mathbf{r})$, respectively, $\{n_k\}$ specifies the complete set of binary lattice variables for the system, and H_{int} describes the interactions between the long- and short-range components of $\phi(\mathbf{r})$.

The energy of the long-range component of $\phi(\mathbf{r})$ is given by,

$$H_L[\{n_k\}] = -\epsilon \sum_{\langle ij \rangle} n_i n_j - \mu \sum_i n_i, \quad (4)$$

where the first summation indicates a sum over all unique nearest-neighbor pairs of lattice sites, ϵ parameterizes the energetic cost of creating a demixed polymer-solvent interface, and μ tunes the relative chemical potential between polymer-rich and polymer-poor domains. These parameters can be estimated from measurable quantities, such as enthalpies of dilution and heat capacities, for polymer solutions.³⁵ We assume that the mixed and demixed phases are near coexistence, *i.e.*,

$\mu \approx -3\epsilon$ (discussion provided in the Supporting Information). We choose a lattice spacing of the long-range density field, $\ell = 0.2\text{nm}$, to correspond roughly to the correlation length for equilibrium polymer density fluctuations. We confine our analysis to a range of nearest-neighbor interaction strengths, ϵ , below the roughening transition where discretization artifacts manifest in simulations.

The energy of the short-range component of $\phi(\mathbf{r})$ is given by,

$$H_S[\delta\phi(\mathbf{r})] = \frac{k_B T}{2} \int_{\mathbf{r}} \int_{\mathbf{r}'} \delta\phi(\mathbf{r}) \chi^{-1}[\mathbf{r}, \mathbf{r}'] \delta\phi(\mathbf{r}'), \quad (5)$$

where k_B is the Boltzmann constant and $\chi[\mathbf{r}, \mathbf{r}']$ is the density-density correlation function defined as,

$$\chi[\mathbf{r}, \mathbf{r}'] = \langle \delta\phi(\mathbf{r}) \delta\phi(\mathbf{r}') \rangle, \quad (6)$$

which is related to the radial distribution function, $g(r)$, via,

$$\chi[\mathbf{r}, \mathbf{r}'] = \bar{\phi} \delta(\mathbf{r} - \mathbf{r}') + \bar{\phi}^2 [g(|\mathbf{r} - \mathbf{r}'|) - 1], \quad (7)$$

where $\bar{\phi}$ is the concentration of the polymer-rich phase, which can differ from ϕ_0 due to the formation of polymer free domains within the system. Notably, $\chi[\mathbf{r}, \mathbf{r}'] = 0$ when $\mathbf{r}$ and $\mathbf{r}'$ reside within such a polymer free domain. Our approach assumes that the characteristics of $\chi[\mathbf{r}, \mathbf{r}']$ do not change upon phase separation and also do not depend on the value of $\bar{\phi}$. Details of how the spectral function is constrained through the course of renormalization are described in the Supplementary Information.

The function $\chi[\mathbf{r}, \mathbf{r}']$ encodes many of the microscopic properties of a solution that are omitted at the level of mean field theory. This includes the depletion interactions and solvophobic effects that drive molecular aggregation and self-assembly.^{36,37} This correlation function is a central ingredient to many condensed phase theories, for instance in the coherent state field theory of supramolecular polymer physics of Fredrickson and Delany.³⁸ The system-specific details of $\chi[\mathbf{r}, \mathbf{r}']$ can be derived based on theory or experiment, and for this work we assign $\chi[\mathbf{r}, \mathbf{r}']$ based on

x-ray diffraction measurements of polyethylene glycol in water. We view this system as a generic representation of a polymer in good solvent.^{39,40}

At the boundary between polymer-rich and polymer-poor domains the effective strength of polymer-polymer interactions are reduced and directionally unbalanced, with larger adhesive forces originating from the polymer rich side of the boundary. These unbalanced interactions can lead to an adjustment of the interfacial density field that is not captured by H_L and H_S alone.⁴¹ These unbalancing effects are captured in H_{int} following the formalism that has been developed to treat aqueous solvation.³³ Specifically, we define

$$H_{\text{int}}[\{n_k\}, \delta\phi(\mathbf{r})] = \left[\int_{\mathbf{r}} u(\mathbf{r}) \delta\phi(\mathbf{r}) \right] + H_{\text{norm}}[\{n_k\}], \quad (8)$$

where the unbalancing potential, $u(\mathbf{r})$, is defined as

$$u(\mathbf{r}) = -2a\bar{\phi}[\langle n(\mathbf{r}) \rangle - 1]. \quad (9)$$

Here, $n(\mathbf{r})$ denotes the value of the binary density variable that contains the position $\mathbf{r}$ and $\langle \dots \rangle$ indicates an equilibrium average. When computing this average, we truncate the range of polymer-polymer interactions at ℓ and compute a weighted average for the binary field variable, $\langle n_i \rangle = \frac{1}{2}n_i + \frac{1}{12} \sum_j' n_j$, where the primed summation runs over all nearest-neighbor sites of site i . Enthalpies of dilution and heat capacities for polymer solutions vary substantially for different solvents and polymer densities. In this study, we confine our analysis to exothermic polymer dilution and choose $a = 4.2 k_B T / \bar{\phi}$ for the adhesive polymer forces. The final term in Eq. 8 describes the influence of the unbalancing potential on Gaussian density fluctuations and is given by

$$H_{\text{norm}}[\{n_k\}] = \frac{k_B T}{2} \int_{\mathbf{r}} \int_{\mathbf{r}'} \beta u(\mathbf{r}) \chi[\mathbf{r}, \mathbf{r}'; \{n_k\}] \beta u(\mathbf{r}'), \quad (10)$$

where $\beta = 1/k_B T$.

Phase Separation and Solvent Cavities

As the system undergoes demixing and the polymer-rich domains solution become more concentrated, it is expected that the formation of a gel-like polymer network will cause the system to exhibit dynamical properties unlike that of an ordinary binary liquid mixture. For example, the ability of network confined solvent domains to diffuse or undergo changes in size and shape will be constrained by the surrounding gel-like polymer network. These solvent domains act as cavities within the polymer density field that can accommodate the inclusion of pore forming additives or template pore formation upon drying. The physical effects that contribute to stabilizing the formation of solvent cavities and limiting their mobility involve collective polymer-polymer and polymer-solvent interactions that are not native to a simple model of binary phase separation.

We account for these interactions empirically, by introducing cavity particles into our model. These fictitious particles are designed to reside preferentially within the polymer-poor domains and limit the fluctuations of their local environment by excluding the polymer density field from a spherical region of volume v centered at their position (*i.e.*, $\phi(\mathbf{r}) = 0$ for $\mathbf{r} \in v$). The properties of cavity particles, such as their size, relative chemical potential, and mobility related to the dynamics of the gel and to can thus be varied to describe different polymer systems. The properties of these particles also play a significant role in determining the driving conditions for demixing and gelation, which have been observed to depend more sensitively on overall polymer concentration than the specific details of polymer chemistry.⁴²

Cavity particles interact with each other as non-overlapping hard spheres. The set of cavity particles in the system combine to establish an excluded volume field,

$$V_{\text{cav}}(\mathbf{r}) = \begin{cases} 1, & \text{if } \mathbf{r} \text{ resides within the volume of a cavity particle,} \\ 0, & \text{otherwise.} \end{cases} \quad (11)$$

The polymer density is constrained to be zero at all points where $V_{\text{cav}} = 1$. The free energetic cost

associated with this constraint can be expressed in terms of an effective potential,

$$H_v[\{n_k\}, V_{\text{cav}}(\mathbf{r})] = \omega \sum_i n_i v_i , \quad (12)$$

where ω is a demixing energy and $v_i = \int_{\mathbf{r} \in i} V_{\text{cav}}(\mathbf{r}) d\mathbf{r}$ is the overlap of the total excluded volume field with site i . This excluded volume field has both a direct and indirect effect on system energy. Because cavity particles in the system reduce the volume available to polymer, their presence leads to an effective increase in the polymer concentration in the regions where $V_{\text{cav}} = 0$, such that

$$\bar{\phi} = \frac{N_{\text{poly}}}{V_{\text{sys}} - v N_{\text{cav}}} , \quad (13)$$

where N_{cav} denotes the total number of cavity particles in the system. The energy of the system depends on the value of this modified polymer density through both $\chi[\mathbf{r}, \mathbf{r}']$ and $u(\mathbf{r})$.

Integrating over the Gaussian fluctuations of the short-range density field yields an expression for the total energy of the model system,

$$\begin{aligned} H[\{n_k\}, V_{\text{cav}}(\mathbf{r}), c(\mathbf{r})] &= H_L[\{n_k\}] + H_v[\{n_k\}, V_{\text{cav}}(\mathbf{r})] + k_B T \ln \sqrt{|2\pi\chi_V|} \\ &\quad - K \int_{\mathbf{r} \in V_{\text{cav}}} u(\mathbf{r}) \bar{\phi} n(\mathbf{r}) + \frac{k_B T}{2} \int_{\mathbf{r} \in V_{\text{cav}}} \bar{\phi} n(\mathbf{r}) c(\mathbf{r}) , \end{aligned} \quad (14)$$

where the integrals are restricted to regions with $V_{\text{cav}} = 1$, and χ_V abbreviates $\chi[\mathbf{r}, \mathbf{r}']$ within these regions. In this expression, $c(r)$ is an auxiliary field that has the property

$$\int_{\mathbf{r}' \in V_{\text{cav}}} \chi(\mathbf{r}, \mathbf{r}') c(\mathbf{r}') = \bar{\phi} n(\mathbf{r}) , \quad \text{for } \mathbf{r} \in V_{\text{cav}} , \quad (15)$$

with $c(\mathbf{r}) = 0$ for all $r \notin V_{\text{cav}}$. We have abbreviated the spectral function for $n(\mathbf{r}) = n(\mathbf{r}') = 1$ with $\chi(\mathbf{r}, \mathbf{r}')$. In the results below, we truncate the spectral function, $\chi(r > 1) = 0$, and fix $c(\mathbf{r})$ with its average value, $c(\mathbf{r}) = \langle N \rangle_V / \sigma_V$ for $\mathbf{r} \in V_{\text{cav}}$. K parameterizes the effective strength of the unbalancing interaction following the integration over the short-range Gaussian density fluctuations.

We choose the value of $K = 0.5$, which has been shown to reproduce the demixing free energy in lattice systems with nearest-neighbor unbalancing interactions.³³

Figure 1: A schematic illustration of our model and the hierarchical renormalization scheme. Left-hand panel depicts the continuous polymer density field along with the inclusion of a cavity particle (shaded in blue). Middle panel depicts the result of integrating over the short-range Gaussian density field, resulting in a binary lattice of mixed ($n_i = 1$) and demixed ($n_i = 0$) regions. The regions where $V_{\text{cav}} = 1$ are indicated with blue shading. The right-hand panel illustrates the renormalized polymer density field $\tilde{n}_{i'}$ following the block averaging of Eq. 23.

Simulating the Dynamics of Polymer-Solvent Demixing

The ability of a specific polymer-solvent mixture to undergo phase separation and form an extended polymer network is determined by a complex combination of system properties. Flory-Huggins theory is a minimal model for describing this phase separation in ideal binary mixtures.^{11–14} Unlike Flory-Huggins theory, which is a macroscopic equilibrium theory, our model includes the effects of molecular scale fluctuations on the properties of the mixture and therefore provides the capability to simulate the nonequilibrium dynamics of phase separation. This capability can be leveraged to identify system properties that contribute to network formation and the microscopic characteristics of the resulting network structure.

Since the energy of the polymer density field depends on $\bar{\phi}$ (via Eq. 14), its increase can induce the onset of a polymer-solvent phase separation. The point at which phase separation occurs depends on the balance of polymer-polymer, solvent-polymer, and solvent-solvent interactions. The former two interactions, parameterized by the value of ϵ , determine the free energy cost for cre-

ating polymer-solvent domain interfaces, with ‘bad solvents’ corresponding to larger values of ϵ . Solvent-solvent interactions affect the internal energy of the polymer solution (analogous to excluded volume Flory-Huggins type interactions) and thus determine the demixing energy, ω , and the spectra of the solvent density-density correlations.

We simulate system dynamics using a grand canonical Monte Carlo algorithm. In this approach we apply a Metropolis acceptance/rejection criteria to trial moves that involve either (1) a change in state of n_i for a randomly chosen site (*i.e.*, $n_i = 0 \rightarrow n_i = 1$ or $n_i = 1 \rightarrow n_i = 0$), (2) the random insertion/removal of a cavity particle, or (3) the diffusion of a randomly selected cavity particle. As described in more detail within the Supplementary Information, the driving force for demixing can be tuned by varying the excess chemical potential for cavity particles, $\delta\mu_{\text{cav}}$. For practical purposes, we confine our analysis to cases where $\delta\mu_{\text{cav}}/k_B T \gg 0$.

In the results presented below, we simulate phase separation dynamics by first initializing the system in a homogeneous semi-dilute state without any cavity particles. We then evolve the system at a fixed temperature of 300 K while driving the removal of solvent via the addition of cavity particles at a fixed excess chemical potential. In order to avoid roughening transitions and account for long wavelength liquid density fluctuations, we fix the radius of the solvent cavity particles to be $r_v = 2.38 \ell$ and the lattice spacing to be $\ell = 0.2$ nm in accordance with estimates for the surface tension, $\gamma = \frac{\epsilon}{\ell^2}$ and the strength of nearest-neighbor interactions. Notably, r_v and ℓ are large enough to represent Gaussian number fluctuations when the binary field is nonzero in an appreciable solvent volume and small enough to avoid simulating nonphysical phase transitions.^{33,34,43}

In our Monte Carlo algorithm, we alternate performing $t_n = 36$ trial insertion/removal of cavity particles, followed by a single sweep of L^3 trial changes to n_i ’s (L is the length of the simulation cell in units of ℓ), and finally a sweep of N_{cav} trial cavity particle displacements, with a maximum displacement of 0.5ℓ . The self diffusion constant of the complex liquid and the correlation time for density fluctuations set the value of t_n and the distribution of trial displacements. Each coarse simulation cell is split into 4^3 fine resolution cells on which the sub-nanometer Gaussian fluctuations are defined. We equilibrate for 20000 steps and collect run statistics every 1000 steps.

Renormalization of the System Hamiltonian

In the vicinity of a sol-gel critical point, physical quantities such as the cluster size, gel fraction, viscosity, and shear modulus have been observed to exhibit power-law scaling.^{17,18,18,24,25,44} If polymer-solvent demixing and phase inversion bring about critical gelation, then divergent correlation lengths become manifest in the long-range density, excluded volume, and auxiliary fields. The scale invariant structure that is responsible for this scaling can be computed through the iterative renormalization of our model. When spanning network structure is present, this renormalization yields interaction parameters that reveal the connection between microscopic and macroscopic system properties. We formulate a hierarchical renormalization of our classical polymer density field using block transformations, analogous to Kadanoff block spin transformations,²⁸ whereby the system is block-averaged to yield a lattice of sites on a renormalized length scale $\tilde{L} = bL$, where b sets the blocking range of the transformation. While our approach neglects the enthalpy of cross-linking, fluctuations in the binary long-range density field determine the physical equilibrium between mixed and demixed phases of the polymer solution.^{5,45} The complete details of our renormalization scheme are described in the Supplementary Information. For clarity, we summarize this formalism below, and illustrate it in Fig. 1.

We begin by transforming the system Hamiltonian into a form that is more generally renormalizable. Specifically, we approximate Eq. 14 with an effective Hamiltonian,

$$H_{\text{eff}} = \sum_i (-\mu' n_i + \omega' u_i + \alpha' g_i + 3\kappa' x_i) - \sum_{\langle ij \rangle} (\epsilon' n_i n_j - \kappa' u_i n_j), \quad (16)$$

where the first summation is taken over all lattice sites and the second is taken over all nearest-neighbor pairs of lattice sites, and the new lattice variables are defined as, $u_i = n_i v_i$, $g_i = n_i v_i c_i$,

where $c_i = \int_{\mathbf{r} \in i} c(\mathbf{r})$, and $x_i = n_i^2 v_i$. The effective interaction parameters are defined as

$$\mu' = \mu, \quad (17)$$

$$\omega' = \omega - 2Ka\bar{\phi}^2 + k_B T(\ell^3/V_{\text{sys}})\bar{\phi}, \quad (18)$$

$$\alpha' = \bar{\phi}/2, \quad (19)$$

$$\kappa' = \frac{Ka\bar{\phi}^2}{3}, \quad (20)$$

$$\epsilon' = \epsilon. \quad (21)$$

This Hamiltonian can be expressed in more a general form,

$$H^{(0)} = \sum_{y=n,u,g,m,x} \left(\sum_i J_{0,y}^{(0)} y_i + \sum_{\langle ij \rangle} J_{1,y}^{(0)} y_i n_j \right), \quad (22)$$

where $m_i = n_i^2$ and the terms $J_{0,y}^{(0)}$ and $J_{1,y}^{(0)}$ indicate the associated first- and second- interactions parameters, respectively (several of which are equal to zero here). The superscript (0) in Eq. 22 indicates that this is the original, unrenormalized Hamiltonian.

To renormalize this Hamiltonian we divide the system into a cubic array of blocks, each containing $b \times b \times b$ sites. We introduce block variables for each site, defined as,

$$\tilde{n}_{j'} = b^{-d} \sum_{i \in j'} n_i, \quad (23)$$

$$\tilde{v}_{j'} = b^{-d} \sum_{i \in j'} v_i, \quad (24)$$

$$\tilde{c}_{j'} = b^{-d} \sum_{i \in j'} c_i, \quad (25)$$

where primed and unprimed indices indicate sites of the blocked and unblocked lattice, respectively. We sample the statistics of these block variables through a Monte Carlo algorithm, as described in the Supplementary Information.

The action of the monte carlo Renormaliztaion Group (MCRG) on a three-dimensional finite simulation volume rounds off critical singularities and many higher order interactions emerge be-

yond those of the original model.⁴⁶ In order to directly renormalize field configurations generated by Monte Carlo sampling, we define a renormalized Hamiltonian for a given blocking level, η ,

$$H^{(\eta)} = \sum_{y=n,u,g,m,x} \left(\sum_{i'} J_{0,y}^{(\eta)} \tilde{y}_{i'} + \sum_{\langle i' j' \rangle} J_{1,y}^{(\eta)} \tilde{y}_{i'} \tilde{n}_{j'} \right) + \mathcal{O}(\text{higher-order interactions}), \quad (26)$$

defined in terms of the renormalized block variables. We describe the classes of higher-order interactions in the SI. Near criticality, we expect the flow of interaction parameters is approximately linear, therefore we solve for the linear stability matrix using second-order cumulants,

$$J_{\alpha,y}^{(\eta+1)} = J_{\alpha,y}^* + \sum_z T_{yz}^{(\eta)} \delta J_{\alpha,y}^{(\eta)}, \quad (27)$$

where $J_{\alpha,y}^*$ is the critical value of the given interaction parameter, $\delta J_{\alpha,y} = J_{\alpha,y} - J_{\alpha,y}^*$, and T_{yz} is the linear stability matrix.

We identify criticality by analyzing changes in average values of the lattice variables upon repeated renormalizations. Specifically, we evaluate the quantity

$$\Delta^2 = \sum_{y=n,u,g,m,x} \left[\frac{\langle \tilde{y} \rangle^{(\eta)} - \langle \tilde{y} \rangle^{(\eta')}}{\langle \tilde{y} \rangle^{(\eta)}} \right]^2, \quad (28)$$

where η and η' represent renormalized lattices with equivalent numbers of sites, and $\langle \tilde{y} \rangle^{(\eta)}$ denotes the average value of the lattice variable computed at blocking level η .

Results and Discussion

Tuning Demixing Dynamics Through Changes in Solvent

We demonstrate the performance of our model by simulating the dynamics of a polymer-solvent mixture near its critical point. We base our model on an aqueous solution of N-isopropylacrylamide (NIPA). We choose this representative system because under certain conditions it is known to form nanoporous gels that exhibit critical scaling similar to that of a simple binary liquid.^{47,48}

For NIPA gels, the conditions that correspond to critical (reversible) gelation are $\bar{\phi}^* = 0.005$ at 307 K.⁴⁹ We thus initiate dynamics from a dilute homogeneous state, free of cavity particles, with $\bar{\phi} = 0.003$ and $T = 307$ K. The introduction of cavity particles into the system corresponds to the removal of solvent and the concomitant increase in $\bar{\phi}$, possibly pushing the system across the critical point. The equilibrium state of the system, and whether it crosses the critical point, depends on the value of $\delta\mu_{\text{cav}}$ and the parameters that specify the choice of solvent. We quantify demixing in terms of the quantity, $\langle N \rangle_v = \bar{\phi} \sum_i n_i v_i$, which quantifies the total occupation of cavity particles in regions of the system that are not demixed in the long-range density field. Larger values of $\langle N \rangle_v$ indicate conditions for which fluctuations in the long-range density field are too short lived to enable the partition of cavity particles into solvent rich domains.

We explore how changes in solvent can influence system dynamics by fixing the value of $\delta\mu_{\text{cav}}$, and systematically varying the solvent parameters ϵ and ω . We set the excess chemical potential for cavity particles to be $\delta\mu_{\text{cav}} = \mu r_v^3 + \delta\mu_{\text{ext}}$, where μ is the chemical potential per volume element between dilute and concentrated polymer phases and $\delta\mu_{\text{ext}}$ is the external potential used to accelerate demixing, which we set to $\delta\mu_{\text{ext}} = 150 k_B T$.

Fig. 2 shows the results of a series of simulations that are each initialized from a homogeneous state at time $t = 0$ and then allowed to relax under different solvent conditions. For the external chemical potential chosen here, the overall bulk density dynamics are roughly independent of the demixing energy and surface tension, as illustrated in the Supporting Information. We observe that at fixed ω , the qualitative behavior of the system transitions from phase separated states at lower values of ϵ to more homogeneous mixed states at larger values of ϵ . In the phase separated states, cavity particles partition into the solvent rich domains, illustrated in the snapshots in Fig. 2 as cavities dominated by $n = 0$ white spheres, giving rise to values of $\langle N \rangle_v \approx 0$. In the mixed state, values of $\langle N \rangle_v > 0$ indicate that the lack of long-range demixing forces cavity particles into domains where they must explicitly constrain the short-range density field, illustrated in the snapshots in Fig. 2 as cavities with a minimal number of $n = 0$ white spheres.

Notably, at intermediate values of ϵ , phase separation is preceded by a transient increase in

$\langle N \rangle_v$, as cavity particles are introduced into the homogeneous system, followed by a decrease as cavity particles migrate into (and possibly facilitate the formation of) demixed regions of the long-range density field. These results highlight the remarkable sensitivity of the structure and dynamics of near-critical polymer solvent mixtures to changes in solvent properties. This sensitivity has consequences that affect macroscopic network structure. We demonstrate this through iterative renormalization in the following subsection.

Figure 2: The evolution of a polymer-solvent mixture initialized in a homogeneous state with different solvent parameters. Panels on the left-hand side contain plots of the value of $\langle N \rangle_v$, averaged over 10 independent trajectories. The isosurfaces displayed on the right-hand side are computed from a volumetric Gaussian density map of all coarse-grained lattice sites with $v_i > 0$, and white spheres centered at lattice site i correspond to $n_i = 0$. The value of ε that causes a transition from a phase separated (lower ε) to mixed state (higher ε) is different for systems with (a) low demixing energies, (b) intermediate demixing energies, and (c) large demixing energies. The turnover in excluded polymer number for moderate and low surface tensions corresponds to transient dense globules that eventually break apart as is shown in the snapshots (right).

Model Renormalization to Distinguish Between First- and Second-Order Gelation

The gelation of a polymer-solvent mixture can proceed through the nascent stages of a binary phase transition. The characteristic network structure of the resulting gel, and thus its mechanical properties, depend on whether this transition is first- or second-order. The hierarchical renormalization of our model can reveal the emergence of scale invariant network structure and thereby be used to identify the molecular scale interactions that ultimately determine macroscopic network characteristics. Our numerical model is limited to finite system sizes and thus cannot fully capture divergent system properties, however, it does offer physical insight that connects microscopic chemical interactions to mesoscale network structure.

To demonstrate how the renormalization of our model can be used to determine critical properties we have applied this method to the model NIPA system with variable solvent conditions from the previous subsection. We consider the renormalization of systems with a range of different solvents of varying polymer-solvent surface tension, ϵ , and demixing energies, ω . We then classify the sol-gel transition based on whether the model exhibits the scale-invariant signatures of a continuous second-order transition or the non-scale invariant structure of a discontinuous first-order transition. We base this classification on the change in the renormalized system properties following a series of 4 consecutive block renormalization procedures. We quantify this change with the parameter Δ , defined in Eq. 28.

We consider values of Δ computed between $L = 16$ (large) and $L = 8$ (small) lattices with

statistics collected at blocking levels $b = 4$ and $b = 2$, respectively, excluding contributions from the auxiliary field. We associate values of $\Delta \approx 0$ with second-order transitions and $\Delta > 1$ (meaning the change in parameters upon renormalization is on the order of the value of the parameter itself) with first-order transitions. We find that the majority of statistical difference between large and small systems arises from principal plane, diagonal plane, and tetrahedral interactions (see SI for more detail).

Fig. 3 contains the results of our renormalization study of the NIPA systems. We find that as the quality of the solvent decreases from good to bad (*i.e.* polymer-solvent surface tension is increased) the characteristics of gelation crosses through a critical point where gelation switches from a first-order to a second-order processes. We also observe that the value of the critical point depends on the demixing energy of the solvent and that there is a critical point for every demixing energy within the range of solvents we considered. Notably, the approximate location of these critical points are consistent with those that distinguished mixed and demixed state of the microscopic system, as illustrated in Fig. 2.

Figure 3: The relative difference in collective coordinates between large and small lattices, $L = 16$ and $L = 8$, with statistics collected at blocking levels $b = 4$ and $b = 2$, respectively, excluding contributions from the auxiliary field.

We can gain further insight into the results of our renormalization study by analyzing the configurations of the renormalized long-range density field. To do this, we compute the principle components of the unrenormalized density field, $\{n_i\}$. Principal components are computed by performing an orthogonal transformation on a centered data matrix whose rows are the sampled configurations of the unrenormalized density field. The principal component weight vectors provided

by the transformation correspond to linearly uncorrelated combinations of unrenormalized binary site density field variables sorted according to their collective variance across the input configurations.

Figure 4: (a) Distribution of eigenvalues of the principal components of the Ising configurations at various points of the phase diagram. Color-coding corresponds to Δ . (b) Distribution of the projection of the first principal component, p_1 , on the Ising configurations.

The eigenvalue of the n th principle component (PC), λ_n , quantifies the relative contribution to the overall variance in the data of that component in the overall configuration. As illustrated in Fig. 4a, the distribution of eigenvalues are qualitatively different for systems with first- and second-order network structure. We find that the eigenvalues for systems with first-order structure are distributed about smaller values than eigenvalues for systems with second-order structure, indicating that the maximum possible variance in polymer density is significantly enhanced for second-order gelation.

The characteristics of first- and second-order structure can be further distinguished by projecting sampled configurations onto their PCs. Fig. 4b contains a histogram of the first PC, p_1 , for randomly sampled configurations generated for a range of different solvent configurations. We observe that systems with second-order structure project less strongly onto the first PC alone but rather distribute variance to a broader set of uncorrelated features.

The transition between first- and second-order structure that we observe in Fig. 3 is not unique

to the NIPA system, and in the SI we demonstrate similar critical behavior in model simulations of organogels. Sommer *et al.* have observed first-order phase separation for polymers in good solvent (a high concentration of cosolvents that enhance polymer condensation).⁵⁰ This observation matches our finding that at low surface tensions the phase separation of semi-dilute and concentrated polymer phases proceeds through a first-order transition. Phase separation reduces the size of polymer clusters but facilitates pore formation within the network. We find that moderate and large surface tension liquids may lead to scale-invariant gelation with divergent correlation lengths, relaxation times, connectivity size, and viscosity. On the other hand, low surface tension liquids are manifestly first-order. Commensurate mixtures of nonsolvents (bad porogens) with good solvents may help tune macroporosity but also weaken the gel's structural integrity by yielding short disconnected polymer chains in the polymer-rich phase.⁵¹

Critical Scaling.

Critical systems are characterized by critical exponents that parameterize their scale-invariant properties. Good solvents inhibit phase separation whereas bad solvents favor demixing.^{52,53} Classical network theories of polymer gels include solvent effects by diluting the concentration of polymer chains and crosslinks, but lack chemical detail and cannot describe nonequilibrium gelation.^{18,54,55} Our hierarchical renormalization identifies critical concentration fluctuations (excluding critical connectivity fluctuations) for a range of demixing energies, as parameterized by ω , and polymer surface tensions, as parameterized by ϵ .

In order to predict power-law scaling we calculate the action of the renormalization Group on the microscopic interactions such as the chemical potential, demixing energy, and the surface tension through a linear analysis of the stability matrix, $T_{yz}^{(\eta)}$ (see Eq. 27). The leading eigenvalue of the even operators gives the thermal eigenvalue critical exponent, $y = 1/\nu$, where ν describes the divergence of the correlation length near criticality. The second-largest eigenvalue gives the correction-to-scaling exponent, ω .⁴⁶ In Fig. 5 we plot the thermal eigenvalue critical exponents at various collective distances from criticality for increasing rank and different blocking levels,

averaging over 10 initial conditions for lattice size $L = 16$. The results using spectral functions for both water and polyethylene glycol (PEG) are provided in order to elucidate possible differences between hydrogels and organogels.

Figure 5: Critical exponents plotted as a function of the total rank of the stability matrix, T , calculated between blocking levels b and $2b$, with coordinate types added along the horizontal axis. The eigenvalues of T are calculated at each phase point and the leading eigenvalue is averaged at $\Delta = \Delta_c \pm 0.1$. We are using balancing (diagonal scaling) to improve the ill conditioned eigenvalues that are sensitive to roundoff errors in the stability matrix. Points are colored according to Δ_c matching the color scheme of the phase diagram. Standard deviation of the $\Delta_c = 0.1$ exponents is shown with a blue dashed line. The critical exponent of the three dimensional Ising model is $\nu = 0.629$ is illustrated using a horizontal black line.

Best estimates for critical exponents come from coarsened blocking of near equilibrium statistics sampled on large lattices (Fig. 5 (c) and (d) with $\Delta \ll 1$ and all interactions included). Excluded volume and auxiliary interactions bring about transient effects but also shift the leading eigenvalue to approximately $y = 1.59$, showing good agreement with the $d = 3$ Ising model and experimental critical scaling for polymer-solvent solutions with good solvent. The similarity between the critical exponents of our model and those of the $d = 3$ Ising model suggests that our model of a polymer-solvent mixture is contained in the same universality class as the $d = 3$ Ising model. We can see from Fig. 5 that transient effects in the mean thermal eigenvalue critical exponent are weaker (and the phase boundary more stable) for organogels than for hydrogels. The estimated critical exponents should not depend very strongly on the choice of blocking level and therefore a more extensive analysis of linearity in the vicinity of the critical points is needed (including finite-size and truncation effects).

Future work is needed to integrate the dynamical arrest of vitrification with our model of demixing and polymer densification in order to simulate the crossover from polydisperse branched aggregates to spanning clusters that exhibit strain softening and pore-pairing at high pore density.^{5,56–58} Renormalized couplings can possibly be used for calculations of mesoscopic gelation in order to significantly reduce the computational cost associated with simulating mesoscopic self-assembly of polymer gels.

Conclusions.

We have presented the development of a model for simulating the equilibrium properties of polymer-solvent mixtures and their nonequilibrium phase separation dynamics. This model introduces several key features that provide novel theoretical capabilities. These features include a discretized field theory that explicitly accounts for sub-nanometer fluctuations and a scheme for hierarchical renormalization that allows for the study of scale invariant network structure. This model thus provides a framework for investigating the emergent relationship between molecular interactions and macroscopic network structure in gel-forming polymer-solvent mixtures. This model can be extended to study the influence of additives and other external perturbations on the processes that drive demixing and polymer network formation.

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Supplementary Information: Polymer-Solvent Phase Separation and Criticality of Gel-Forming Systems

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Coexistent Dilute and Concentrated Polymer Phases.

For the results presented in this manuscript we have parameterized the model to represent a mixture of polyethylene glycol and water. The parameters of the long-range Ising-like density field are chosen to reflect the characteristics of the demixed solution. We set the nearest-neighbor spacing of the cubic lattice sites to the correlation length for density fluctuations in bulk liquid water, $\ell = 0.21$ nm.¹⁻⁴ In this model, the value of ϵ sets the effective surface tension between demixed phases,

$$\gamma = \frac{\epsilon}{\ell^2} \quad (1)$$

which we treat here as a free parameter.⁵ We assume that the solvent-rich and polymer-rich phases are near coexistence,⁶ *i.e.*, that,

$$\mu = \mu_{\text{coexist}} + \Delta\mu, \quad (2)$$

where $\mu_{\text{coexist}} = -3\epsilon$ for cubic lattice gas and $|\Delta\mu| \ll |\epsilon|$. Coarse-grained simulations of polymer solvent mixtures with both long and short polymer chains can also be used to estimate the chemical potential of coexistent liquid polymer phases.⁷

The internal energy of a homogeneous polymer solution sets the energy scale for unbalancing interactions, ϵ' , where the polymer density differs significantly from its expected value in the bulk semi-dilute phase and⁸⁻¹⁰

$$a = \frac{z\epsilon'}{2\bar{\phi}^2\ell^3} , \quad (3)$$

with $z = 6$ for cubic lattice gas. If we assume that a critical temperature between coexistent semi-dilute and concentrated polymer phases, T_c , exists then the internal energy at room temperature is

$$U = -a\bar{\phi}^2\ell^3 \approx \Delta H_{dilute}(T_c) + \int_{T_c}^{298 \text{ K}} C_p dT . \quad (4)$$

Polymer gelation and polymer melting are known to be exothermic and endothermic, respectively, with the former occurring just above room temperature. Typical enthalpies of dilution and heat capacities for polymer solutions motivate our choice of a model interaction between the chemical potential and nearest-neighbor interaction strength,¹¹ $\mu \approx -3\epsilon$. Having motivated a parameterization similar to models of hydrophobic solvation of small solutes, we fix $a = 4.2 k_B T / \bar{\phi}$ and $K = 0.5$.

Renormalization

The partition function can be discretized by first integrating over $\delta\phi(r)$ with the excluded volume constraint,

$$Z = \sum'_{\{n_i, v_i, c_i\}} e^{-\beta H_{eff}[\{n_i, v_i, c_i\}]} . \quad (5)$$

The constrained summation, $\sum'_{\{n_i, v_i, c_i\}}$, obeys

$$\sum_j \chi_{ij} c_j v_j = \bar{\phi} n_i . \quad (6)$$

The Gaussian renormalization energy, $k_B T \ln \sqrt{2\pi\chi_V}$, is difficult to incorporate into the block transformations of the MCRG, but is small relative to the total energy and can be approximated by a reorganization-like term, $k_B T(\ell^3/V_{\text{sys}})\langle N \rangle_V$, for a concentrated polymer phase where the Ising

field is mostly unity. This condition is satisfied in the domain of critical second-order gelation, so we absorb the Gaussian renormalization energy into the effective reorganization energy,

$$\omega' = \omega - 2Ka\bar{\phi}^2 + k_B T(\ell^3/V_{\text{sys}})\bar{\phi} \ , \quad (7)$$

for the purposes of hierarchical renormalization.

The MCRG directly renormalizes the field configurations through a linearization along the collective coordinates depicted in Fig. 1 along with the potential-like terms described previously.¹²

Figure 1: Classes of collective coordinates in which combinations of Ising, excluded volume, and auxiliary field variables can be grouped.

We have not described an exhaustive list of collective coordinates, but rather the most likely candidates for relevant interactions.

Sampling Equilibrium Polymer Phases.

To simulate the dynamics of the model system, we apply Grand Canonical Monte Carlo sampling to the configurations of the coarse-grained density field and to the cavity particles. Specifically, we evolve the system by performing Monte Carlo moves that either modify the state of the long-range density field, through variations in the n_i variables, or the state of the excluded volume field, $V(\mathbf{r})$, through changes in the number and/or positions of cavity particles in the system.

Phase separation can be described using a complex Langevin equation,^{13–16} but we construct a unified framework of Monte Carlo sampling in order to simulate the phase inversion of N_p polymer segments and N_s solvent molecules in the Grand Canonical ensemble,

$$\begin{aligned} \Xi(\{\mu\}, V_{\text{sys}}, T) &= \\ &= \int V_{\text{cav}} \delta \left[\int d\mathbf{r} (V_{\text{cav}}(\mathbf{r}) - V_{\text{cav}}) \right] e^{\beta \mu_{\text{cav}} N(V_{\text{cav}})} Z[n(\mathbf{r}), V_{\text{cav}}(\mathbf{r}), c(\mathbf{r})] , \end{aligned} \quad (8)$$

having abbreviated the chemical potential energy of the polymer-solvent phase when the total excluded volume and the bulk density are approximately constant,

$$\mu_{\text{cav}} N(V_{\text{cav}}) = \mu_p N_p + \mu_s N_s (1 - V_{\text{cav}}/V_{\text{sys}}) . \quad (9)$$

Inserting a solvent cavity (excluding polymer from a sphere of radius r_V) reduces the volume available to the polymer by $(\frac{4}{3}\pi r_V^3)$ and reduces the solvent number by $(\frac{4}{3}\pi r_V^3 d_s)$. To simulate an effective ensemble where the number of cavities (N_{cav}) fluctuates, we cast the chemical potential energy in terms of the number of solvent cavities, with $\mu_p/\mu_s \ll 1$, and

$$\mu_s N_s = \mu_s d_s \overline{V_{\text{cav}}} . \quad (10)$$

$d_s V_{\text{sys}}$ is the initial number of solvent molecules and

$$\overline{V_{\text{cav}}} = V_{\text{sys}} - \left(\frac{4}{3}\pi r_V^3 \right) N_{\text{cav}} . \quad (11)$$

We absorb the constant shift into Ξ and arrive at the effective partition function

$$\Xi_{eff}(\{\mu\}, V_{sys}, T) = \int V_{cav} \delta \left[\int d\mathbf{r} (V_{cav}(\mathbf{r}) - V_{cav}) \right] \dots e^{\beta(\delta\mu_{cav} N_{cav})} Z[n(\mathbf{r}), V_{cav}(\mathbf{r}), c(\mathbf{r})] , \quad (12)$$

where the effective chemical potential for cavities is

$$\delta\mu_{cav} = \mu' - \mu_s d_s \left(\frac{4}{3} \pi r_V^3 \right) , \quad (13)$$

and μ' is an external potential to accelerate demixing. For practical purposes, we confine our analysis to cases where $\mu' \gg 0$ and choose $\delta\mu_{cav} = \mu r_v^3 + \delta\mu_{ext}$ where $\delta\mu_{ext}$ is the external potential used to accelerate demixing which we set to $\delta\mu_{ext} = 150 k_B T$.

Uncorrelated Percolation through a Porous Medium.

We elucidate the connection between percolation and porosity using a simpler model of site-site uncorrelated percolation in order to bolster the claim that continuous gelation persists when co-solvents and porogens are added to the system. Nonporous gels, such as those synthesized from N-isopropylacrylamide (NIPA), exhibit critical scaling similar to that of a three-dimensional Ising model.^{17,18} Although percolation is not a sufficient condition for gelation,¹⁹ percolation models well estimate critical exponents and site-bond correlated percolation models incorporate rudimentary solvent effects.^{20,21} Porous polymer gels self-assembled with guest-host complexation (e.g. cyclodextrin and adamantane) aggregate in such a way that both microscopic structure and the macroscopic pore size is controlled by chemical crosslinking and solvation but the overall void fraction is primarily a function of the initial polymer concentration.^{22,23}

To evaluate this dependence we consider a simple model of site-site uncorrelated percolation in order to gauge whether or not criticality persists when complex liquids are demixed (i.e. accommodate large excluded volume). Here, demixing is represented using two-dimensional and

three-dimensional square lattices populated with non-overlapping spherical voids in which the site probability is naught. In Fig. 2 we plot percolation statistics for porous two dimensional systems with varying exclusion volumes and void radii. Snapshots of spanning clusters on two-dimensional lattices are identified using a burning algorithm.

Figure 2: (a) The percolation threshold plotted as a function of the site probability, p . Percolation of two dimensional ($L = 48$) porous systems with periodic boundary conditions is averaged over 200 void configurations with 1, 4, and 7 inserted voids shown in blue, green, and red, respectively. A cluster is considered spanning if it spans the diagonal. (b) A snapshot comparison of percolation networks on large ($L = 128$) and small ($L = 32$) two-dimensional lattices that span the diagonal near and far from the critical threshold, $p = 0.63$ and $p = 0.67$, respectively. The total excluded volume is $v/V_{sys} = 0.2$ in all cases and the void radius is $r_v = 4$.

By excluding volume in which the polymer can gel we dampen the self-assembly of spanning clusters that can reach from one end of the simulation volume to the other. We can see from Fig. 2 that a percolation threshold persists (scale invariance when $p = p_c$) for large excluded volumes ($v/V_{sys} \gg 0$) and that the total excluded volume, not the size of the voids, is primarily responsible for the shift in the percolation threshold to larger site probabilities. In both two and three dimensions the percolation threshold scales linearly with the total excluded volume for weak porosity, up until the point that spanning clusters are rare. This site percolation model lacks chemical detail and is inadequate to describe microscopic effects such as the entropic penalty of excluding polymer from a demixed solvent volume. Next, we discuss polymer gelation simulated with our microscopic model in which the demixing energy, polymer surface tension, and density-density correlations are explicit.

Phase Inversion of Organogel Solutions.

The solutions that yield organogels and hydrogels not only differ in their surface tension and demixing energy but also in the sub-nanometer density fluctuations that govern the entropic penalty of polymer exclusion from a solvent domain. We test the densification profiles and equilibrium structure using two spectral data sets, water and polyethylene glycol, in order to simulate hydrogels and organogels.^{24,25} Spatial correlations can also be simulated using the Polymer Reference Site Interaction Model (PRISM).²⁶ We can see from Figs. 3 and 4 that the way in which polymer and solvent phase-separate and polymer densifies is qualitatively insensitive to the choice of density-density correlation function.

Figure 3: The bulk polymer density as a function of time for hydrogel (left) and organogel (right) solutions.

Figure 4: The excluded polymer number statistics as a function of time for organogel solutions.

Critical points of organogelation are identified in Fig. 5 using the collective distance, Δ .

Figure 5: The relative difference in collective coordinates between large and small lattices, $L = 16$ and $L = 8$, with statistics collected at blocking levels $b = 4$ and $b = 2$, respectively, excluding contributions from the auxiliary field.

(a)

(b)

Figure 6: (a) Distribution of eigenvalues of the principal components of the Ising configurations at various points of the phase diagram. Color-coding corresponds to Δ . (b) Distribution of the projection of the first principal component, p_1 , on the Ising configurations.

We can see from Fig. 5 that there exists a domain of potential criticality for large surface tensions for organogels, as was the case for hydrogels. The distributions of PC eigenvalues and first PC projections in Fig. 6a and Fig. 6b show that, although the maximum possible variance is smaller for first-order gelation as was the case for hydrogels, neither first- nor second- order gel structure projects strongly onto the first PC. First-order organogels also exhibit greater variance and reduced first PC weight relative to simulated hydrogel structure.

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