Coarsening of Bicontinuous Microstructures via Surface Diffusion

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Surface diffusion is thought to be the primary transport mechanism for coarsening of bulk nanoporous metals, materials which consist of bicontinuous networks of pores and metallic ligaments. To better understand coarsening dynamics in these materials, we simulate coarsening via surface diffusion of bicontinuous three-dimensional structures using a phase field model. The simulated structures are characterized in terms of topology (genus density), the interfacial shape distribution, and autocorrelations of phase and mean curvature. At nominal volume fractions of 50%-50% and 36%-64%, we observe self-similar evolution of morphology and topology and agreement with the expected power law for dynamic scaling, in which the characteristic length increases over time proportionally to \( t^{1/4} \). To understand the effect of transport mechanism on coarsening dynamics, we compare the surface-diffusion structures to structures undergoing self-similar coarsening via bulk diffusion, which follows a \( t^{1/3} \) power law for dynamic scaling. While we observe the expected difference in the coarsening kinetics, differences in scaled morphology and topology due to coarsening mechanism are found to be surprisingly small. We find that bicontinuous structures coarsened via surface diffusion have slightly lower scaled genus density and slightly more spatially correlated mean curvature at short ranges when compared to structures coarsened via bulk diffusion. These small differences are larger at 36% volume fraction than at 50% volume fraction, indicating that the manner in which the coarsening mechanism affects the morphology depends on the volume fraction.

I. INTRODUCTION

Bulk nanoporous metals fabricated by electrochemical [1] or melt [2] dealloying have garnered significant interest for applications such as catalysis [3], sensing [4], and energy storage [5]. The high ratio of surface area to volume in nanoporous materials enables these applications, but it also provides a large driving force for coarsening [6]: evolution that reduces surface area leading to an increase in the size scale of individual features. Nanoporous materials will therefore coarsen rapidly at elevated temperatures where transport mechanisms such as surface diffusion or bulk diffusion are active [7, 8]. This coarsening may result in performance degradation during operation (such as a reduction in catalytic activity [3]), or it may be controlled via an annealing process to tune scale-dependent mechanical properties [9]. Surface diffusion is typically activated at lower temperatures than bulk diffusion, and therefore it is the most relevant coarsening mechanism for many bulk nanostructured materials.

Despite its importance, coarsening via surface diffusion is not well understood, particularly when compared to coarsening via bulk diffusion. For coarsening via bulk diffusion, an extensive theoretical literature exists for systems of particles (reviewed in Ref. [10]), building upon the seminal work of Lifshitz and Slyozov [11] and Wagner [12] for the limit of low volume fraction. These theories predict particle size distributions that evolve self-similarly. During self-similar evolution resulting from bulk diffusion, the particle size distribution is time-independent when scaled by a characteristic length scale \( L \) that obeys the temporal power law \( L \propto t^{1/3} \) [11]. This power law is expected to apply to any morphology that evolves self-similarly as a result of bulk diffusion [13]. Self-similarly evolving morphologies are important because they represent the late-time limiting morphology for a range of initial states, and are thus more likely to be observed experimentally. Theories of coarsening via bulk diffusion that apply to more complex three-dimensional (3-D) structures (e.g., Ref. [14]) cannot yet predict morphologies that will evolve self-similarly. Instead, simulations have been used to obtain coarsening kinetics and self-similar morphologies of complex 3-D structures [15].

For coarsening via surface diffusion, the power law for self-similar coarsening is \( L \propto t^{1/4} \) [13]. Self-similarity has been reported experimentally in nanoporous gold based on a comparison between structures coarsened at different temperatures [16]. However, comparisons between coarsened and as-dealloyed structures have found changes in scaled morphology [17, 18], which indicate non-self-similar coarsening. Simulations provide a well-controlled way to test whether structures can coarsen self-similarly via surface diffusion. Coarsening via surface diffusion has been simulated extensively in two dimensions (2D) [19–21], but this may not accurately represent the dynamics in three dimensions (3D). The only existing 3-D simulation study examined coarsening of porous nanoparticles [22]. These particles differ from bulk nanoporous materials due to the presence of a curved exterior surface that will drive densification (reduction in the volume of pore phase). In fact, Ref. [22] observed substantial densification as well as coarsening, and thus their
findings (particularly the absence of self-similarity during evolution) may not extend to coarsening of bulk nanoporous materials.

In the present study, we therefore seek to test whether self-similar coarsening via surface diffusion arises in a hypothetical bulk nanoporous material, which we emulate via a large computational domain with periodic boundary conditions. We simulate phase separation and coarsening via surface diffusion and characterize the morphology and topology of the resulting structures. To gain fundamental insight into the effects of coarsening mechanism on morphology, we also compare these results to simulations of coarsening via bulk diffusion.

Diffusion is driven by differences in chemical potential within the structure. These differences in chemical potential result from spatially varying interfacial curvatures, since the curvature and chemical potential are related by the Gibbs-Thomson effect [23]. In coarsening via surface diffusion, diffusional flux is proportional to the surface gradient of mean curvature (assuming interfacial energy is isotropic). The resulting interfacial velocity is proportional to the surface divergence of this flux, the surface Laplacian of mean curvature [24]:

\[ v_n = \alpha \nabla^2 \mathcal{H}, \tag{1} \]

where \( v_n \) is interfacial velocity, \( \mathcal{H} \) is mean curvature, and \( \alpha \) is a constant that depends on the interfacial energy and surface diffusivity. In the dynamics described by Eq. 1, interfaces can only interact with their immediate neighborhood on the surface. This differs from coarsening via bulk diffusion, in which interfaces or particles separated by a matrix phase can still interact with each other through that phase. This difference in dynamics between surface and bulk diffusion is known to substantially affect coarsening kinetics through the difference in power laws for self-similar evolution, \( L \propto t^{1/3} \) for bulk diffusion and \( L \propto t^{1/4} \) for surface diffusion [13]. However, it has not been possible to theoretically determine how the differences in coarsening mechanism affect morphology. Using simulations, Kwon et al. [25] found a significant difference in morphology between structures undergoing self-similar coarsening via bulk diffusion and via nonconserved dynamics (mean curvature flow). Our simulations enable us to determine whether such a difference exists between coarsening via surface diffusion and via bulk diffusion.

To simulate the coarsening of complex structures, we employ phase field models, which represent interfaces implicitly as a region over which one or more field variables smoothly transition. The models we use are based on the Cahn-Hilliard equation, which describes the evolution of a single concentration field that can represent a two-phase system [26, 27]. With constant mobility, the dynamics of the Cahn-Hilliard equation correspond to phase separation followed by coarsening via bulk diffusion [28]. To model coarsening via surface diffusion, we employ the model of Rätz, Ribalta, and Voigt [29], which includes a modification to the classical Cahn-Hilliard chemical potential as well as a concentration-dependent mobility. We describe these phase field models and our simulation and characterization methods in the following section.

II. METHODS

A. Phase field model

To model coarsening via bulk diffusion, we employ the Cahn-Hilliard equation, which can be expressed as the generalized diffusion equation [27]

\[ \frac{\partial \phi}{\partial t} = \nabla \cdot M \nabla \mu, \tag{2} \]

where \( \phi \) is a scaled concentration and \( \mu \) is the chemical potential of \( \phi \). This chemical potential \( \mu \) is the variational derivative with respect to \( \phi \) of the Cahn-Hilliard free energy functional [26]

\[ F[\phi, \nabla \phi] = \int_{\Omega} \left[ f(\phi) + \frac{\epsilon^2}{2} |\nabla \phi|^2 \right] dr, \tag{3} \]

where \( \Omega \) represents the domain, \( \epsilon \) is the gradient energy coefficient, a scalar parameter, and the function \( f(\phi) \) represents the volumetric free energy density of a bulk (i.e., compositionally homogeneous) phase. Evaluating this variational derivative to find \( \mu \) in Eq. 2 results in

\[ \frac{\partial \phi}{\partial t} = \nabla \cdot M \nabla \left[ f'(\phi) - \epsilon^2 \nabla^2 \phi \right]. \tag{4} \]

We additionally specify \( f(\phi) \) to be the double-well potential [30],

\[ f(\phi) = \frac{W}{4} \phi^2 (1 - \phi)^2, \tag{5} \]
where the bulk equilibrium concentrations of the phases are \( \phi^+ = 1 \) and \( \phi^- = 0 \), and the height of the energy barrier between them is set by the parameter \( W \). Our model for coarsening via bulk diffusion thus consists of Eq. 4 with constant mobility \( M \) and the bulk free energy \( f(\phi) \) given by Eq. 5.

Phase field models for surface diffusion typically include a concentration-dependent mobility that must be nonzero within the interface and zero at the bulk equilibrium concentrations of the two phases, \( \phi^+ \) and \( \phi^- \) [19–21, 29, 31]. However, this approach will still allow some slow bulk diffusion if concentrations in the bulk deviate from \( \phi^+ \) and \( \phi^- \) [32–34]. Such deviations in concentration are expected to occur during coarsening due to the Gibbs-Thomson effect, which relates interfacial curvature to chemical potential and thus to concentration [28]. Rätz, Ribalta, and Voigt (RRV) [29] proposed a model that reduces these changes in concentration (and the bulk diffusion that they permit) by modifying the chemical potential with a stabilizing function [29, 35]. The RRV model thus converges to coarsening via surface diffusion (Eq. 1) in the asymptotic limit \( \epsilon \to 0 \) [29, 36].

The form of the RRV model that we implement consists of Eq. 4 with the following modifications [29]: the variationally derived chemical potential is divided by a stabilizing function, \( g(\phi) \propto f(\phi) \), and the mobility is made concentration-dependent, with \( M(\phi) \) proportional to \( f(\phi) \) and \( g(\phi) \). We use \( M(\phi) = g(\phi) = \phi^2 (1 - \phi)^2 \) [32]. The resulting governing equation is

\[
\frac{\partial \phi}{\partial t} = \nabla \cdot M(\phi) \nabla \left( \frac{1}{g(\phi)} \left[ f'(\phi) - \epsilon^2 \nabla^2 \phi \right] \right). \tag{6}
\]

The stabilizing function \( g(\phi) \) eliminates the effect of interfacial curvature on concentration in the bulk due to the Gibbs-Thomson effect, thereby ensuring that \( M(\phi) \) is zero in the bulk. (We consider the effect of \( g(\phi) \) on dynamics in greater detail in the Supplemental Material [37].) Based on asymptotic analysis of Eq. 6 in the limit \( \epsilon \to 0 \), the kinetic coefficient \( \alpha \) in the sharp interface model (Eq. 1) is related to the phase field model parameters by [29]

\[
\alpha = \frac{\epsilon}{(\phi^+ - \phi^-)} \int_{\phi^-}^{\phi^+} \frac{M(\phi)}{\sqrt{2f(\phi)}} d\phi \int_{\phi^-}^{\phi^+} \frac{\gamma}{g(\phi)} d\phi. \tag{7}
\]

where \( \gamma \) is the interfacial energy, which is given by

\[
\gamma = \epsilon \int_{\phi^-}^{\phi^+} \frac{1}{\sqrt{2f(\phi)}} d\phi. \tag{8}
\]

This expression for \( \gamma \) is also valid for the bulk diffusion case.

### B. Simulation parameters and numerical methods

The RRV model (Eq. 6) was used to simulate phase separation and coarsening via surface diffusion. Parameters of the phase field model were \( W = 0.4 \) and \( \epsilon^2 = 0.2 \), which correspond to a sharp interface kinetic coefficient \( \alpha = 1/6 \). Singularity of \( 1/g(\phi) \) was avoided by the addition of a small positive constant, \( \sigma = 10^{-12} \), to the denominator: \( 1/g(\phi) \approx 1/[g(\phi) + \sigma] \).

Simulations were conducted within a cubic domain, \( L_x = L_y = L_z = 1024 \), with periodic boundary conditions. The domain was discretized by a uniform Cartesian grid with \( \Delta x = 1 \), which resulted in 3-5 points through the interface. Equation 6 was solved numerically using the finite difference method. Explicit (forward Euler) timestepping was used with \( \Delta t = 0.04 \). The Laplacian in Eq. 6 was discretized using the standard seven-point stencil, and the term \( \nabla \cdot M(\phi) \nabla \mu \) was approximated by calculating \( M(\phi) \nabla \mu \) on half-points and taking a centered difference to find the divergence \( \nabla \cdot M(\phi) \nabla \mu \) on grid points. Simulations were initialized with random noise, and two average system compositions were examined, \( \langle \phi \rangle = 0.50 \) and \( \langle \phi \rangle = 0.36 \), which correspond to nominal volume fractions of 50%-50% and 36%-64% of the \( \phi = 1 \) and \( \phi = 0 \) phases, respectively.

Simulations of coarsening via bulk diffusion were conducted using Eq. 4 with constant mobility, \( M = 1 \). The timestep of these simulations was \( \Delta t = 0.05 \), and other phase field and numerical parameters were the same as the surface-diffusion case. All simulation parameters are nondimensional.

### C. Characterization methods

After an initial period to allow for phase separation (\( t < 1.6 \times 10^4 \) for surface diffusion and \( t < 10^4 \) for bulk diffusion), structures were extracted from the simulation output and characterized. The length scale of the simulated
structures was quantified by the ratio of domain volume $V$ to total interfacial area $A_T$, $S_V^{-1} = V/A_T$ [8]. This is a natural choice of length scale for coarsening since it is inversely proportional to the total interfacial energy of the system, $\gamma A_T$. Thus, $S_V^{-1}$ will monotonically increase during coarsening, regardless of other morphological changes. Statistics of interfacial curvature, topology, and autocorrelations of phase and curvature were calculated for each structure, and are reported with the appropriate scaling by the characteristic length to evaluate self-similarity of the structures.

1. Interfacial morphology

To accurately determine interfacial curvature, concentration data resulting from the simulation was first post-processed using a level-set based method [38]. The interface of each structure was approximated as a triangular mesh of the $\phi = 0.5$ isosurface. Mean curvature $H$ and Gaussian curvature $K$ were calculated on the simulation grid as described in Ref. [38] and interpolated to the centers of mesh triangles. Surface integrals were discretized using the mesh faces: $\int_S q dA = \sum_i q_i A_i$, where $A_i$ and $q_i$ correspond to the area of the $i$th mesh face and the value of the integrand $q$ at the center of the $i$th mesh face, respectively. Likewise, the total interfacial area was calculated as $A_T = \sum_i A_i$. This method was used to calculate statistics of interfacial morphology, including average mean curvature ($H$), standard deviation of mean curvature $\sigma_H$, and the interfacial shape distribution (ISD). The ISD [39] is a probability density function for the probability of finding a point on the interface with a specific pair of principal curvatures, $(\kappa_1, \kappa_2)$, which are related to $H$ and $K$ by $H = (\kappa_1 + \kappa_2)/2$ and $K = \kappa_1 \kappa_2$. We express the ISD as

$$P(\kappa_1, \kappa_2) = \frac{1}{A_T} \frac{\partial^2 F_A(\kappa_1, \kappa_2)}{\partial \kappa_1 \partial \kappa_2},$$

where $F_A(\kappa_1, \kappa_2)$ is a cumulative area distribution function, defined as the total area within the structure having first and second principal curvatures less than or equal to $\kappa_1$ and $\kappa_2$, respectively. We discretize the ISD in rotated coordinates $x' = (\kappa_1 + \kappa_2)/\sqrt{2}$ and $y' = (\kappa_2 - \kappa_1)/\sqrt{2}$ to avoid having bins that are split by the line $\kappa_1 = \kappa_2$ (since $\kappa_2 > \kappa_1$ by convention, such bins would consist partially of a ‘forbidden’ region of the ISD). Bin sizes for the ISDs are $\Delta x'/S_V = \Delta y'/S_V = 0.125$. The sign convention for mean curvature is such that convex bodies (e.g., spheres) of the $\phi = 1$ phase have positive mean curvature.

2. Topology

Topology of the structures was primarily evaluated in terms of the genus density $g_V$ of the $\phi = 1$ phase, the ratio of genus $g$ to domain volume $V$, $g_V = g/V$. In general, the topology of a phase in 3D can be quantified by the Betti numbers, $\beta_0$, the number of independent particles/regions of phase, $\beta_1$ (equivalent to the genus, $g$), the total number of ‘handles’ if the particles are deformed into spheres with handles, and $\beta_2$, the number of internal voids or cavities enclosed in the phase [40]. The number of independent particles $\beta_0$ was calculated using the LABEL_REGION function in IDL and an algorithm to take into account connections through the periodic boundaries. The genus was evaluated by calculating the Euler characteristic, $\chi$ and applying the Euler-Poincaré formula, $\chi = \beta_0 - \beta_1 + \beta_2$, where $\beta_2 = 0$ as no voids were detected. The Euler characteristic of the interface mesh, $\chi_m$ (twice the Euler characteristic of each phase, $\chi_m = 2\chi$) was calculated with the Euler-Poincaré formula, $\chi_m = N_V - N_E + N_F$, where $N_V$ is the number of vertices, $N_E$ the number of edges, and $N_F$ the number of faces [41]. The formula for the genus is then $g = \beta_0 - \chi_m/2$.

We calculate $g$ as an extensive property of a structure, such that a much larger structure that contains $n$ unit cells will have a genus of $ng$. For $g$ to be an extensive property, we must avoid over-counting topological features that are shared by multiple unit cells. Therefore, we exclude one half of the contributions from edges and vertices on domain faces to $\chi_m$ in the Euler-Poincaré formula [40]. When calculating $\beta_0$, we take advantage of the periodicity of the structures to determine whether regions of the $\phi = 1$ phase are connected to the main bicontinuous region of the $\phi = 1$ phase through domain boundaries. We also exclude the bicontinuous region itself from $\beta_0$, since it is shared between all unit cells. Thus, a periodic bicontinuous structure has $\beta_0 = 0$ when evaluated by our method. Genus density is related to Gaussian curvature $K$ via the Gauss-Bonnet theorem, which is expressed as

$$g_V = -\frac{1}{4\pi V} \int_S K dA$$

for a bicontinuous structure.
3. Autocorrelations

Two-point statistics methods can be used to capture information about the spatial distribution of features in a microstructure, unlike other descriptors that treat each data point as an independent sample. Recent work [42–44] extends on methods that only provide information about the correlation between quantities in the bulk of the microstructure to also include interfacial quantities, such as the mean curvature. Of particular interest is the two-point Pearson correlation function, which quantifies the degree of correlation between two spatial fields and allows identification of both positive and negative correlations. The discretized two-point Pearson correlation is defined as

\[ h[u, u'; q] = \frac{1}{|S[q]|} \frac{1}{\sigma[q] \sigma[q']} \sum_{p \in S} (u[p] - \bar{u}) c[p] \cdot (u'[p + q] - \bar{u}') c[p + q] \]  

(11)

where \( u \) and \( u' \) are local attributes of interest in the microstructure, such as the interfacial curvature; for autocorrelation, \( u = u' \). The symbol \( q \) denotes the vector defining the separation of the two points being correlated, \( p \) is the index of the spatial bins, \( S \) is the entire set of spatial bins, and \(|S[q]|\) is the total number of spatial bins in \( S[q] \). The total number of spatial bins in \( S[q] \) is given by

\[ |S[q]| = \sum_{p \in S} c[p] c[p + q] \]  

(12)

where \( c \) is a mask function, which tracks the voxels that should be included in the statistics calculation. In the case of a cubic periodic data set, this mask function will include the entire data set when \( u \) is a quantity in the bulk and will only include voxels on the interface when \( u \) is an interfacial quantity. The standard deviations of \( u \) and \( u' \) are given by \( \sigma \) and \( \sigma' \) and their means are given by \( \bar{u} \) and \( \bar{u}' \). Further mathematical details are provided in [42]. The two-point Pearson correlations range from -1 to 1, where \( h[u, u'; q] = 1 \) is perfect correlation, \( h[u, u'; q] = -1 \) is perfect anti-correlation, and \( h[u, u'; q] = 0 \) is no correlation. The evolution of the interface is controlled primarily by \( H \), the interfacial mean curvature, thus two-point Pearson autocorrelations will be calculated of \( H \). We shall also determine the spatial autocorrelation of the segmented phases, where voxels are binarized to values of zero or one if \( \phi \leq 0.5 \) or \( \phi > 0.5 \), respectively.

For computational efficiency without loss of accuracy, the data is downsampled from \( 1024^3 \) to \( 512^3 \) voxels for calculation of the autocorrelations. As the simulated dynamics are isotropic, a radial average of the autocorrelations is calculated as a function of the radial distance. The radial average of \( h[u, u'; q] \) at each \( r \) is the average of all values on a sphere with radius \( r \) centered at the origin. The radial average was calculated in equidistant bins with size \( \Delta r = 2 \) (i.e., one voxel-width in the downsampled structure). The autocorrelations were calculated for the latest available simulation time as self-similarity was confirmed across each simulation.

4. Scaling

We report morphological and topological quantities that are scaled by an evolving characteristic length scale, such that invariance of scaled quantities during evolution is indicative of self-similarity. We employ \( S_V^{-3} \) to scale curvatures and genus density. Scaled mean curvature is therefore \( H/S_V \), scaled Gaussian curvature is \( K/S_V^2 \), scaled genus density is \( g_V S_V^{-3} \), and the ISDs are reported in terms of scaled principal curvatures \( \kappa_1/S_V \) and \( \kappa_2/S_V \). The Gauss-Bonnet theorem (Eq. 10) expressed in terms of scaled quantities is

\[ -\frac{1}{4\pi} \int_S K S_V^{-2} dA / A_T = g_V S_V^{-3}. \]  

(13)

That is, the scaled genus density \( g_V S_V^{-3} \) is proportional to the average of the scaled Gaussian curvature \( K/S_V^2 \) over the interface.

To scale radial distance in the phase and \( H \) autocorrelations, we employ a length scale based on Porod’s Law [45], which states that the first derivative of \( h(r) \), the radially averaged phase autocorrelation, at \( r = 0 \) is related to \( S_V^{-1} \) and the volume fraction of the minority phase, \( V_f \), by

\[ h'(0) = -\frac{1}{4V_f(1-V_f)} S_V^{-1}. \]  

(14)

(see e.g. Ref. [46] for a derivation in English). Based on Eq. 14, scaling \( r \) by the length scale \( L_p = 4V_f(1-V_f)S_V^{-1} \) ensures that all of the phase autocorrelations have the same slope at \( r = 0 \). They will have the same value at \( r = 0 \)
as well, since \( h(0) = 1 \) for any Pearson autocorrelation. Thus, scaling \( r \) by \( L_p \) ensures that the phase autocorrelations of all cases have the same behavior near \( r = 0 \). By accounting for the known effect of volume fraction in Eq. 14, this scaling allows us to observe more subtle differences between the autocorrelations of different cases.

### III. RESULTS AND DISCUSSION

In this section, we show how the scaled morphology and topology of the different structures converge to self-similar states, and how the kinetics of the surface-diffusion cases converge to the \( t^{1/4} \) power law predicted for self-similar coarsening. We then analyze the self-similarly evolving structures in greater detail and discuss possible explanations for the differences we observe between surface and bulk diffusion.

#### A. Convergence to self-similar coarsening

1. Evolution of scaled morphology and topology

Figure 1 shows the average scaled mean curvature \( \langle H/S_V \rangle \), standard deviation of scaled mean curvature \( \sigma_{H/S_V} \), and scaled genus density \( g_V S_V^{-3} \) plotted against the characteristic length, which enables a direct comparison between the morphologies resulting from surface and bulk diffusion despite their different kinetics. In the structures with \( \langle \phi \rangle = 0.50 \), scaled genus density converges quickly, and the average and standard deviation of mean curvature (Fig. 1a and 1b) undergo little if any evolution. This indicates that the morphologies resulting from phase separation are close to the self-similar coarsening morphologies. More substantial evolution is observed at \( \langle \phi \rangle = 0.36 \); for both coarsening mechanisms, the average and standard deviation of scaled mean curvature decrease while scaled genus density increases. In all four cases (bulk and surface diffusion with \( \langle \phi \rangle = 0.50 \) and \( \langle \phi \rangle = 0.36 \)), there is a late time/large \( S_V^{-1} \) regime during which all of the quantities plotted in Fig. 1, namely \( \langle H/S_V \rangle \), \( \sigma_{H/S_V} \), and \( g_V S_V^{-3} \), appear to be stable.

To define a converged regime for each structure for further analysis, we applied an ad hoc convergence criterion based on the evolution of \( g_V S_V^{-3} \) with respect to \( S_V^{-1} \) (i.e., the series plotted in Fig. 1c). We focus on \( g_V S_V^{-3} \) since the cases with \( \langle \phi \rangle = 0.50 \) have transient behavior in \( g_V S_V^{-3} \) that is less apparent in \( \langle H/S_V \rangle \) or \( \sigma_{H/S_V} \). Our criterion resulted in converged regimes starting from \( S_V^{-1} = 19.1 \) and \( S_V^{-1} = 32.4 \) for the surface-diffusion \( \langle \phi \rangle = 0.50 \) and \( \langle \phi \rangle = 0.36 \) structures, respectively, and \( S_V^{-1} = 21.5 \) and \( S_V^{-1} = 46.7 \) for the bulk-diffusion \( \langle \phi \rangle = 0.50 \) and \( \langle \phi \rangle = 0.36 \) structures, respectively. To assess whether evolution was in fact self-similar in these regimes, we examined the difference between the average ISD over the converged regime, \( \bar{P} \), and the ISD at each output step, \( P(t) \). The integrated absolute difference between \( P(t) \) and \( \bar{P} \) (the \( L^1 \) normed difference \( ||P - P(t)||_1 \) ) remained small in the converged regimes for each structure, verifying that evolution within them is self-similar. Details regarding the convergence criterion and the evolution of the ISDs are provided in the Supplemental Material [37].

2. Kinetics

The time evolution of \( S_V^{-1} \) is shown in Fig. 2 for the surface-diffusion simulations. During self-similar coarsening via surface diffusion, the time evolution of the characteristic length \( S_V^{-1} \) must follow the \( t^{1/4} \) power law, which can be expressed as

\[
S_V^{-4}(t) = k(t - t_0),
\]

where \( k \) is the coarsening rate constant, \( t \) is simulation time, and the time offset \( t_0 \) is related to the initial characteristic length \( S_V^{-1}(0) \) by \( t_0 = S_V^{-4}(0)/k \). Figure 2 plots \( S_V^{-4} \) against \( (t - t_0)^{1/4} \). To evaluate whether coarsening kinetics agree with Eq. 15 during self-similar coarsening, the linear fits to the data within the converged regime to Eq. 15 are shown by solid black lines. The equations of fit are \( S_V^{-4} = 1.59 t + 1.08 \times 10^5 \) for \( \langle \phi \rangle = 0.36 \) and \( S_V^{-4} = 1.05 t + 1.30 \times 10^4 \) for \( \langle \phi \rangle = 0.50 \). Coefficients of correlation are \( R^2 = 0.99986 \) for \( \langle \phi \rangle = 0.36 \) and \( R^2 = 0.99998 \) for \( \langle \phi \rangle = 0.50 \), indicating excellent agreement between the data and Eq. 15 within the converged regime, as is expected for self-similar coarsening via surface diffusion. Prior to the converged regime, transient kinetics are observed: the coarsening rate constant decreases over time to its self-similar value. This decrease in coarsening rate constant is larger for the \( \langle \phi \rangle = 0.36 \) case, which correlates to its more substantial evolution prior to convergence in Fig. 1. In agreement with the existing literature [15], coarsening kinetics of the bulk-diffusion simulations were found to agree with the theoretically predicted \( t^{1/3} \) power law. Details are provided in the Supplemental Material [37].
B. Self-similar morphologies

We now compare self-similar morphologies from the surface- and bulk-diffusion cases. We expect that these morphologies represent those that are reached after a sufficient amount of evolution from a range of initial morphologies. Therefore, the comparison should be free of the effect of the initial morphologies generated by the different phase separation dynamics, isolating the effect of coarsening mechanism for a given system composition/volume fraction.
TABLE I. Scaled topology and morphological statistics of self-similar structures.

|               | surface | bulk | surface | bulk |
|---------------|---------|------|---------|------|
| ⟨H/S_v⟩      | 0.00    | 0.00 | 0.41    | 0.38 |
| σ_{H/S_v}^2  | 0.30    | 0.32 | 0.36    | 0.37 |
| g_vs_{V}^{-3} | 0.128   | 0.132| 0.114   | 0.129|

1. Structures

Figure 3 shows samples of the surface-diffusion structures from the latest available times with the same scaled volume, (8S_v^{-1})^3. The ⟨φ⟩ = 0.50 structure at t = 9.6 × 10^5 is shown in Figs. 3a-c, and the ⟨φ⟩ = 0.36 structure at t = 3.2 × 10^6 is shown in Figs. 3d-f. The interfaces (i.e., the φ = 0.50 isosurfaces) are depicted with the φ = 1 phase capped at the sample boundary in Figs. 3a and 3d, colored by scaled mean curvature H/S_v in Figs. 3b and 3e, and colored by scaled Gaussian curvature K/S_v² in Figs. 3c and 3f.

Overall, the ⟨φ⟩ = 0.36 structure has more area with positive H/S_v than the ⟨φ⟩ = 0.50 structure (Figs. 3b and 3e, respectively). This is a direct consequence of the reduced volume fraction of the φ = 1 phase in the ⟨φ⟩ = 0.36 case, as it leads to more compact structures of the φ = 1 phase and, by our sign convention, convex regions of the φ = 1 phase have positive mean curvature. In Figs. 3c and 3f, most features having large |K| are necks, which have highly negative Gaussian curvature and mean curvature of either sign. Interfaces with negative Gaussian curvature are hyperbolic interfaces, and their principal curvatures κ_1 and κ_2 have opposite signs. During coarsening, necks shrink and pinch off, leaving behind ‘caps’ with highly positive or negative mean curvature and positive Gaussian curvature. Some caps with positive mean curvature can be seen in the ⟨φ⟩ = 0.36 structure (Figs. 3e and 3f). In general, interfaces with positive Gaussian curvature are elliptic interfaces, and their principal curvatures have the same sign. While more elliptic interfaces are visible in the ⟨φ⟩ = 0.36 structure than in the ⟨φ⟩ = 0.50 structure, they are less common than hyperbolic interfaces in both structures.

The structures in Fig. 3 appear to be bicontinuous. This was confirmed for the ⟨φ⟩ = 0.50 structure, in which no independent particles were detected. In the ⟨φ⟩ = 0.36 structure, two independent particles persist during the converged regime of evolution. These particles of the φ = 1 phase are a negligible component of the overall topology of the structure, which has g ≥ 1116 for all simulation outputs, and comprise a negligible fraction of the total volume, V_f < 10^{-4}. These isolated particles cannot evolve by surface diffusion after reaching their equilibrium shape unless they rejoin the main region of phase. Since isolated particles cannot evolve, the evolution of the ⟨φ⟩ = 0.36 surface-diffusion case corresponds to that of a bicontinuous structure consisting of its continuous regions of the φ = 0 and φ = 1 phases.

2. Scaled topology and morphological statistics

Table I compares the average scaled mean curvature ⟨H/S_v⟩, standard deviation of scaled mean curvature σ_{H/S_v}, and scaled genus density g_v S_v^{-3} over the converged regime for all four cases: surface and bulk diffusion with ⟨φ⟩ = 0.50 and ⟨φ⟩ = 0.36. The structures at ⟨φ⟩ = 0.50 are quantitatively similar; the surface-diffusion case has lower σ_{H/S_v} and slightly lower g_v S_v^{-3}, with no difference in ⟨H/S_v⟩. (⟨H/S_v⟩ = 0 is expected at this volume fraction due to the symmetry between the phases). At ⟨φ⟩ = 0.36, we again observe lower g_v S_v^{-3} and σ_{H/S_v} for surface diffusion, but the difference in g_v S_v^{-3} is much larger than at ⟨φ⟩ = 0.50 and there is now a nonzero difference in ⟨H/S_v⟩, with the surface diffusion case having higher ⟨H/S_v⟩. At both volume fractions, coarsening via surface diffusion results in smaller g_v S_v^{-3} and σ_{H/S_v} than the bulk-diffusion cases, while no trend can be confirmed for ⟨H/S_v⟩ because both mechanisms have ⟨H/S_v⟩ = 0.00 at ⟨φ⟩ = 0.50. Differences due to coarsening mechanism are smaller than the differences due to volume fraction, except in the case of scaled genus density, which is very similar between the bulk-diffusion structures at ⟨φ⟩ = 0.50 and ⟨φ⟩ = 0.36.

3. Interfacial shape distributions

The converged average ISDs ˆ{P(κ_1/S_v, κ_2/S_v)} introduced in Section III A 1 are shown in Fig. 4. Figures 4a-c depict the ⟨φ⟩ = 0.50 cases, while Figs. 4d-f depict the ⟨φ⟩ = 0.36 cases. The surface-diffusion ISDs are given in Figs. 4a and 4d, the bulk-diffusion ISDs are given in Figs. 4c and 4f, and Figs. 4b and 4e show the differences between them. The
line $\kappa_1 = -\kappa_2$ corresponds to zero mean curvature ($H = 0$), and is indicated on the ISDs by a dashed line extending from the origin. The lines $\kappa_1 = 0$ and $\kappa_2 = 0$ correspond to zero Gaussian curvature ($K = 0$), where the interfacial shape corresponds to that of a cylinder.

Hyperbolic interfaces lie in the quadrant $\kappa_1 < 0$, $\kappa_2 > 0$, and they comprise the majority of interfaces in all four ISDs. The differences between ISDs solely due to volume fraction are relatively large, with the normed difference $||P_{0.50} - P_{0.36}||_1$ equal to 0.99 for surface diffusion and 0.94 for bulk diffusion. The $\langle \phi \rangle = 0.50$ ISDs are concentrated closely around the $H = 0$ line, while the $\langle \phi \rangle = 0.36$ ISDs are shifted toward the upper right, indicating larger populations of interfaces with larger $H$. This is consistent with the differences in $\langle H/S_V \rangle$ in Table I and the differences in $H/S_V$ between structures in Fig. 3, where the $\langle \phi \rangle = 0.36$ structure has substantially more areas with positive mean curvature than the $\langle \phi \rangle = 0.50$ structure. Additionally, the $\langle \phi \rangle = 0.36$ ISDs are more diffuse, which is consistent with their higher values of $\sigma_{H/S_V}$ in Table I.

At $\langle \phi \rangle = 0.50$, the difference between ISDs due to coarsening mechanism (Fig. 4b) is very small. Quantitatively, the normed difference $||P_{surf} - P_{bulk}||_1$ between the ISDs is 0.04, only slightly larger than variations in the ISDs over time, which are in the range $0.01 - 0.03$ [37]. The surface-diffusion ISD has more low-curvature area near the origin, including more elliptic area, and its higher-curvature areas are more closely concentrated about the $H = 0$ line than in the bulk-diffusion ISD, which may result in its lower $\sigma_{H/S_V}$ in Table I.

The difference between surface- and bulk-diffusion ISDs at $\langle \phi \rangle = 0.36$ is shown in Fig. 4e. Quantitatively, $||P_{surf} - P_{bulk}||_1 = 0.09$, which is substantially larger than the variation in time of either ISD ($0.02 - 0.04$ [37]). The line $H/S_V = 0.38$, representing $\langle H/S_V \rangle$ of the bulk-diffusion case, has been drawn onto Fig. 4e as a dotted line. The surface-diffusion ISD contains more area to the upper right of this line (with higher $H/S_V$) and less area to the lower left of it (with lower $H/S_V$). This decrease in area at lower $H/S_V$ corresponds primarily to hyperbolic interfaces with highly negative $K$, such as the necks observed in Fig. 3. Much of the increase in area at higher $H/S_V$ corresponds to an increase in elliptic areas with $\kappa_1 > 0$ (and thus $K > 0$ and $H > 0$), which can be attributed to the caps that form after necks pinch off. Both the decrease in hyperbolic area and the increase in elliptic area are expected to reduce $g_V S_V^{-3}$ in the surface-diffusion structure because of the Gauss-Bonnet theorem (Eq. 13), matching the trend in Table I.
4. Two-point Pearson autocorrelations

Figure 5a shows the Pearson phase autocorrelation for all four cases: surface and bulk diffusion with \( \langle \phi \rangle = 0.50 \) and \( \langle \phi \rangle = 0.36 \). In each case, there is a peak at \( h(0) = 1 \) from which the phase autocorrelations decrease with the slope given by Porod’s Law (Eq. 14), \( h'(0) = -1/L_p \). As \( r/L_p \) increases, the phase autocorrelations decay below zero and then oscillate about zero with decreasing amplitude. As shown in [43], the distance between neighboring phases, the center-to-center distance between channels of the same phase, is approximately given by the location of the first local maximum of the phase autocorrelation. This local maximum occurs around \( r = 2.8L_p \) for all cases. The interphase distance (the space between the center of channels of opposite phase) is given by half the value of \( h \). Although these distances are the same for each structure, \( L_p \) is different. Thus the differences between cases due to volume fraction are encapsulated in the scaling factor, \( L_p = 4V_f(1 - V_f)S_V^{-1} \). No substantial differences due to coarsening mechanism are observed.

Figure 5b displays the Pearson \( H \) autocorrelation for all four cases. For each structure, the \( H \) autocorrelation is less oscillatory than the phase autocorrelation and shows a large region of anti-correlation. However, locations of extrema are similar between the phase and \( H \) autocorrelations, despite the extrema themselves differing in magnitude and sign. Differences in \( H \) autocorrelations due to volume fraction are largely captured by the scaling factor \( L_p \) in the bulk-diffusion cases (as was observed for the phase autocorrelations in all cases), but the surface-diffusion cases do show an effect of volume fraction not captured by \( L_p \). The effect of coarsening mechanism on the \( H \) autocorrelations is shown in the inset to Fig. 5, which plots the difference between the \( H \) autocorrelations for each mechanism, \( h_{surf}(r/L_p) \) and \( h_{bulk}(r/L_p) \), at \( \langle \phi \rangle = 0.36 \) and \( \langle \phi \rangle = 0.50 \). (We do not show the corresponding plot for phase autocorrelations as the differences between them are very small, at most 0.01 between any two cases.) The difference \( h_{surf} - h_{bulk} \) at each volume fraction peaks near \( r/L_p = 0.7 - 0.8 \), then decays to a negative value as \( r/L_p \) increases, and finally converges toward zero at large \( r/L_p \). The initial peak value is approximately twice as large at \( \langle \phi \rangle = 0.36 \) as at
Coarsening via surface diffusion at nominal volume fractions of 36% and 50% (system compositions of $\langle \phi \rangle = 0.36$ and $\langle \phi \rangle = 0.50$, respectively) resulted in self-similarly evolving structures that are quite close to those evolving via bulk diffusion. However, quantitative characterization of the structures revealed differences in morphology and topology due to the underlying coarsening mechanism. The surface-diffusion structures have lower scaled genus density, lower standard deviation of scaled mean curvature, and lower short-range spatial variation in $H$, as assessed by its autocorrelation. The ISDs for surface diffusion contained relatively more elliptic area than the bulk-diffusion ISDs, which is consistent with their lower scaled genus density.

The differences in morphology and topology between the surface- and bulk-diffusion cases are surprisingly subtle given the significant difference in dynamics between them. To fully understand why this is the case, we would need to develop a better theoretical connection between coarsening dynamics and morphology. One approach, recently applied to hydrodynamic coarsening of viscous fluids [47], is to examine the topological changes that occur during coarsening. Since all of the structures have a substantial genus density and a negligible number of particles, the dominant
mechanism of topological change is the pinching-off of necks. Since this process results in hyperbolic interfaces (necks) turning into elliptic areas (caps), the higher fraction of elliptic area in the surface diffusion structures (and the lower scaled genus density) may represent slower evolution of caps compared to necks relative to the bulk-diffusion case. Caps typically flatten rapidly due to their high mean curvature relative to the surrounding structure, and it seems reasonable that restricting transport to the surface could slow this flattening process disproportionately to the pinching-off process. However, while pinching-off of necks has been analyzed for surface diffusion [48], and for bulk diffusion when the diffusivities of the phases are highly dissimilar [49], it has not yet been examined for bulk diffusion with uniform mobility. Such investigation is needed in order to fully assess the impact of topological changes on coarsening morphology evolution.

In addition to the overall effects of coarsening mechanism on morphology, we have found an interestingly strong interaction between coarsening mechanism and volume fraction: differences in morphology between surface and bulk diffusion are larger at $\langle \phi \rangle = 0.36$ than at $\langle \phi \rangle = 0.50$. We observe this trend in several microstructural characteristics: ISDs, $H$ autocorrelations, scaled genus densities, and average scaled mean curvature. Only the standard deviation of scaled mean curvature provides a possible counterexample, with a slightly larger difference between coarsening mechanisms at $\langle \phi \rangle = 0.50$ than $\langle \phi \rangle = 0.36$. To explain this trend, we examine differences between coarsening mechanisms that might result in a volume fraction dependence in the bulk diffusion case but not in the surface diffusion case. While surface diffusion only allows diffusion between neighboring points on the interface, bulk diffusion allows interfaces to interact nonlocally. In the latter, the local chemical potential at a point on the interface can affect the local interfacial velocity far from that point. To approximate these interactions, a uniform mean-field chemical potential is often introduced. In bicontinuous structures, this potential can be reasonably assumed to be proportional to the local interfacial velocity far from that point. To approximate these interactions, a uniform mean-field chemical potential is often introduced. In bicontinuous structures, this potential can be reasonably assumed to be proportional to $\langle H \rangle$ [50, 51] (see also the Supplemental Material [37]). Since $\langle H/S_V \rangle$ changes considerably between $\langle \phi \rangle = 0.50$ and $\langle \phi \rangle = 0.36$ (from zero to 0.38-0.41), the effect of a mean-field chemical potential is one possible explanation for the greater difference between coarsening mechanisms at $\langle \phi \rangle = 0.36$ compared to $\langle \phi \rangle = 0.50$. While our study focused on comparisons between coarsening mechanisms at the same volume fraction, we also note that the differences in self-similar morphology and topology due to changes in nominal volume fraction are smaller for bulk diffusion than for surface diffusion. This effect is most apparent in $g_V S_V^{-3}$ and the $H$ autocorrelations, but it is also found to a lesser extent in the ISDs, $\langle H/S_V \rangle$, and $\sigma_{H/S_V}$. Thus, the mean-field chemical potential in the bulk-diffusion case may have a stabilizing effect on the morphology and topology of bulk-diffusion structures as volume fraction decreases.

When examining effects of volume fraction, one question that is worth exploring is whether there is a volume-fraction-dependent scaling length that would eliminate the volume-fraction dependence. In this study, $L_p$ has been used to account for the volume-fraction effect when examining the autocorrelations. The fact that it yields proper scaling implies that the autocorrelation depends on the volume fraction as $V_f (1 - V_f)$, which is the volume-fraction-dependent term in $L_p$. However, this scaling would not be appropriate for other microstructural characteristics examined here. For example, average scaled mean curvature $\langle H/S_V \rangle$ cannot be proportional to $V_f (1 - V_f)$ because $\langle H/S_V \rangle$ must change sign at $V_f = 0.5$ due to the sign convention for $H$ and the inversion symmetry between $\langle \phi \rangle = V_f$ and $\langle \phi \rangle = 1 - V_f$. When scaled by $S_V^{-3}$, genus density is already essentially constant between $V_f = 0.50$ and $V_f = 0.36$ for coarsening via bulk diffusion, and thus any volume fraction scaling would lead to disagreement. Standard deviation of scaled mean curvature does appear to scale with volume fraction, but not precisely according to $V_f (1 - V_f)$: $\sigma_{H/L_p}$ for the four simulations falls in a slightly narrower range (0.30-0.34) than $\sigma_{H/S_V}$ does in Table I (0.30-0.37). Thus, for the microstructural characteristics considered here, we find that $L_p$ provides improved scaling compared to $S_V^{-1}$ only for the autocorrelation distance $r$. Further theoretical basis would be needed to develop proper scaling lengths for volume-fraction-dependent microstructural characteristics.

IV. CONCLUSIONS

We have conducted three-dimensional phase field simulations of phase separation and coarsening via surface diffusion at nominal volume fractions of 36% and 50% (average concentrations of $\langle \phi \rangle = 0.36$ and $\langle \phi \rangle = 0.50$). Simulations of coarsening via bulk diffusion were also conducted to examine the effects of coarsening mechanism on morphology. All of the simulations resulted in bicontinuous microstructures, with no independent particles at 50% and a negligible volume and number of particles at 36%. Scaled genus density was used to define convergence to self-similar coarsening for each structure, an approach that was validated by examining convergence of interfacial shape distributions (ISDs). Kinetics of coarsening via surface and bulk diffusion were found to agree with their respective power laws for self-similar evolution, $S_V^{-1} \propto t^{1/3}$ and $S_V^{-1} \propto t^{1/3}$.

Self-similar structures coarsening via surface and bulk diffusion were compared to isolate the effects of the difference in coarsening dynamics. Average scaled mean curvature, standard deviation of scaled mean curvature, and scaled genus density were averaged over the self-similar regime, and ISDs and Pearson autocorrelations of phase and interfacial mean curvature were also compared between self-similar structures. Overall, the structures coarsening by surface
diffusion are remarkably similar to those coarsening by bulk diffusion, despite the different kinetics. However, a close examination of these structures reveals that structures coarsening via surface diffusion had slightly lower scaled genus densities and standard deviations of scaled mean curvature, slightly more elliptic area (area with positive Gaussian curvature) in their ISDs, and greater spatial correlations of mean curvatures at relatively short distances. Phase autocorrelations were also nearly identical across all volume fractions and coarsening mechanisms when the distance was scaled by \( L_p = 4V_f(1 - V_f)S^{-1} \), a factor based on Porod’s law that eliminates the first-order effect of volume fraction. In most other metrics, there was a strong interaction between the effects of volume fraction and coarsening mechanism, with much larger differences at 36\% than at 50\%. We have hypothesized possible explanations for the effect of coarsening mechanism on morphology (and its interaction with the effect of volume fraction), but more rigorous theoretical development is needed before they are fully understood. Our results provide direct insight into the coarsening dynamics of complex microstructures as well as a basis for comparison to future experimental or theoretical investigations.

**DATA AVAILABILITY**

Analysis results presented in this work and selected raw simulation output will be released on Materials Commons (materialscommons.org) prior to publication.

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Supplemental Information: Coarsening of Bicontinuous Microstructures via Surface Diffusion

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I. COARSENING DYNAMICS WITHOUT THE STABILIZING FUNCTION

In the course of our investigation, we also examined the dynamics of the Cahn-Hilliard equation with a concentration-dependent mobility but without the modification to the chemical potential that distinguishes the RRV model. We will refer to this as a solubility-permitting (S-P) model for surface diffusion: the primary difference between it and the RRV model is that in the S-P model, concentration in the bulk can deviate from \( \phi_0^+ = 1 \) and \( \phi_0^- = 0 \) due to the Gibbs-Thomson effect [S1, S2], which can be expressed as

\[
\phi = \phi_0^+ + \frac{2\gamma H}{(\phi_0^+ - \phi_0^-)^2 f''(\phi)},
\]

(S1)

where \( H \) is mean curvature and \( \gamma \) is interfacial energy. The designation ‘solubility-permitting’ also excludes models employing the double-obstacle potential for \( f(\phi) \), in which discontinuities in \( f'(\phi) \) at \( \phi_0^\pm \) inhibit changes in concentration in the bulk. Previous analyses of S-P models in the context of coarsening theory [S3] and in the asymptotic limit of a sharp interface [S1, S4] have found that they do not completely eliminate transport through the bulk. Instead, S-P models slow down bulk diffusion such that surface diffusion becomes the primary transport mechanism in a well-connected or bicontinuous structure. A type of slow bulk diffusion is still present in the sharp interface limit of S-P models, but it is at the same or higher order (depending on the form of the mobility) compared to surface diffusion in the asymptotic expansion of the dynamics [S4]. In systems of isolated particles that cannot coarsen via surface diffusion, this slow bulk diffusion still allows coarsening, but with a power law that depends on the form of the mobility (and is never faster than the \( t^{1/4} \) power law expected for surface diffusion [S3]). To avoid this ambiguity in the coarsening dynamics, we employed the RRV model to generate the principal results of this paper. However, our results with the S-P model do illustrate important differences between surface and bulk diffusion, and they may be of broader interest to the phase field modeling community; therefore, the results are summarized below.

The S-P model we examine here is the Cahn-Hilliard equation (Eq. 4 of the main text) with the concentration-dependent mobility \( M(\phi) = 16\phi^2(1 - \phi)^2 \) and the double-well bulk free energy (Eq. 5 of the main text). Neglecting the contribution from bulk diffusion, this model results in a sharp interface kinetic coefficient [S5]

\[
\alpha = \frac{c_0^2}{(\phi_0^+ - \phi_0^-)^2} \int_{\phi_0^-}^{\phi_0^+} \frac{M(\phi)}{\sqrt{2f(\phi)}} d\phi,
\]

(S2)

where the interfacial energy \( \gamma \) is given by Eq. 8 of the main text. We present the results of a single simulation in a cubic domain, \( L_x = L_y = L_z = 800 \), with an average system composition of \( \langle \phi \rangle = 0.36 \) and periodic boundary conditions in each direction. Simulation parameters were \( c_0 = 0.2 \) and \( W = 0.4 \), which result in \( \alpha = 4/45 \) according to Eq. S2. The explicit finite differences scheme introduced in the main text was used with \( \Delta x = 1 \) and \( \Delta t = 0.05 \).

Coarsening kinetics of the S-P and RRV models are compared in Fig. S1, which plots \( V^{-1/2} \) against a scaled time, \( t' = \alpha t \). With this time scaling, both models have the same scaled surface diffusion equation in the sharp interface limit,

\[
\frac{\partial \phi}{\partial t'} = \nabla^2 \phi,
\]

(S3)

and the remaining difference in kinetics can be attributed to the additional dynamics (bulk solubility and bulk diffusion) present in the S-P model. As one might expect, Fig. S1 shows more rapid coarsening kinetics for the S-P model. However, the difference in dynamics can affect kinetics both directly, by allowing more mass transport, and indirectly, by altering the morphology in a way that affects coarsening kinetics. We find significant differences in morphology between the S-P and RRV models (see below), and thus neither of these effects can be ruled out in Fig. S1.
FIG. S1. Comparison of coarsening kinetics between the S-P model (red triangles) and RRV model (blue diamonds) for surface diffusion at \( \langle \phi \rangle = 0.36 \). Characteristic length to the fourth power, \( S^{-4} \), is plotted against scaled time \( t^* = t\alpha \), where \( \alpha \) is the sharp interface kinetic coefficient.

FIG. S2. Comparison of morphological evolution with \( \langle \phi \rangle = 0.36 \) between the RRV model (blue diamonds) and S-P model (red leftward-pointing triangles) for surface diffusion, and the bulk-diffusion case (yellow downward-pointing triangles). (a) and (b) depict evolution of average scaled mean curvature and scaled genus density respectively. In (c), volume fraction of the \( \phi = 1 \) phase is plotted against \( S^{-1} \), while (d) plots the same relationship except that the quantity \( \frac{1}{3} \langle H \rangle \) from Eq. S5 has been added to the volume fractions of the S-P and bulk-diffusion cases to account for the mean-field Gibbs-Thomson effect.

Figure S2 compares the evolution of morphological and topological statistics between the S-P and RRV models for surface diffusion and the bulk-diffusion case. Figures S2a and S2b show the evolution of scaled average mean curvature \( \langle H/SV \rangle \) and scaled genus density \( gV_S^{-3} \), respectively. At the earliest time (i.e., immediately following phase separation), the S-P structure has values of \( \langle H/SV \rangle \) and \( gV_S^{-3} \) that are much closer to the bulk-diffusion structure than the RRV structure. The S-P structure also has a substantially longer transient regime than the RRV structure despite having more rapid evolution of \( \langle H/SV \rangle \) and \( gV_S^{-3} \) with respect to \( S^{-1} \). In fact, the S-P structure never converges to a self-similar state during this simulation. Figure S2c depicts the evolution with respect to \( S^{-1} \) of the volume fraction of the \( \phi = 1 \) phase. The S-P structure and bulk-diffusion structure start at substantially lower volume fractions than both the RRV structure and the nominal volume fraction of 0.36. Volume fraction converges toward 0.36 over time in all three cases, but the volume fractions of the S-P and bulk diffusion structures always remain less than the volume fraction of the RRV structure.
Based on Fig. S2a-c, the differences in topology and morphology between the RRV case and the S-P and bulk-diffusion cases are to an extent correlated to the differences in volume fraction between them. This is especially true for the initial morphology, where volume fraction differs the most and the bulk-diffusion and S-P cases are most similar, but the greater evolution of volume fraction over the course of the S-P and bulk-diffusion simulations also matches the longer transient evolution they have in \( \langle H/S_V \rangle \) and \( \sigma_W S_V^{-3} \). The observed differences in volume fraction are in fact a predictable consequence of the lack of solubility in the RRV model. Since \( \phi \) is conserved, below-nominal volume fractions are caused by increased average compositions of the phases. This relationship can be expressed by the lever rule,

\[
V_f = \frac{\langle \phi \rangle - \phi^-}{\phi^+ - \phi^-}.
\]

In the RRV case, the below-nominal volume fraction in S2c is likely a diffuse interface effect: at early times, the interface takes up a non-negligible fraction of the total volume, and the criterion \( \phi > 0.5 \) does not necessarily divide this interfacial volume equally between the two phases. This effect may occur in the S-P and bulk-diffusion structures as well, but it should be similar in magnitude between structures with similar \( S_V^{-1} \) and \( \langle H/S_V \rangle \), and thus it cannot explain the large difference in volume fraction between them and the RRV structure. However, unlike the RRV structure, the bulk-diffusion and S-P structures also have changes in the bulk concentration due to the Gibbs-Thomson effect, Eq. S1. The magnitude of these changes can be estimated by employing a mean-field assumption, specifically by assuming that the average change in concentration can be obtained from Eq. S1 with \( \langle H \rangle \) substituted for the local mean curvature \( H \). Substituting this mean-field concentration into Eq. S4 and substituting the parameters for our system results in

\[
V_f = \langle \phi \rangle - \frac{1}{3} \langle H \rangle.
\]

To test our understanding of how volume fraction evolves, we compare the evolution of \( V_f \) for the RRV case to the evolution of \( V_f + \frac{1}{3} \langle H \rangle \) for the S-P and bulk-diffusion cases in Fig. S2d. As expected, all three cases are very similar when the change in bulk concentration due to the Gibbs-Thomson effect is taken into account. Since this mean-field Gibbs-Thomson effect is proportional to \( \langle H \rangle \), it is largest early in the simulations, when feature sizes are small. In this way, the presence or absence of bulk solubility causes the large initial difference in volume fraction between the S-P and bulk-diffusion cases and the RRV case that correlates with their initial differences in morphology and topology.

Overall, we find that the concern raised in previous work [S1] regarding S-P models for surface diffusion is warranted for the type of coarsening simulation conducted here. The presence of solubility in the S-P model affected both morphology and kinetics during coarsening and resulted in a longer transient regime that prevented us from obtaining a self-similar morphology. However, the effect of solubility decreases as the length scale of microstructural features increases, raising the possibility that the S-P model will accurately describe surface diffusion when microstructural features are very large compared to the width of the interface. Finally, we note that the evolution of volume fraction that we have observed may help to explain differences in transient coarsening between cases in the main text: not only does the bulk-diffusion structure at \( \langle \phi \rangle = 0.36 \) converge more slowly than the RRV structure, but both structures at \( \langle \phi \rangle = 0.36 \) converge slowly compared to those at \( \langle \phi \rangle = 0.50 \), where symmetry constrains the volume fraction to be \( V_f = 0.50 \) at all times.

II. CONVERGENCE CRITERION AND ISD EVOLUTION

In this section, we describe the criterion for convergence of \( g_V S_V^{-3} \) with which we define the converged regimes for each structure. We then verify self-similarity of morphologies within the converged regime by examining the evolution of the ISDs. The metric we use to quantify convergence of \( g_V S_V^{-3} \) is its standard deviation within a moving window \( 10 S_V^{-1} \) wide centered at the value of \( S_V^{-1} \) at time \( t \). We denote this quantity \( \sigma_W(t) \), and plot it against \( S_V^{-1} \) in Fig. S3a. Structures are considered converged for all \( S_V^{-1} \) greater than the \( S_V^{-1} \) at which \( \sigma_W \) initially drops below a set value, \( \sigma_W(t) = 10^{-3} \), which is indicated by the dotted line in Fig. S3a. All of the structures subsequently stay below \( \sigma_W = 10^{-3} \) except for bulk diffusion at \( \langle \phi \rangle = 0.36 \), which may have more variability due to the smaller statistical sample size of interfacial area implied by its high \( S_V^{-1} \). Based on this criterion, the surface-diffusion \( \langle \phi \rangle = 0.50 \) and \( \langle \phi \rangle = 0.36 \) structures converged by \( S_V^{-1} = 19.1 \) and \( S_V^{-1} = 32.4 \) respectively, while the bulk-diffusion \( \langle \phi \rangle = 0.50 \) and \( \langle \phi \rangle = 0.36 \) structures converged by \( S_V^{-1} = 21.5 \) and \( S_V^{-1} = 46.7 \) respectively.

To demonstrate that the criterion \( \sigma_W(t) \leq 10^{-3} \) adequately represents convergence of the morphology, Fig. S3b shows the convergence of the ISDs. To determine a ‘converged’ ISD with reduced statistical variation, we calculate an average ISD for each simulation using ISDs from all of its outputs within the temporal range corresponding to its
FIG. S3. Measures of convergence of (a) the scaled genus density and (b) the scaled ISD, both plotted against characteristic length. In (a), the quantity $\sigma_W(t)$ represents the standard deviation of $g_v S_v^{-1}$ within a moving window $10 S_v^{-1}$ wide centered at the value of $S_v^{-1}$ at time $t$. The critical value of $\sigma_W(t)$ used to assess convergence, $10^{-3}$, is indicated by the dotted line. In (b), the quantity $||\bar{P}(t) - \bar{P}_s||_1$ is the integrated absolute difference (i.e., the $L^1$ normed difference) between a converged average ISD $\bar{P}$ and the time-dependent ISD $P(t)$. All four conditions are shown in (a) and (b): bulk diffusion $\langle \phi \rangle = 0.36$ (yellow downward-pointing triangles), surface diffusion $\langle \phi \rangle = 0.36$ (blue diamonds), bulk diffusion $\langle \phi \rangle = 0.50$ (purple rightward-pointing triangles), and surface diffusion $\langle \phi \rangle = 0.50$ (red squares).

The values of $||\bar{P} - P(t)||_1$ within the converged regimes may signify statistical variation around a stationary, self-similarly-evolving ISD or, alternatively, non-self-similar evolution of the ISD at a slower rate. Since the statistical sample size for the ISD (the total interfacial area) decreases with time during coarsening, we expect that this decrease in statistics results in an increase in statistical variability of the ISD over the course of each simulation. This is because, in order to simplify quantitative comparisons between them, all of our ISDs employ the same discretization of the scaled curvature space. Since the bin size of the discretization is constant, changes in statistical sample size will affect statistical variability in ISDs that sample the same underlying distribution, with smaller statistical sample sizes leading to more variability. Thus, we expect that $P(t)$ for structures within their self-similar regimes will contain an increasing amount of statistical variability as $S_v^{-1}$ increases, matching the slow, slight increases in $||\bar{P} - P(t)||_1$ in Fig. S3b after convergence. To demonstrate this effect, the differences $P(t) - \bar{P}$ are plotted in Fig. S4 in the middle of the converged regime for each of the four cases: (a) surface diffusion at $\langle \phi \rangle = 0.50$, (b) bulk diffusion at $\langle \phi \rangle = 0.50$, (c) surface diffusion at $\langle \phi \rangle = 0.36$, and (d) bulk diffusion at $\langle \phi \rangle = 0.36$. The cases are ordered such that characteristic length $S_v^{-1}$ increases from (a) to (d), accompanied by the increase in $||\bar{P} - P(t)||_1$, which matches the behavior observed in Fig. 2b of the main text after convergence. The larger differences present at larger $S_v^{-1}$ (Figs. S4c and S4d) appear to be uncorrelated and fluctuate rapidly in sign, supporting the hypothesis that $||\bar{P} - P(t)||_1$ consists primarily of statistical noise in this regime.

Even if the ISDs were evolving during the converged regime, we note that the magnitude of any such evolution is limited by the triangle inequality: $||\bar{P}(t_1) - \bar{P}(t_2)||_1 \leq ||\bar{P} - P(t_1)||_1 + ||\bar{P} - P(t_2)||_1$. Taking the $\langle \phi \rangle = 0.50$ bulk-diffusion case as an example, with $t_2$ as the beginning of the converged regime and $t_2$ as the final output step, this inequality suggests that $||\bar{P}(t_1) - \bar{P}(t_2)||_1 \leq 0.016 + 0.025 = 0.041$. Thus, this ISD has changed by at most 4.1% over the entire converged regime. (Again, since $||\bar{P}||_1 = 1$ by definition, $||\bar{P}(t_1) - \bar{P}(t_2)||_1$ and $||\bar{P} - P(t)||_1$ can both be interpreted as relative differences.) We therefore conclude that the average ISDs within the converged regime are most likely representative of self-similar coarsening, and the values of $||\bar{P} - P(t)||_1$ within the converged regime provide an approximate measure of their uncertainty. For the $\langle \phi \rangle = 0.50$ structures, $||\bar{P} - P(t)||_1$ is in the range 0.01 – 0.03 after convergence, and for the $\langle \phi \rangle = 0.36$ structures, it is in the range 0.02 – 0.04.
FIG. S4. Differences between time-averaged and time-dependent ISDs, \( P(t) - \bar{P} \), in the middle of the converged regime for each of the four cases considered: (a) surface diffusion, \( \langle \phi \rangle = 0.50 \), (b) bulk diffusion, \( \langle \phi \rangle = 0.50 \), (c) surface diffusion, \( \langle \phi \rangle = 0.36 \), and (d) bulk diffusion, \( \langle \phi \rangle = 0.36 \). The corresponding norm of the difference, \( ||P(t) - \bar{P}||_1 \), and the characteristic length \( S^{-1}_V \) are noted in each figure.

III. KINETICS OF COARSENING VIA BULK DIFFUSION

The time evolution of \( S^{-3}_V \) in the bulk-diffusion simulations is shown in Fig. S5. During self-similar coarsening, this evolution is expected to follow a \( t^{1/3} \) power law, which can be expressed as

\[
S^{-3}_V(t) = k(t - t_0),
\]

where \( k \) is the coarsening rate constant and \( t_0 = S^{-3}_V(0)/k \). Figure S5 plots \( S^{-1}_V \) against \( (t - t_0)^{1/3} \). Since Eq. S6 is not guaranteed to hold when evolution is not self-similar, we fit it only to data within the converged regime. Fits of Eq. S6 to data within the converged regimes are shown as solid black lines in Fig. S5. The equations of fit are \( S^{-3}_V = 0.245t + 1.84 \times 10^4 \) for \( \langle \phi \rangle = 0.36 \) and \( S^{-3}_V = 0.180t + 1.40 \times 10^3 \) for \( \langle \phi \rangle = 0.50 \). Coefficients of correlation are \( R^2 = 0.99960 \) for \( \langle \phi \rangle = 0.36 \) and \( R^2 = 0.99996 \) for \( \langle \phi \rangle = 0.50 \), indicating excellent agreement between the data and Eq. S6 within the converged regime. Similar qualitative trends are found in Fig. S5 compared to the surface-diffusion cases considered in the main text: the rate constants \( k \) decrease during transient evolution prior to the converged regime, and the \( \langle \phi \rangle = 0.36 \) case has both a longer transient regime and a larger steady-state rate constant than the \( \langle \phi \rangle = 0.50 \) case.

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FIG. S5. Kinetics of coarsening via bulk diffusion at \( \langle \phi \rangle = 0.36 \) (yellow downward-pointing triangles) and \( \langle \phi \rangle = 0.50 \) (purple rightward-pointing triangles). Characteristic length \( S_{\text{V}}^{-1} \) is plotted against \( (t - t_0)^{1/3} \), the cube root of simulation time \( t \) offset by \( t_0 \). Fits of Eq. S6 to data within the converged regimes are shown as solid black lines.

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