

Chapter 1

Introduction

This chapter provides a general overview of phase-separating binary mixtures in contact with surfaces, which we explore in this thesis. We briefly introduce the associated problems and the methodologies used to deal with them in section 1.1. In the subsequent sections, we provide the basic concepts and theories that will help us understand the content of the later chapters.

1.1 Kinetics of Phase Transitions

This thesis focuses on the kinetic pathways the system prefers to evolve from a thermodynamically unstable or metastable state to a globally stable state. The instability or metastability occurs due to sudden changes in external parameters, like temperature, pressure, etc. Subsequently, the system exhibits *far-from-equilibrium* unstable states, characterized by complex *spatio-temporal patterns*, where the patterns account for domains enriched in the preferred states. Thus, the system's kinetics toward the new states is driven by nonlinearities in the form of defects costing free energy, such as domain interfaces. The system then proceeds further by minimizing these defects following nonequilibrium dynamics commonly referred to as *domain growth*, *coarsening kinetics*, or *phase-ordering kinetics* [1–4].

Lately, nonequilibrium ordering, phase separation, and pattern formation have also been investigated in active matter systems [5–8], borrowing equivalent tools and mathematical frameworks from their passive counterparts. The study of phase-separation kinetics in active matter systems, being nascent, poses challenges more complicated than the passive cases, exhibiting novelties like reverse Ostwald ripening, microphase separation, moving interfaces, etc. Thus, the concept of phase-ordering kinetics has far more reaching applicability and relevance than it was envisaged initially. As the discipline has grown exceedingly refined and nuanced, it faces challenges from this new arena, celebrated as active phase separation.

An extensively used paradigm for coarsening kinetics is phase separation in a homogeneous binary (AB) mixture quenched below its miscibility curve. If the

quenched mixture is unstable to small composition fluctuations ($n_A - n_B$, where n_α is the local density for the species α), the phase separation is spontaneous and is known as *spinodal decomposition* [4, 9]. Otherwise, the quenched mixture is metastable and decomposes into pure phases only for small-scale high-intensity concentration fluctuations, where segregation occurs via *nucleation and growth* [9, 10]. The problems about phase separation first appeared in metallurgy and materials science, but they soon became relevant in complex fluids and later in biological physics. A phase separation process is a recurring phenomenon in many *far-from-equilibrium* systems. One of the primary focuses of this thesis is to analyze the commonalities and distinctions in these systems.

A new problem set emerges when symmetry-breaking elements are introduced in the phase-separating mixtures. The common ones are the boundaries, where accounting for their presence becomes indispensable in critically understanding the process. The mixture phase separating in a container or contact with a surface is commonplace in metallurgy and chemical and biological systems. In many cases, the surfaces preferentially attract one of the species from the binary mixture. If the fluid remains miscible, then an enrichment layer of the preferred component forms over the surface, and its thickening in time is referred to as *surface-enrichment kinetics* (SE) [11–15].

In contrast, if the mixture is immiscible, the thoroughly mixed system demixes into coexisting phases rich in either component, and the surface becomes the origin of composition waves, known as *surface-directed spinodal decomposition* (SDSD) waves [4, 14, 16–22]. The SDSD waves are composed of alternating segments of the wetting (rich in the preferred component) and depletion layers (lack of the preferred component). Another closely related phenomenon is the *dewetting* in the thin film settings, where the unstable wetting layer deteriorates, exposing the dry area of the surface [14, 15, 23–25]. The kinetics of SE, SDSD, and *dewetting* are of great technological and scientific importance and provide a way to curate and design functional materials by enabling control over their domain morphologies.

Statistical theories and microscopic experimental studies are highly developed fields that complement each other in exploring complex physical and biological processes. Statistical theories provide a robust framework to describe the emergent properties and collective behavior in systems with many interacting components, ranging from complex fluids to condensed matter physics. Whereas, advances in microscopic experimental techniques, such as high-resolution microscopy, spectroscopy, and scattering methods, enable precise observation and measurements at atomic and molecular scales [26]. However, such advances still face challenges in bridging length and time scales and capturing nonequilibrium systems [27].

Although advanced experimental techniques offer direct, often high-resolution, observations of phenomena with the least assumptions, they face challenges in controlling all of the state variables, interpreting data in complex environments, or accessing specific time or length scales. In contrast, molecular simulations excel

in providing detailed atomistic insights into the system under controlled conditions. Molecular simulations often allow researchers to examine system properties and investigate mechanisms in situations that cannot be isolated in experiments. Moreover, such simulations can sample rare events that are relatively hard to replicate in experiments. However, the simulation’s underperformance is linked to the accuracy of the models and force fields, which limits its predictive reliability for complex or poorly understood systems. Without the explicit use of macroscopic assumptions, these simulations can be understood as a bottom-up approach and are invaluable for hypothesis generation and testing. Conversely, the experiments are inherently top-down approaches, interpreting the data using macroscopic laws and theories after probing at the microscopic level. Thus, experiments remain essential for validating and grounding theoretical predictions in reality [28]. This thesis utilizes the bottom-up approach of molecular simulations to explore phase-separation kinetics in a nonequilibrium system.

The three basic simulation techniques are of *Monte Carlo* (MC), *molecular dynamics* (MD), and *Langevin* simulations. In principle, the simulations are classified into two main classes of *stochastic* and *deterministic* simulations [28–30]. The MC and *Langevin* simulations are stochastic, while MD is deterministic. The MC simulations use random sampling to explore only the configurational space and calculate equilibrium properties based on statistical mechanics. In the MD method, the configurational and the whole phase space are probed by solving Newton’s equation of motion, which preserves the system’s dynamics. The generated atomistic trajectories in MD are then utilized to study the systems’ dynamical properties, e.g., radial distribution functions (RDF), transport coefficients, structural and time-dependent correlation functions, etc. The *Langevin* simulations augment the MD method with additional stochastic and frictional force terms to model systems in contact with a thermal bath. A similar contact with a thermal bath is emulated in MD by coupling the system with an external thermostat. Which could be either explicit or implicit in the implementations, e.g., Langevin thermostat, velocity-rescaling, Andersen thermostat, etc., are explicitly added by changing the velocities on the fly [28, 31–33]. In contrast, thermostats like Nosé-Hoover are implicitly included in the system’s Hamiltonian itself [28, 31].

Molecular methods have contributed to studying phase-ordering kinetics in far-from-equilibrium systems [34–37]. These methods provide insights into the microscopic mechanisms governing domain growth, interface dynamics, and defect annihilation, which are challenging to access experimentally. MD is particularly effective in exploring the role of external driving forces, temperature quenches, and confinement effects on the kinetics of phase separation. Furthermore, its ability to simulate systems under varying nonequilibrium conditions makes it invaluable for investigating phenomena like spinodal decomposition and the nucleation process. Through its atomistic resolution, MD bridges the gap between microscopic interactions and macroscopic behaviors [28], offering a comprehensive framework

for understanding phase ordering in complex systems.

This chapter offers a detailed overview of the domain growth in the most straightforward system of phase-ordering kinetics, i.e., bulk phase separation in a binary mixture. We provide the requisite theory and the details of tools and methodologies applied to study the domain growth in such systems, which we also use in the subsequent chapters. The quantitative measures to characterize the domain growth in the systems exhibiting phase ordering are correlation functions, structure factors (Fourier transform of the correlation function), domain distribution functions, etc. During the late stages of domain growth, the system enters a dynamical scaling regime, where the coarsening patterns exhibit a characteristic time-dependent length scale $L(t)$. This results in the scaling of the correlation function $C(r, t) = f[r/L(t)]$, where $f(x)$ is the scaling function. The resultant patterns seem statistically self-similar in time if rescaled by the length scale $L(t)$.

The next part of this chapter is structured as follows. The upcoming section is a thermodynamic discourse on phase transitions, which sets the stage for subsequent discussion on the phase-separation kinetics in bulk and at surfaces. In Sec. 1.3, we briefly discuss the phase-separation kinetics in the bulk of a binary mixture and associated domain growth laws. Section 1.4 deals with the phase-separation kinetics in mixtures at surfaces. Finally, we provide an overview of this thesis in the last section 1.5.

1.2 Theoretical Background

Here, we give the details of phase separation happening in a bulk binary mixture (AB), where the bulk stands for the absence of any surfaces. During the transient process of phase separation, the homogeneously mixed state demixes into states composed of domains rich in either A or B components. This state transition is triggered by a sudden change in the system's thermodynamical control parameters, like temperature, pressure, etc., which makes the homogeneous phase unstable. Furthermore, for closed systems in equilibrium with external heat baths, the approach to the new equilibrium is guided by the minimization of Helmholtz free energy $F = U - TS$, where U and S commonly refer to internal energy and entropy, respectively. The governing forces and current towards the new equilibrium are generated from the derivatives of the free energy [2, 9, 38]. The section below summarizes the free energy forms and their components used to construct a continuum phase separation model.

1.2.1 Free Energy and Phase Diagram

Landau's phase transition theory is invoked to study phase separation in the continuum limits. Here, the system's state near the critical point is described by

Landau local free energy [39], f_{local} , expressed as a power series of the order parameter (ψ):

$$f_{local} = \frac{a}{2}(T - T_c)\psi^2 + \frac{b}{4}\psi^4. \quad (1.1)$$

For phase-separating binary mixture, ψ is the density difference ($n_A - n_B$) defined locally. The prefactors a and b are completely determined by symmetry conditions and convergence of f_{local} near the critical point [9].

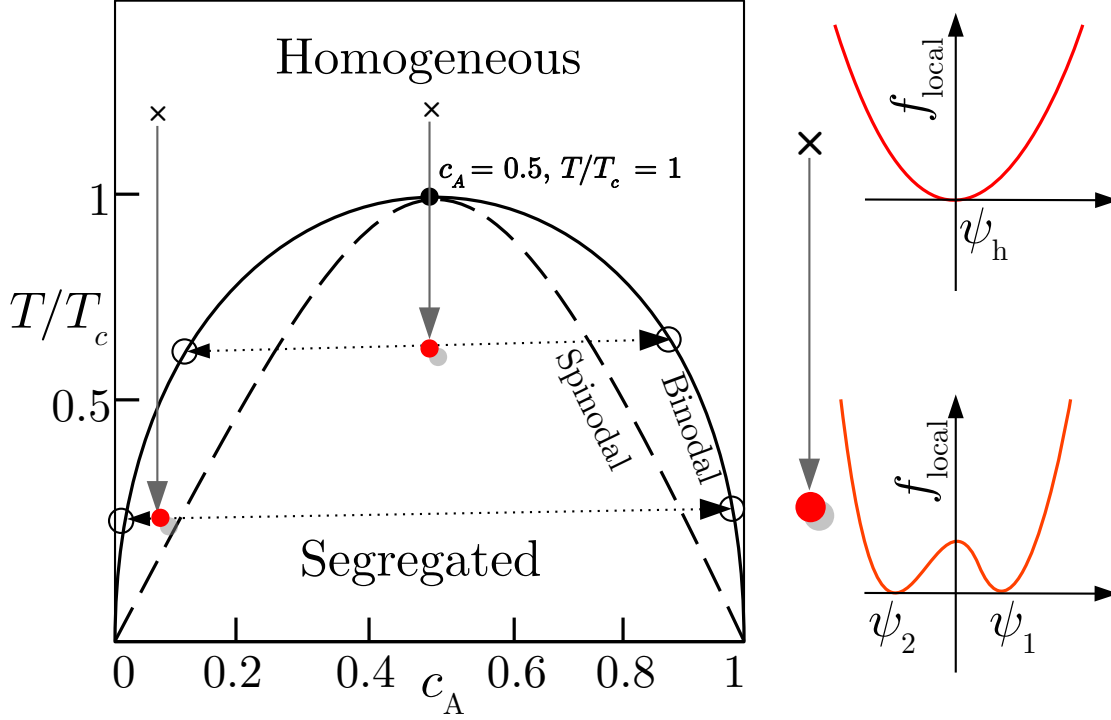


Figure 1.2.1: *Left:* A schematic phase diagram of a bulk binary mixture (AB) in the composition (c_A) and temperature plane. The solid line marked as binodal is the boundary separating the system's homogeneous and coexisting thermodynamic states. The spaced line marked as spinodal denotes an open boundary of an unstable segregated state, distinguishing it from a metastable demixed state also lying in the coexisting region. The symbols $\times$ and red circle represent states before and after the quench, respectively; a vertical line with a downward arrow highlights the transitions. In equilibrium, the compositions of the demixed phases after the quench are the binodal values (open circles) decided by the tie lines shown as horizontal dotted lines. A black-filled circle with $c_A = 0.5$ at the critical temperature shows a second-order critical point. *Right:* The behavior of Cahn-Hilliard free energy with the order parameter is shown right before (above T_c) and after the quench (below T_c).

Now, let us take a moment to see the behavior of f_{local} from the phase diagram of bulk systems. For binary mixtures, the phase diagram is typically plotted in terms

of temperature and species concentration c_A or c_B as shown in Fig. 1.2.1, where c represents the total concentration of a species. The homogeneous region in the phase diagram corresponds to the completely mixed states where f_{local} has only one minimum at $\psi_h = c_A - c_B$ ($\psi_h = 0$ for $T > T_c$ at critical composition $c_A = 0.5$). When the system is quenched to a state point (red circles) located inside the segregated region, f_{local} develops two minima located at ψ_1 and ψ_2 (corresponding to c_A values marked by the horizontal dotted lines for each quenched state point shown). The double minima in f_{local} denotes that the system exists as *two-phase* state with *A-rich* ($\psi_1 > \psi_h$) and *B-rich* ($\psi_2 < \psi_h$) domains. The volume fraction (x) covered by, let say *A* species, is calculated from the lever rule $\psi_h = x\psi_1 + (1 - x)\psi_2$.

A system undergoing a shallow quench may end up in the metastable region lying in between the spinodal and the binodal lines of Fig. 1.2.1, and the phase separation could only proceed via *nucleation and growth*. This region in the phase diagram is called the nucleation regime, where the metastable system is unstable only to high-amplitude, small-wavelength concentration fluctuations. However, for a deeper quench below the spinodal curve, the system becomes unstable even to small-amplitude, large-wavelength fluctuations, and therefore the phase separation proceeds spontaneously. This spontaneous phase segregation is known as the *spinodal decomposition*. The spaced spinodal line in Fig. 1.2.1 denotes that there is no clear boundary between phase separation via the *nucleation and growth* and *spinodal decomposition* [40]. Furthermore, the growth in the *spinodal decomposition* could also be explained in terms of negative free energy curvature, as the minimum of f_{local} suddenly changes to a maximum after the quench. Also, negative diffusion emerges here as the phase separation is driven by increased concentration differences, which is the opposite of usual pure diffusion evolving towards a system of uniform concentration differences.

Landau theory [9], just like any mean-field theory, does not account for non-local order-parameter fluctuations as it presumes a system free from any nonuniformities. However, the phase-separating binary mixtures exhibit concentration gradients when we move across the domain interfaces, separating different phases. The characteristic wavelength of these gradients grows with the domain coarsening. Near the critical point, these length scales blow up, and their inclusion in the system's large-wavelength effective Hamiltonian becomes necessary. Cahn and Hilliard have shown that the free energy functional $F[\psi(r)]$ in such a non-uniform system can be approximated as [41–43]

$$F = \int_V \left(f_{local} + \frac{1}{2} \kappa (\vec{\nabla} \psi)^2 \right) d\vec{r}. \quad (1.2)$$

Here, $\frac{1}{2} \kappa (\Delta \phi)^2$ term is the non-local contribution to the free energy. The parameter κ is the stiffness coefficient for the free energy gradients forming the

interfaces. It has the interfaces' enthalpic (concentration-independent) and entropic (concentration-dependent) contributions. The concentration-independent contributions are due to the effective interactions between the mixture components and account for the contact between the incompatible components. Whereas the concentration-dependency is related to configuration constraints associated with the system components, e.g., for polymer mixtures, it is the constrained number of configurations of the constituent polymer in the interfaces [44, 45]. Reasonable efforts are made to derive the form of κ , which provides experimentally validated interfacial energy. De Gennes first used random phase theory for the form of κ and explained the phase separation of polymer systems in a simple way [46].

1.2.2 Dynamical Models

Different dynamical models are listed in the classification scheme of Hohenberg and Halperin [47]. The formulation of these models is based on the conservation laws and the underlying physical mode of material transportation for the coarsening process [1, 48, 49]. For the diffusion-limited transportation modes and conservation of material [48, 50], as in binary alloys, the dynamics takes the form of a continuity equation $\partial\psi/\partial t = -\vec{\nabla}\cdot\vec{J}$. The current term is the diffusive flux vector $\vec{J} = -M\vec{\nabla}(\delta F/\delta\psi)$ due to the thermodynamical driving forces derived from the free energy functional. It ultimately takes the form of a Cahn-Hilliard-type phase-field model [9], and it reads

$$\frac{\partial\psi}{\partial t} = \vec{\nabla}\cdot\left(M\vec{\nabla}\frac{\delta F}{\delta\psi}\right), \quad (1.3)$$

where M is the phenomenological parameter related to the mobility of the constituent components in the concentration gradient. For simplicity, M here is a constant, and the equation assumes the same mobility for components in the two phases, with zero cross-mobility. However, M can also be temperature and concentration dependent. Furthermore, thermal fluctuations can be incorporated into the Cahn-Hilliard equation by including a Gaussian stochastic noise term $\vec{\eta}$, which obeys the fluctuation-dissipation theorem. The resultant model is the Cahn-Hilliard-Cook equation and is classified as *model B* in the Hohenberg-Halperin classification scheme [47].

Another relevant model is *model H* in the classification scheme, which accounts for diffusion and convective modes of material transportation [49, 51]. In this case, the generalized mass flux becomes $\vec{J} = -M\vec{\nabla}\delta F/\delta\psi + \psi\vec{v}$, here, the first term is the usual diffusion. The latter term describes the convection of the order parameter by a mean fluid velocity $\vec{v}$. The mean velocity itself is governed by the momentum-conserving generalized Navier-Stokes equations [52]. Other numerical schemes like molecular dynamics (MD) [28, 30] and Lattice-Boltzmann methods [53] inherently

incorporate hydrodynamics and are now widely used to understand the kinetics of phase separation in fluid mixtures, accounting for both diffusive transport and flow-induced demixing. In this thesis, we employ MD methods to highlight the importance of fluid flow in growth and coarsening.

1.3 Phase-Separation Kinetics of Binary Mixtures in Bulk

As a pedagogical exercise, we perform molecular dynamic simulations of spinodal decomposition in a bulk mixture to familiarize ourselves with the relevant tools for analyzing domain growth. We model phase separation in a symmetric binary mixture using the Lennard-Jones (LJ) potential to describe pairwise interactions. The LJ potential is given by

$$U(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right], \quad (1.4)$$

where r is the interparticle distance, ϵ represents the interaction strength, and σ is the characteristic length scale. For a symmetric binary mixture with components A and B , interaction parameters are set to $\epsilon_{AA} = \epsilon_{BB} = \epsilon_{AB} = \epsilon$ and $\sigma_{AA} = \sigma_{BB} = 2\sigma_{AB} = \sigma$, ensuring spontaneous phase separation below a critical temperature. The system is quenched to a reduced temperature $T^* = \frac{k_B T}{\epsilon}$, where k_B is the Boltzmann constant. In our bulk simulations, we have fixed the quench depth to $T^* = 1 = 0.7T_c$, where $T_c = 1.434$ is the bulk critical temperature [54, 55]. The quench drives the system into a two-phase region, leading to spinodal decomposition characterized by the growth of A -rich and B -rich domains over time [54, 56, 57].

The MD snapshots in Fig. 1.3.1 are of the 3d phase-separating binary mixture that captures the system's morphology after quenching it below the critical temperature. Analyzing these snapshots, we observe the evolution from a homogeneous phase-state to states with distinct domains of A -rich and B -rich phases. Also, the domains seem interconnected, bicontinuous structures characteristic of spinodal decomposition. The domain boundaries reflect the formation of interfaces due to phase separation. On average, the growing size of the domains shows evidence of coarsening, with larger structures dominating the field while smaller ones vanish. These snapshots vividly illustrate the dynamic interplay between diffusion and interfacial tension in shaping the emerging patterns.

1.3.1 Morphological Characterizations: Correlation Function and Structure Factor

Building upon the insights from the MD snapshots, domain morphologies in phase-separating binary mixtures can be quantitatively characterized using the equal-

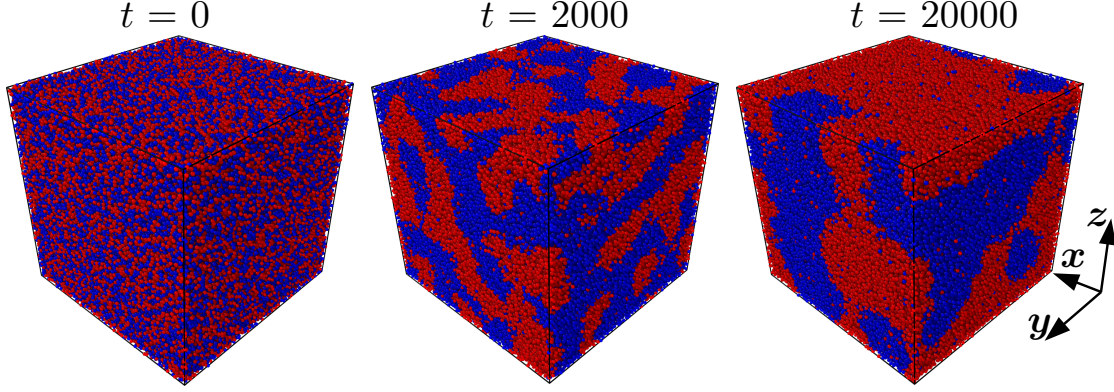


Figure 1.3.1: Snapshots from molecular dynamics (MD) simulations depicting the temporal evolution of phase separation in bulk binary mixtures after a deep quench in the phase diagram. The simulation box volume is $L^3 = 64^3$, with periodic boundaries in all directions. The emergent domain morphologies consist of bicontinuous A - and B -rich structures, particles shown in different colors, spanning the complete simulation box. The coarsening is highlighted by the size of growing domains in time from $t = 0$ to $t = 20000$.

time two-point correlation function $C(\vec{r}, t)$. This function is defined as

$$C(\vec{r}, t) = \langle \psi(\vec{R}, t) \psi(\vec{R} + \vec{r}, t) \rangle - \langle \psi(\vec{R}, t) \rangle \langle \psi(\vec{R} + \vec{r}, t) \rangle, \quad (1.5)$$

measures the spatial correlation of the order parameter ψ , such as concentration difference, over a distance $|\vec{r}| = r$. The decay of $C(r, t)$ (spherically-averaged $C(\vec{r}, t)$ for isotropic systems) with the distance r reflects the characteristic domain size $L(t)$. In practice, $L(t)$ is extracted as the distance where $C(r, t)$ falls to half its maximum value, providing an approximate measure of average domain size. It effectively measures the growth dynamics and the domain coarsening observed in the snapshots.

Further structural insights can be gained through the structure factor $S(\vec{k}, t)$, obtained as the Fourier transform of $C(\vec{r}, t)$:

$$S(\vec{k}, t) = \int e^{i\vec{k} \cdot \vec{r}} C(\vec{r}, t) d\vec{r}, \quad (1.6)$$

where k is the wavevector. $S(\vec{k}, t)$ highlights the spectral distribution of domain structures, with its peak indicating the dominant length scale in the system. The characteristic length $L(t)$ can also be derived from spherically-averaged $S(\vec{k}, t)$ to

obtain $S(k, t)$ for isotropic phase ordering and use its first moment:

$$L(t) = 2\pi \frac{\int_0^{k_m} S(k, t) k^{-1} dk}{\int_0^{k_m} S(k, t) dk}, \quad (1.7)$$

where k_m corresponds to the largest wave vector in the first Brillouin zone. $S(k, t)$ provides a complementary perspective, capturing the average domain size while accounting for contributions across all scales. The peak of $S(k, t)$ occurs at a wavevector $k^* \sim 1/L(t)$, and as the system evolves, the peak shifts with time, reflecting the growth of the characteristic domain size.

In systems where a single length scale dominates, the formed patterns exhibit a self-similarity feature in time, which is shown in the scaling behavior of $C(r, t)$ and $S(k, t)$. The scaling becomes particularly simple and can be described by universal scaling functions [58]. For $C(r, t)$ and $S(k, t)$ the scaling takes the form

$$C(r, t) = f\left(\frac{r}{L(t)}\right), \quad (1.8)$$

$$S(k, t) = L^d g(kL(t)), \quad (1.9)$$

where d is the dimension and $f(x)$ and $g(x)$ are the scaling functions that describe the distribution of domain sizes. The scaling thus captures the emergence of a single dominant length scale in the system, with the behavior of both $C(r, t)$ and $S(k, t)$ governed by the evolution of $L(t)$. Moreover, the functional form of $f(x)$ and $g(x)$ highlights the prevalent domain morphologies (droplet or bicontinuous) in the system.

The other general feature of the domain patterns is sharp interfaces, apart from the self-similarity, where Porod's law gives the corresponding statistical measure [59]. Porod's law dictates the short-distance singularities in the correlation function and structure factor, whose exact form was obtained by Bray and Humayun [60]. Their results show that for sharp interfaces, the structure-factor tail decays with a power-law form of $g(p) \sim p^{-(d+1)}$.

We demonstrate the dynamical scaling and Porod's law for domain morphologies presented in Fig. 1.3.1. To analyze the correlation functions and structure factors on MD trajectories, we coarse-grained the simulation box into a cubic lattice consisting of voxels (as shown in Fig. 1.3.2) and assigned $\psi(\vec{r})$ values to their centers. The $\psi(\vec{r})$ values were further refined by acknowledging contributions from neighboring voxels using the majority spin rule, effectively removing noise [61]. This approach ensured a more accurate representation of the spatial variations in the order parameter for subsequent analysis. Conservation constraints cause the scaled correlation functions for a critical composition to oscillate around the global order parameter ($\psi_0 = 0$), highlighting the bicontinuous domain morphology.

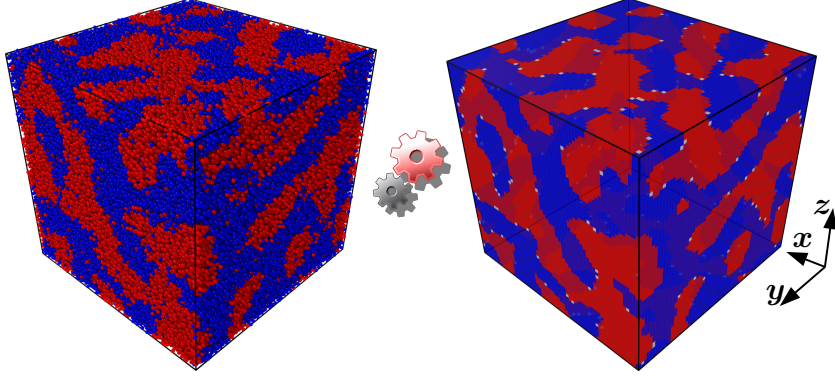


Figure 1.3.2: A schematic to explain the post-processing of raw MD trajectories (shown on the left) into a coarse-grained cubic lattice (shown on the right) consisting of voxels. We use the lattice to compute the correlation function and structure factor. The voxels represent unit cells with coordinates (i, j, k) and hold the order-parameter values $(\rho_A - \rho_B)$ after calculating it in that unit volume. The $\psi_{i,j,k}$ values are also processed further to remove the noise using the majority-spin rule explained in the text.

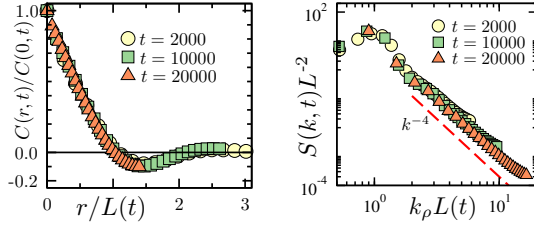


Figure 1.3.3: Scaled correlation functions (left) and structure factor plotted on a log-log scale (right) for the evolution shown in Fig. 1.3.1. The data is averaged over 20 independent runs with distinct initial states. The corresponding time for each data curve is shown as timestamps in each subplot. Porod's law is demonstrated as a spaced line having a slope of (-4) , characteristic of three-dimensional defects with sharp interfaces. The data overlap results from dynamical scaling, emphasizing the presence of a single length scale.

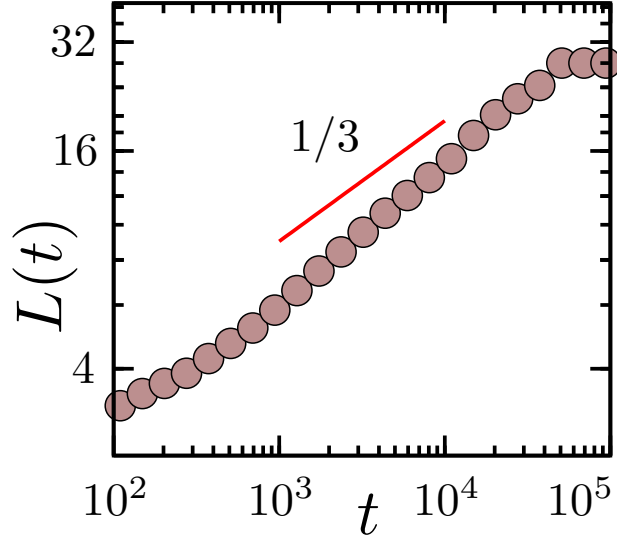


Figure 1.3.4: The growth of the length scale, $L(t)$, plotted vs. time, t , on a log-log plot. $L(t)$ is calculated as the first-zero crossing of correlation functions $C(r, t)$ analogous to what shown in Fig. 1.3.3. The solid line has a slope of $1/3$, denoting the LS growth law. The simulations were carried out with the particle velocities controlled by the Andersen thermostat, which does not conserve momentum at the local level.

1.3.2 Growth Laws

Considering only a single length scale operational in the phase-ordering system, its growth could be deduced up to the growth exponent from the governing dynamics just using the scaling hypothesis [48, 49, 62–66]. The diffusive current due to the chemical potential (μ) gradient is given by Eq. (1.3), which simply is written as $\vec{J} = M(\vec{\nabla}\mu)$, M being a constant. The system with an average domain size of $L(t)$ will have chemical potential at the surface given by the Laplace pressure $\mu \sim \gamma/L(t)$ (γ being the interfacial tension), and the spatial gradient term will contribute additional $1/L(t)$ because of the fluctuations with the characteristic wavelength $k^{-1} \sim L(t)$. That gives net current across the interface proportional to $|\vec{\nabla}\mu| \simeq \gamma/L(t)^2$, which in return drives the interface with a velocity equal to $v_{\text{int}} = dL(t)/dt \propto \gamma/L(t)^2$. The moving interfaces correlate with the domain growth where the domain average size grows as $L(t) \sim t^{1/3}$, and the interface velocity decreases as $v_{\text{int}} \sim t^{-2/3}$. The underlying diffusive growth mechanism belongs to *Ostwald ripening* or *evaporation-condensation process*, which is modeled by the Lifshitz-Slyzov-Wagner theory where the bigger domains (low curvature) feed on the domains of smaller size (high curvature) [62]. The domain growth results from our MD simulation in Fig. 1.3.4 closely follow the Lifshitz-Slyzov growth law [62]. Here, the reduced length scale data (expressed on the scale of σ) is plotted with reduced time (expressed on a scale of $t_{\text{LJ}} = \sqrt{m\sigma/\epsilon} = 1$) on

a log-log scale. We switch off the hydrodynamic environment by employing the Andersen thermostat [32] in the simulations, whose data we present in Fig. 1.3.4. The Andersen thermostat does not conserve momentum at the smaller length scales appropriate to sustain the hydrodynamics, as it frequently truncates the trajectories in the phase space.

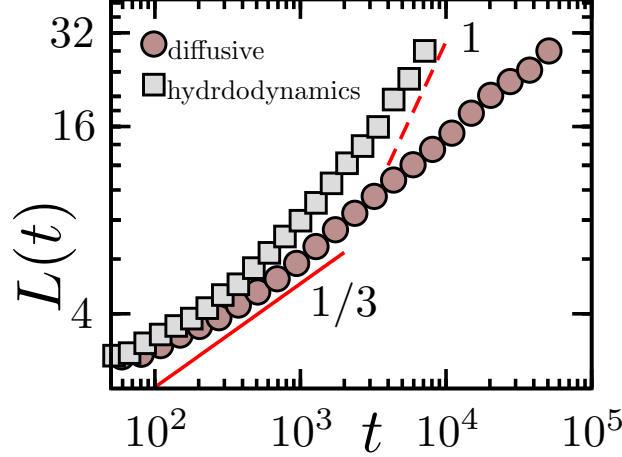


Figure 1.3.5: Length scale growth vs. time is analogous to what is shown in Fig. 1.3.4. The hydrodynamics results belong to the simulations implementing Nosè-Hoover thermostat, known to conserve momentum locally. The dashed and solid lines with slopes 1 and 1/3 denote the viscous-hydrodynamics and diffusive growth regimes, respectively.

Hydrodynamic Effects

To extend the understanding of the length scale growth beyond the diffusive dynamics as described by Lifshitz-Slyozov (LS) theory, we analyze the systems where the material could also be transported via fluid flow [48–51, 67–69]. The resultant dynamical model incorporating advection is referred to as *model H* in the Hohenberg-Halperin classification scheme (discussed in section 1.2.2) [47]. The flow field velocities $\vec{v}$ responsible for the advection of the order parameter is governed by the momentum conservation equations of Navier-Stokes [70], given as:

$$\rho \left(\frac{\partial \vec{v}}{\partial t} + \vec{v} \cdot \nabla \vec{v} \right) = -\nabla p + \eta \nabla^2 \vec{v}, \quad (1.10)$$

where $\vec{v}$ is the velocity field, p is the pressure, η is the dynamic viscosity, and ρ is the density. Effects of the fluid flow on the domain coarsening are further classified in regimes according to the Reynolds flow number (Re). Re for the flow in fluids parameterized by η , γ , and ρ is defined as the ratio of inertial forces to viscous drag, given in terms of the characteristic velocities ($v^* = \gamma/\eta$) as $Re = \rho v^* L / \eta = \rho \gamma L / \eta^2$. In the low Reynolds number regime ($Re \ll 1$), viscous forces

dominate, and the nonlinear term $\vec{v} \cdot \nabla \vec{v}$ is negligible. Balancing the viscous term $\eta \nabla^2 \vec{v} \sim \gamma/L^2$ with the pressure term $\nabla p \sim \nabla \mu$, the characteristic velocity scales as $v \sim \gamma/\eta$. Upon substituting the velocity into the advection length scale relation $dL/dt \sim v$, the length scale growth is derived as $L(t) \sim (\gamma/\eta)t$. This linear growth regime is known to be *surface-tension-driven*. In the high Reynolds number regime, i.e., $Re \gg 1$, which gives a crossover length scale of $L \gg \eta^2/\gamma\rho$, inertial forces dominate, and the viscous term is negligible. Here, the nonlinear term $\vec{v} \cdot \nabla \vec{v} \sim v^2/L$ balances with the chemical potential gradient term, $\nabla p \sim \gamma/\rho L^2$. From this balance, the velocity shows the scaling of $v \sim (\gamma/\rho)^{1/2} L^{1/2}$. When we substitute the scaling into the advection relation $dL/dt \sim v$, the length scale follows the *inertial hydrodynamics regime* with a growth of $L \sim (\gamma/\rho)^{1/3} t^{2/3}$ [49].

In Fig. 1.3.5, we provide the MD results contrasting the length scale during the diffusion-limited and hydrodynamic-enabled simulations. We replace the Andersen thermostat with the Nosé-Hoover thermostat as it is known to have hydrodynamic conserving capabilities [28, 69, 71]. The data in Fig. 1.3.5 clearly shows the contrast between the late-time growth regime due to viscous hydrodynamics versus one with only diffusive transport. However, the contrast is asymptotically true because there is a crossover regime for times earlier than that, where the length scale for both hydrodynamics-enabled and diffusion-limited studies shows similar diffusive growth. In this case, the interfaces are poorly developed to induce flow fields. The crossover to the viscous hydrodynamics occurs when the interface velocity $v_{\text{int}} \sim t^{-2/3}$ decays to match the characteristic velocities of the fluid [1].

Composition Effects

The mixture composition affects the domain coarsening process and the length scale growth. As shown in Fig. 1.3.6, quenches with an off-critical mixture produce disconnected domain morphology, where the domains are not interconnected, and the droplets of the minority phase are dispersed in the matrix of the majority phase. The minority droplets profoundly affect the length scale growth in fluids, as the hydrodynamics is ineffective for such disconnected domains. The difference is shown in Fig. 1.3.6, where we have added hydrodynamic-enabled simulation results for the bulk mixtures with the composition ratio of $A : B = 80 : 20$. Compared to the length scale growths for a critical composition, the viscous hydrodynamic regime is absent for the off-critical quench. The main reason is the absence of capillary effects for droplet morphologies. However, some other distinct coarsening mechanisms are active for such disconnected morphologies. Binder and Stauffer [58], Binder [65], and Siggia [63] came forward with mechanisms where the droplets may coalesce (facilitated by diffusion or hydrodynamics) into one another as they perform Brownian motion; however, the mechanism for 3d droplets leads to a growth regime of $L(t) \sim (k_B T t / \eta)^{1/3}$ [58, 63, 65], similar to that of the LS mechanism. Another mechanism arises on the pretext of many-body interac-

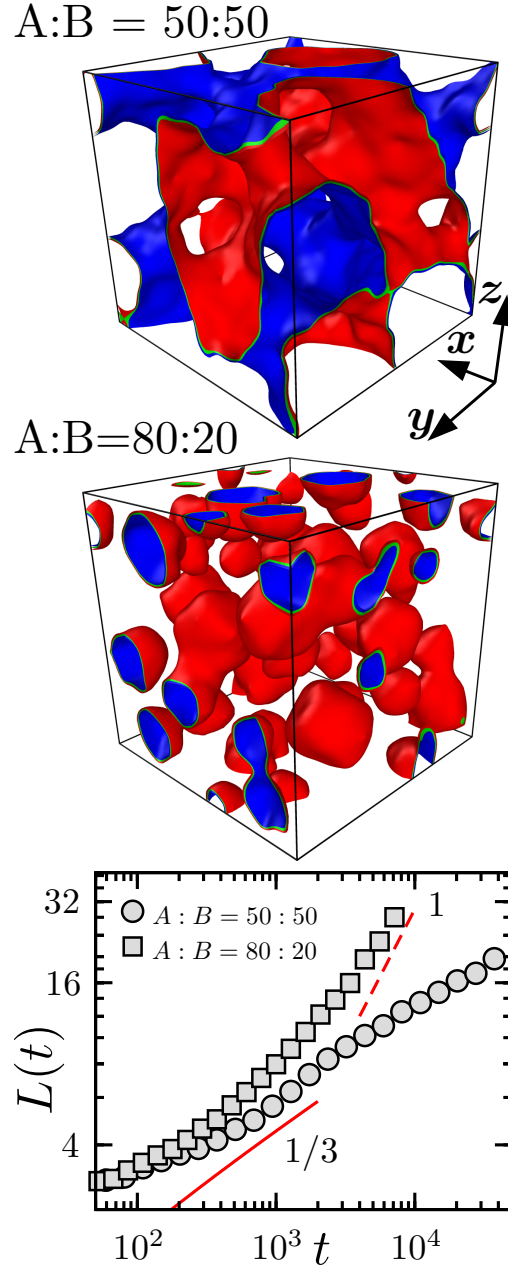


Figure 1.3.6: Domain morphologies in the phase-separating binary mixtures are shown as isosurfaces of A -rich (Red) and B -rich (Blue) phases for the critical ($A : B = 50 : 50$ or $\psi_0 = 0$) and off-critical quenches ($A : B = 80 : 20$ or $\psi_0 = 0.6$). The green isosurface represents the interfaces. The Length scale growth $[L(t)]$ analogous to the growth shown in Fig. 1.3.5, but for hydrodynamics-enabled simulations. The data corresponds to the critical quench and the off-critical quench. Slower growth in the off-critical quench highlights the role of domain connectivity in the viscous hydrodynamic regime (surface-tension-driven growth).

tions and hydrodynamics. It is known as coalescence-induced-coalescence [72–74], which, one more time, leads to a similar growth exponent of the LS growth law. For a non-hydrodynamic environment, like in alloys, the growth is LS for critical and off-critical quenches.

The literature on the growth exponents for solids and fluids is enormous and includes liquid-gas and liquid-liquid transitions, where density plays the role of composition in the former. We specifically highlight the works of Das and co-workers [69, 71, 75, 76] on liquid-liquid phase transitions in bulk mixtures, in which the authors have exhaustively addressed the role of mixture composition and the presence of a hydrodynamic environment on the growth dynamics and scaling laws. The results shown in the above figures completely agree with Das *et. al.* works. Finally, we provide a summary of the different growth regimes for fluids [1, 4, 77]:

$$\begin{aligned}
 L(t) &\sim (D\gamma t)^{1/3}, \quad L \ll (D\eta)^{1/2}, \quad (\text{diffusive regime}) \\
 &\sim \frac{\gamma t}{\eta}, \quad (D\eta)^{1/2} \ll L \ll \frac{\eta^2}{\rho\gamma}, \quad (\text{viscous hydrodynamic regime}) \\
 &\sim \frac{\gamma t^{2/3}}{\rho}, \quad \frac{\eta^2}{\rho\gamma} \ll L, \quad (\text{inertial hydrodynamic regime}).
 \end{aligned} \tag{1.11}$$

1.4 Phase-Separation Kinetics of Binary Mixtures at Surfaces

This section addresses the systems where the bulk phase separation occurs in contact with a surface [78]. We will familiarize ourselves with the equilibrium properties of wetting at a surface, the experimentally relevant features to explore, and the available theoretical models. Moreover, there has been a long-standing interest in the phase diagram of binary mixtures at surfaces [79–83]. However, the objectives of this thesis are directed towards the corresponding *far-from-equilibrium* problem. We consider a homogeneous binary mixture AB (at a high temperature) in contact with a surface that prefers A -rich phase. The system is quenched deep below the miscibility curve at the start, initiating the phase separation and simultaneous surface wetting by A . The dynamic interplay between these two processes of phase separation and wetting is referred to as *surface-directed spinodal decomposition* (SDSD). For over half a century, the SDSD has garnered intense theoretical [4, 18, 19], computational [1, 4, 77, 84, 85], and experimental [16, 17, 83, 86] interest.

Generally, the wetting surface under consideration can have any geometry with edges and sides contributing to the process. But, for simplicity, we stick to surfaces with semi-infinite geometries (no edges exposed to the process). The preferential

wetting by A may result in a partially wet (PW) or completely wet (CW) domain morphology at the surface. Where the angle made by the contact line between the preferred phase of A and non-preferred phase of B and the surface (S) is determined by Young's condition [78]

$$\gamma_{AB}\cos\theta = \gamma_{AS} - \gamma_{BS}. \quad (1.12)$$

Here $\gamma_{\alpha\beta}$ is the surface tension between the α and β domains ($\alpha, \beta \in A, B$ and S). If $\gamma_{AS} - \gamma_{BS} > \gamma_{AB}$, the preferred phase (A -type particles) completely wets the surface and might grow into a macroscopic wetting layer of thickness $R_1(t)$. Otherwise, domains of both phases coexist over the surface, forming a PW morphology, where the interfaces of A -rich and B -rich phases are not parallel, but make an angle $\theta > 0$ with the surface.

1.4.1 Experimentally Relevant Features

The first significant experimental study on SDSD was conducted by Jones et al. [16]. They investigated the coarsening behavior of critical mixtures of poly (ethylene-propylene) (PEP) and perdeuterated poly(ethylene propylene) (d-PEP) in contact with an open surface that exhibited a preferential attraction for d-PEP. Their observations revealed the emergence of composition waves (SDSD waves) originating at the surface and propagating into the bulk. These results, illustrated in Fig. 1.4.1, demonstrate the propagation of SDSD waves into the bulk, with wave vectors perpendicular to the surface. The wave denotes the formation of a multi-layered structure composed of successive wetting and depletion layers. The wetting layers, as shown in Fig. 1.4.1, have more dPEP than their average value in the bulk. The converse is true for the depletion layers. The first wetting-layer thickness, $R_1(t)$, is the depth at which the wave crosses the bulk value from above and is referred to as the *first-zero crossing*. Similarly, the *second-* [$R_2(t)$] and *third-zero crossing* [$R_3(t)$] can be extracted as the wave oscillates about the global composition value (the bulk value), representing the different length scales. A similar system was studied by Krausch et al. [86] using different experimental techniques. They observed that the *first-zero crossing*, $R_1(t)$, of the SDSD waves (as shown in Fig. 1.4.1) followed the LS growth law, $R_1(t) \sim t^{1/3}$. Krausch et al. also provided a detailed review of experimental techniques related to this phenomenon [17, 86].

Before proceeding, we summarize the key experimentally relevant aspects that any reasonable theoretical framework for SDSD must address [4, 11]:

1. The preferred component quickly enriches the surface, initiating SDSD waves that propagate into the bulk.
2. The morphology and evolution of these waves are critically influenced by whether the surface potential leads to a complete wetting (CW) or partial wetting (PW) morphology at equilibrium.

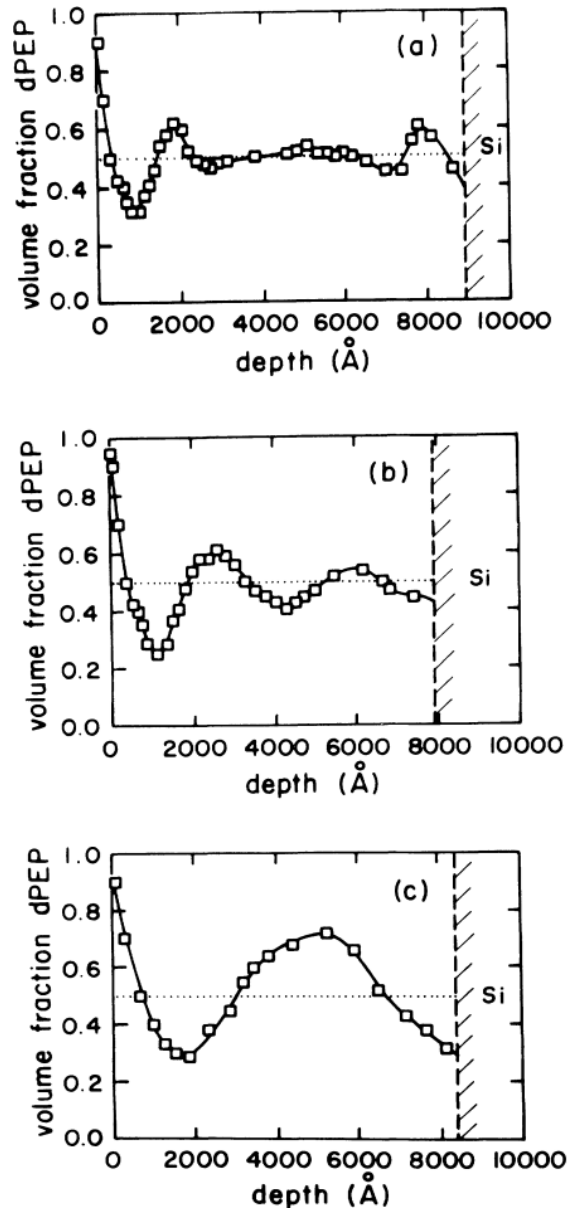


Figure 1.4.1: The SDSD process in an unstable polymer mixture of PEP and d-PEP is examined in an open surface preferentially wetted by d-PEP. The frames illustrate the depth-dependent, laterally-averaged volume fraction of d-PEP at three different times following the quench: (a) 19,220 seconds, (b) 64,440 seconds, and (c) 172,800 seconds. The dotted line represents the average composition. (Adapted from Ref. [16]).

3. The characteristics of domain growth near the wetting layer must be identified, including growth laws that govern coarsening parallel and perpendicular to the surface.
4. The interplay between surface interactions and bulk dynamics and how this shapes the overall phase separation process must be considered.

1.4.2 Theoretical Model of Surface-Directed Spinodal Decomposition (SDSD)

We briefly describe here the numerical models developed to study the SDSD. Puri-Binder (PB) [87, 88] gave the first successful on-lattice model for SDSD. Their approach involved deriving a Cahn-Hilliard-Cook (CHC) type coarse-grained equation of motion for the local density difference $\psi(\vec{r}, t)$. The evolutionary equations constitute free energy derived from a master equation that entails the microscopic details of the system. Further, the surface effects were modeled via two appropriate boundary conditions, and the surface's preference towards a particular species was enabled by a depth-dependent attractive potential included in the free energy functional. The beginning is owed to Binder and Frisch [89], who applied the master equation approach to the kinetic Ising model and developed a phenomenological model for the SDSD. They incorporated a delta-function surface potential for semi-infinite surface geometry. PB later refined this model, which explicitly introduced a zero-current boundary condition. Let us derive the PB model starting from general considerations.

In dimensionless form, the free energy functional for an unstable binary mixture AB in contact with a surface S (at $z = 0$) is expressed as [4, 19]:

$$\begin{aligned} \mathcal{F}[\psi] &\simeq \int d\vec{r} \left[-\frac{\psi^2}{2} + \frac{\psi^4}{4} + \frac{1}{4}(\vec{\nabla}\psi)^2 + V(z)\psi \right] \\ &+ \int d\vec{\rho} \left[-\frac{g}{2}(\psi(\vec{\rho}, 0))^2 - h_1\psi(\vec{\rho}, 0) - \gamma \frac{\partial\psi(\vec{\rho}, z)}{\partial z} \Big|_{z=0} \right], \quad (1.13) \\ &\simeq \mathcal{F}_B + \mathcal{F}_S \end{aligned}$$

where $\vec{r} \equiv (\vec{\rho}, z)$, and $\vec{\rho}$ and z denote coordinates parallel and perpendicular to the surface, respectively. In Eq. (1.13), the bulk free energy $\mathcal{F}_B$ includes the usual ψ^4 term from Cahn-Hilliard free energy plus a surface potential $V(z)$. The surface contribution $\mathcal{F}_S$ incorporates phenomenological parameters g , h_1 , and γ , which characterize the dimensionless surface field. $V(z)$ starts behind the surface so that any singularity in the potential does not lay at the surface. The term $\partial_z\psi|_{z=0}$ arises due to the absence of neighboring atoms below the surface (for $z < 0$). This expansion is rigorously justified near criticality, where the amplitude of ψ is small. However, we will use this free energy for parameter ranges far from criticality,

ensuring experimental relevance.

The corresponding coarse-grained dynamical model for phase separation driven by diffusion evolves the bulk order parameter according to the Cahn-Hilliard-Cook (CHC) equation:

$$\frac{\partial \psi(\vec{r}, t)}{\partial t} = \vec{\nabla} \cdot \left[\vec{\nabla} \left(-\psi + \psi^3 - \frac{1}{2} \nabla^2 \psi + V(z) \right) + \vec{\theta}(\vec{r}, t) \right], \quad (1.14)$$

where $\vec{\theta}(\vec{r}, t)$ represents Gaussian white noise satisfying the fluctuation-dissipation relation.

The corresponding dimensionless boundary conditions are as follows:

$$\frac{\partial \psi(\vec{r}_{\parallel}, 0, t)}{\partial t} = h_1 + g\psi(\vec{r}_{\parallel}, 0, t) + \gamma \frac{\partial \psi}{\partial z} \Big|_{z=0} + \tilde{\gamma} \nabla_{\parallel}^2 \psi(\vec{r}_{\parallel}, 0, t), \quad (1.15.1)$$

$$0 = \left\{ \frac{\partial}{\partial z} \left[-\psi + \psi^3 - \frac{1}{2} \nabla^2 \psi + V(z) \right] + \theta_z \right\} \Big|_{z=0}, \quad (1.15.2)$$

where $\tilde{\gamma}$ is a phenomenological parameter. Equation (1.15.1) ensures the rapid relaxation of ψ (can be replaced by a static version $\partial_t \psi = 0$) at the surface to its equilibrium value, while Eq. (1.15.2) reflects the absence of z -component flux at the surface. In systems where lateral diffusion dominates, the term $\tilde{\gamma} \nabla_{\parallel}^2 \psi(\vec{r}_{\parallel}, 0, t)$ in Eq. (1.15.1) can often be neglected, however, for CW cases it vanishes. The surface potential and the phenomenological parameters h_1 , g , γ , $\tilde{\gamma}$ determine the equilibrium phase diagram of the surface wetting [18, 87].

The diffusion-limited dynamical models inaccurately handle SDS in fluids; meanwhile, most experiments are done on fluids composed of polymers or low molecular weight mixtures. The hydrodynamics plays a significant role in the wetting kinetics [77, 90], as it does for phase separation in bulk mixtures. Therefore, one can consider microscopic models, like molecular dynamics (MD) and dissipative particle dynamics (DPD) [91, 92], which inherently include hydrodynamics. Alternatively, one can explicitly add the effects of a hydrodynamic environment by solving for the fluid flows as done in mesoscopic simulation techniques of lattice-boltzmann [53], stochastic-rotational dynamics [93], and *model H* framework listed in the Hohenberg and Halprin classifications scheme [47]. The appropriate boundary conditions governing the behavior of the order-parameter and velocity fields at the surfaces have to be implemented. The most common condition used for velocity fields is *no-slip* boundaries, where the velocities vanish at the surface. The phase separation at the surface has attracted considerable theoretical and experimental interest; however, an understanding from the microscopic perspective is preliminary. Our thesis leverages the credible ability of MD simulations to explore and unfold the dynamic interplay between wetting kinetics and phase separation in a hydrodynamic environment.

1.4.3 Phenomenological Theory of SDS

PB [87, 88] also developed a phenomenology theory to explain the experimentally observed growth kinetics of the wetting layer thickness, $R_1(t)$, along with the numerical simulations supporting it. Although the methodology we chose incorporates hydrodynamics naturally, the theory seems valid for other instances, such as off-critical mixture compositions and times before the onset of the viscous hydrodynamics growth regime. Hydrodynamic coarsening modes are absent in the former due to disconnected domain morphology, as seen for bulk systems undergoing SD in Sec. 1.3.2.

The phenomenology constitutes a current J_z in the z -direction (normal to the surface), which signifies the gradient in the depth profiles and has the form:

$$J_z \simeq - \left. \frac{dV(z)}{dz} \right|_{z=R_1} - \frac{\gamma}{Lh}. \quad (1.16)$$

The first term is the force contribution due to the surface potential $V(z)$. Consider a long-range potential with a power-law form of $V(z) = -\epsilon_a/z^n$ for $z > 0$, where z denotes the distance from the surface, n is the potential range, and ϵ_a is the potential strength at the surface ($V(z=0) = -\epsilon_a$). The second term represents the intrinsic chemical potential of the bulk domains, owing to the surface tension (γ) differences between them and the flat wetting layer separated by a depletion layer of width $h(t)$. The depletion layer width $= R_2(t) - R_1(t)$, where $R_1(t)$ and $R_2(t)$ are the first and second-zero crossing of the depth profiles at time t , analogous to what is shown in Fig. 1.4.1. Further approximating the multilayered morphology by a bilayer ($R_1(t) + h(t)$) and considering that it maintains the overall initial composition ψ_0 [94, 95], the depletion layer width could be approximated as $h(t) \simeq [(1 - \psi_0)/(1 + \psi_0)]R_1(t)$.

Upon substituting the forms of $h(t)$ and $V(z)$ in Eq. (1.16), we get

$$J_z \simeq - \frac{n \epsilon_a}{R_1^{n+1}} - \frac{\gamma}{L R_1} \left(\frac{1 + \psi_0}{1 - \psi_0} \right), \quad (1.17)$$

where the current leads to the wetting layer growth, *i.e.* $J_z = -dR_1/dt$. Depending upon the dominance of the two terms, we finally get the following growth regimes [4, 94],

$$R_1(t) \sim \begin{cases} (\epsilon_a t)^{1/(n+2)}, & t \ll t_c \text{ (potential-dependent regime)} \\ \sqrt{\frac{(1 + \psi_0)}{f(\psi_0)(1 - \psi_0)}} (\gamma t)^{1/3}, & t \gg t_c \text{ (diffusive regime)} \end{cases} \quad (1.18)$$

where $f(\psi_0)$ is the prefactor in bulk length scale growth $L(t) = f(\psi_0)(\gamma t)^{1/3}$ and

its exact expression is given in Ref [94]. The crossover time t_c between the two growth regimes can be obtained by equating the early-time and late-time length scales as (for $n > 1$)

$$t_c \sim h_1^{3/(n-1)} \gamma^{-(n+2)/(n-1)} \left[\frac{f(\psi_0)(1 - \psi_0)}{(1 + \psi_0)} \right]^{3(n+2)/[2(n-1)]}. \quad (1.19)$$

From the above equation, it is evident that the potential-dependent regime [$R_1(t) \sim t^{1/(n+2)}$] depends on the surface field strength ϵ_a as well as the exponent n , but is independent of the composition ratio of the system.

We have seen that during the diffusive regime, the symmetry exhibited by the bulk binary mixtures (AB), under the interchange of A and B species, results in the same growth exponent impervious to the nature of the minority and majority phases. This means that the systems with off-critical compositions where A is in the minority and B forms the majority, or vice versa, will have domains that grow similarly. However, for the wetting layer growth, the symmetry is violated by the sign of the surface-tension term γ in Eq. (1.16) for the off-critical quenches ($A : B \neq 50 : 50$). This sign change gives rise to two critical cases of the wetting layer growth for the diffusive regime referred to as the *minority wetting* and *majority wetting*. The *minority wetting* corresponds to the case of the wetting phase having a lower composition than the nonwetting phase. In this case, the droplets of the wetting phase (A) form in bulk [34, 96] and feed the wetting layer growth as the chemical potential difference is positive.

In contrast, during the *majority wetting*, droplets of the non-wetting phase (B) have a lower chemical potential than the wetting layer. This causes a negative chemical potential difference and reverses the direction of the current J_z . This time, the wetting layer feeds the droplets of the minority phase (B) [94].

1.5 Thesis Overview

The thesis chapters use molecular dynamic simulations to provide detailed insights into wetting kinetics and phase separation, emphasizing the role of hydrodynamics in understanding the complex and multiscale phenomena of SDS. Throughout, hydrodynamics-incorporated simulations play a pivotal role in capturing the subtleties of the domain coarsening near the surface from the early to late stages.

Chapter 2 focuses on the early-time potential-dependent growth of the wetting layer during critical quenches, exploring the influence of long-range and short-range interaction potentials. The simulations reveal growth exponents depending upon the potential range, followed by distinct growth regimes, offering insights into the existence of hydrodynamics at the early stage of wetting kinetics.

In Chapter 3, the study shifts to the early-time growth dynamics for the off-critical quenches involving the majority- and minority-wetting scenarios. By ex-

tending the investigation to asymmetric compositions, the simulations provide a nuanced understanding of the reasons for deviations from the Puri-Binder phenomenological theory of wetting layer growth.

The fourth chapter examines both early- and late-time wetting kinetics, emphasizing the dynamic interplay between wetting processes and phase separation on amorphous surfaces. Replacing the flat walls used in the first two chapters with a rough, amorphous wall enabled us to procure length scales at the late stages of the domain growth. Further, the study provides a comprehensive view of how hydrodynamics influence these intertwined dynamics across time scales in contrast to the diffusive dynamical models.

Finally, Chapter 5 explores the effects of surface chemical heterogeneity or patterning on the phase-separation kinetics in the bulk and near the surface. Through hydrodynamically resolved MD simulations, the influence of surface inhomogeneities on wetting and phase behavior is elucidated, offering a detailed understanding of how patterned surfaces can modulate kinetic and structural evolution during phase separation.

In summary, this thesis demonstrates how hydrodynamic-enabled numerical simulations are indispensable for revealing the intricate mechanism of wetting and phase separation across various conditions, advancing our understanding of these fundamental processes. This understanding participates in developing methods to create functional materials for advanced technological applications.

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