

Chapter 4

Critical Quenches Over an Amorphous Wall

In this chapter, we employ molecular dynamics simulations to investigate the dynamic interplay of wetting kinetics and phase separation on an amorphous wall. The mixture does not exhibit surface-induced crystallization by choosing an amorphous wall, as seen for integrated flat walls implemented in the previous two chapters. This change enabled us to examine the wetting kinetics at larger length scales present in the late stages of SDSD. For a phase-separating binary mixture (AB), complete wetting occurs over the wall by the A -type particles, and a macroscopic wetting layer of thickness $R_1(t)$ forms over it. Using morphological characterization, we identify relevant length scales of phase ordering in the direction parallel [$L_{||}$] and perpendicular [$L_{\perp}$] to the wetting wall. Our results on the length scale growth (R_1 , $L_{\perp}$, and $L_{||}$) show a power-law form ($\sim t^{\alpha}$) with the same growth exponents α for a given coarsening regime ($\alpha = 1/3$ and 1 for the diffusive and viscous hydrodynamics regime, respectively), but with varying magnitudes of growth. Diffusion-limited studies show asymmetric domain coarsening near the wetting wall, apparently due to the orientational effects of the wetting and depletion layers. In contrast, no such asymmetrical domain coarsening occurs in our MD results with or without hydrodynamics. We provide phenomenological arguments for the contrasting results obtained in our simulations.

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*Interaction of wetting kinetics and spinodal decomposition in
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4.1 Introduction

As emphasized in previous chapters, the phase-separating binary mixture (AB) showcases interesting kinetics of pattern formation comprising domains of A -rich and B -rich phases when quenched far below its spinodal temperature [1–4]. Not surprisingly, various pattern morphologies exist for mixtures undergoing spinodal decomposition that appear for distinct mixture compositions and geometrical confinements. Fully symmetric critical mixtures ($N_A/N_B : 50/50$, where N_A and N_B are the total numbers of A -type and B -type particles, respectively), at late times, decompose into a bicontinuous structure with the domains of ordered phases demarcated by sharp interfaces. The bulk patterns are isotropic and are characterized by two-point equal-time correlation functions and structure factors [1], defined as:

$$C(r, t) = \langle \psi(\vec{r}_1, t) \psi(\vec{r}_2, t) \rangle - \langle \psi(\vec{r}_1) \rangle \langle \psi(\vec{r}_2) \rangle, \quad (4.1.1)$$

$$S(k, t) = \int d\vec{r} e^{i\vec{k} \cdot \vec{r}} C(r, t). \quad (4.1.2)$$

Here, ψ is the local density difference and is commonly used as the order parameter for phase separation studies in binary mixtures. For systems where the domains grow symmetrically in all directions, the associated length scale can be calculated from the structure factor $S(k, t)$ as $L(t) = 2\pi \int S(k, t) dk / \int k S(k, t) dk$.

The domain patterns are complex entities imbued with interesting physical properties like self-similarity, percolation thresholds, interface roughness, topological defects, etc. During the coarsening process, the self-similarity of patterns is exhibited in the dynamical scaling [5] of correlation functions and structure factors:

$$C(r, t) = g\left[\frac{r}{L(t)}\right], \quad (4.2.1)$$

$$S(k, t) = L(t)^d f[kL(t)]. \quad (4.2.2)$$

The time dependence in the spatial correlations for d -dimensional patterns is only a matter of scale factor; as a result, during the dynamical scaling regime, all correlation curves collapse onto a universal master curve irrespective of the microscopic details of the coarsening process. Besides, $L(t)$ grows with a power-law form of $d_0 t^\alpha$, where the exponent α underlines the physical process and conservation laws, and the prefactor signifies the role played by the local properties of the system. The exponent also decides the form of the scaling functions $g(x)$ and $f(x)$, which are time-independent.

In fluids, the physics of spinodal decomposition involves capillary effects, viscous dissipation, and inertial forces, as asserted by Siggia and Furukawa [6–9]. Thus, a fluid with physical parameters such as the self-diffusion coefficient D ,

fluid mass density ρ , shear viscosity η , and interfacial tension γ , show different growth laws at different length and time scales. For length scales $L(t) \ll (D\eta)^{1/2}$, the diffusion is the dominant force and $L(t)$ grows as $(D\sigma t)^{1/3}$ ($\alpha = 1/2$ for non-conserved order parameter). For intermediate times, when the surface energy density and the viscous dissipation balances each other, $(D\eta)^{1/2} \ll L(t) \ll \eta^2/\rho\gamma$, the creeping flow accelerates the coarsening process and generates a growth of $L(t) \propto (\sigma/\eta)t$. The creeping flow, commonly called surface-tension-driven flow, sustains flows only in a low Reynolds number regime. Later, for higher Reynolds number flows ($\eta^2/\rho\gamma \ll L(t)$), the nonlinearity due to fluid inertia makes the fluid more turbulent, and the coarsening process enters the inertial regime. In this regime $L(t)$ grows like $(\gamma/\rho)^{1/3} t^{2/3}$. Most of these growth regimes and the crossovers are accessible via experiments and mesoscopic simulations. However, some still evade the confirmations from molecular simulations due to the excessive computational demands.

A boundaryless demixing emulates a bulk behavior with the growth of isotropic composition fluctuations. However, as stated previously, such systems are not free of effects induced by the surrounding surfaces. Notably, surface effects are not limited to the thickness of some molecular length scales, but are felt at a higher order of molecular distances [2, 10, 11]. During surface-directed spinodal decomposition (SDSD), the wetting evolves to either a completely wet or a partially wet equilibrium morphology, governed by the *Young's condition* [12]:

$$\gamma_{AB}\cos(\theta) = \gamma_{BS} - \gamma_{AS}, \quad (4.3)$$

here, γ_{AS} and γ_{BS} are surface tensions between the A -rich and B -rich phases and S (wall's surface), respectively, and $\gamma_{AS} < \gamma_{BS}$ (preferential attraction of A particles towards the surface). Equation (4.3) has no solution for $\gamma_{BS} - \gamma_{AS} > \gamma_{AB}$, and thus the B -phase is expelled completely resulting into a completely wet surface of an A -rich wetting layer of macroscopic size (away from the critical point). In response, the wetting process produces composition waves normal to the wall, called the SDSD wave, that disappear deep inside the bulk [13, 14]. The SDSD is inevitable during the fabrication of metal oxide semiconductors [15] and organic electronics [16–18] via processes like atomic layer deposition and solvent evaporation (drying). Therefore, it finds utilization in developing high-dielectric gate transistors [15], bulk heterojunctions in organic electronics [18–25], etc. There are many other applications that we have already listed in our earlier publications [26].

Because the wall breaks the system's symmetry in the z -direction (wall placed in xy plane), we decompose $L(t)$ into parallel $[L_{\parallel}(z, t)]$ and perpendicular length scales $[L_{\perp}(y, t)$ or $L_{\perp}(x, t)]$ that correspond to wavelengths of the characteristic fluctuations (proportional to the average domain sizes) parallel and perpendicular to the wall. Moreover, an additional length scale is added to the system in the form of the wetting layer thickness $R_1(t)$, which has been the subject of intense scrutiny

via experiments [10, 18, 23, 27–32], theory [33–39], and simulations [2, 3, 13, 40–58]. The presence of different length scales may occur due to the finite simulation time and box size. Therefore, we are interested in the scaling hypothesis and growth laws for these length scales during our simulation time. However, they should converge to a single-length scale at late times.

We recall here an investigation of Puri and Binder [59] focused on the phase-separation kinetics of a critical binary mixture with the surface exerting a long-range attraction $V(z) \sim z^{-n}$, where n denotes the range. In their numerical simulations, the wetting layer thickness $R_1(t)$ grew as $t^{1/(n+2)}$ (potential-dependent growth) for early times, and it later makes a crossover to the universal diffusive regime $t^{1/3}$. Furthermore, the depth-dependent parallel length scale exhibits growth of $L_{\parallel}(z, t) \sim t^{1/2}$ in layers close to the wetting wall. For their diffusion-limited model, the growth exponent of $1/2$ was greater than the diffusive exponent of $1/3$. Therefore, they called this growth an accelerated growth regime. From this point on, we will stick to this terminology. Their results also exhibited an asymmetric domain growth in the composition of wave-affected layers, which they attributed to the orientational effects of the lateral phase ordering. The asymmetric coarsening results in elongated domains oriented parallel to the wetting wall, which improves the chances of droplet-droplet coalescence parallel to the wall and produces the accelerated growth regime of $t^{1/2}$. Their results form a benchmark for diffusion-limited investigations of SDS. However, our current endeavor looks for the deviations that hydrodynamic forces will bring to the complex interaction between wetting kinetics and phase separation. We are concerned not only with the changes at asymptotic length and time scales that are already established [7, 9], but also for very early times where the experiments with polymer mixtures have exhibited controversial fast mode ($\alpha \approx 3/2$) [2, 30–32, 34, 35, 53, 60].

As pointed out in previous chapters, there are MD studies of SDS for various geometries and confinements, like semi-infinite geometry [13, 26, 46, 53, 61–63], thin films [13, 64–66], etc. The works of Jaiswal *et al.* [26, 46, 61, 62] are parallel to our current setup but carry a critical difference. All of these MD works share the common feature of representing the surface by an integrated Lennard-Jones potential. The integrated potential smoothens the surface’s roughness to a tiny scale, unnoticed by the fluid. This smooth surface model exhibited stacking of particles in layers near the surface [53, 63, 64], which induces anisotropic density fluctuations in the direction parallel and perpendicular to the wall. For instance, Jaiswal *et al.* [26, 46] could access a wetting layer thickness of 2.5 times the particle size under the complete wetting and 5 times the particle size for the partial wetting before the mixture completely crystallizes into layers and solidifies into a crystalline state. Furthermore, some studies have used structured walls with face-centered cubic (FCC) lattice to investigate SDS in thick films using MD [63], and in thin films and nanopores via dissipative particle dynamics (DPD) simulation [67, 68]. However, the crystalline state of the wall also produced similar

layering effects.

This chapter focuses on eliminating the layering effects by replacing the integrated wall with an amorphous wall composed of particles. The latter increases the surface's roughness up to the fluid particle scale. Our effort to make rougher walls has been fruitful, and we could capture the wetting layer growth for larger lengths and time scales. Relaxed fluid density near the walls means removal of the particle layering and consequently lowers the chances of wall-induced crystallization of the mixture. We foresee that attempts will be made to investigate phase separation kinetics in thick and thin films [13, 14, 64–66, 66] with these new features of rough walls. Subsequently, we investigate the domain coarsening parallel and perpendicular to the wall, extracting the growth exponents and examining the key questions on the existence of the *fast-mode kinetics* and the anisotropic domain coarsening near the wetting wall.

4.2 Methodology and Numerical Details:

We have simulated SDSD on an amorphous substrate using molecular dynamics (MD) simulation. We use the LAMMPS [69] engine to run MD for our setup in parallel mode, which enables us to efficiently obtain asymptotic length and time scales. We begin with a simulation box of volume $L_x \times L_y \times L_D$, where the box is compartmentalized into the regions of fluid and walls. The fluid is confined between walls present in the z -direction, while the simulation box is periodic in the xy directions.

The particle-particle interaction is modeled via the standard 12-6 Lennard-Jones (LJ) potential, given as

$$U_{\alpha\beta}(r) = 4\epsilon_{\alpha\beta} \left[\left(\frac{\sigma_{\alpha\beta}}{r} \right)^{12} - \left(\frac{\sigma_{\alpha\beta}}{r} \right)^6 \right], \quad (4.4)$$

where $\epsilon_{\alpha\beta}$ and $\sigma_{\alpha\beta}$ set the interaction strength and overlap distance for different particle pairs ($\alpha, \beta \in \{A, B\}$). We set $\epsilon_{AA} = \epsilon_{BB} = 2\epsilon_{AB} = \epsilon$ and $\sigma_{AA} = \sigma_{BB} = \sigma_{AB} = \sigma$ to model phase separation in a symmetric binary mixture, following the previous MD simulations of SD and SDSD [46, 61, 62, 70, 71]. The wetting occurs by tuning the interaction strength between the wall particles and the fluid. The bottom wall prefers A -type, whereas the top substrate is neutral. Moreover, the top and bottom walls are neutral to B -type particles. The neutral interactions are modeled via Weeks-Chandler-Andersen (WCA) [72] form, given by

$$\phi_{WCA}(r) = \begin{cases} 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] + \phi_c, & r < 2^{1/6}\sigma \\ 0, & r \geq \sigma \end{cases} \quad (4.5)$$

where we truncate the potential at its minimum and then shift the potential by a

constant such that $\phi_c(2^{1/6}\sigma) = 0$. The parameters for $U_{\alpha\beta}$ and ϕ_{WCA} between the wall atoms and the fluid are set to $\epsilon_{AS} = \epsilon_{BS} = \epsilon$ and $\sigma_{AS} = \sigma_{BS} = \sigma$. Recall that the neutral interaction does not attract any fluid particles. Therefore, the fluid particles are repelled by the neutral walls. The current set of parameters results in complete wetting of the bottom wall (at $z = 0$) by A -type particles. Furthermore, all measurements are expressed in the basic units of energy ($\epsilon = k_B T$), distance (σ), and mass (m), which we further set to 1. That gives us the reduced time $t = \sqrt{m\sigma^2/\epsilon} = 1$. Also, we followed the standard procedure of truncating and shifting the potential in Eq. (4.4), such that both the potential and the force approach zero smoothly at the cutoff $R_c = 2.5 \sigma$ [73].

The volume of the fluid box is set to $128 \times 128 \times 128 \sigma^3$, and the walls of size $128 \times 128 \times 2 \sigma^3$ are placed at the top ($z = 66$) and at the bottom ($z = 0$) of the fluid box. We fix the number density of the fluid particles to $\rho_N = 1$ to make it incompressible, which, together with the chosen temperature, avoids the liquid-gas phase transition. It is known from previous investigations [71, 74] of bulk phase separation that the scaling laws describing the growth of average domain size are not affected until the latter reaches the size of the box itself. For the chosen simulation box and periodic boundary conditions, we could emulate the bulk behavior in the xy -direction with the average domain size reaching a maximum of $32\sigma = 1/4$ ($L_x = L_y = 128\sigma$). Furthermore, the current wetting parameters correspond to the first-order wetting transition [62], producing a finitely thick wetting layer in equilibrium. Thus, we avoid difficulties that arise in critical transitions, where the length scale associated with the fluctuations blows up. In our investigation, the maximum value of wetting layer thickness is equal to the size of bulk domains, after which we could see its saturation due to the finite size of the simulation box.

Next, we discuss the simulation protocol that we used. We start by equilibrating the fluid mixture at a high temperature for $t < 0$ to have a homogeneously mixed state with walls in place. At $t = 0$, we change the temperature to $0.7T_c$ (T_c is the bulk critical temperature $\simeq 1.423$) [75, 76] in our thermostat. The system is instantly brought to the lower temperature, and the fluid starts demixing for $t > 0$ in the presence of the walls. The velocity-verlet [73, 77] integrator was used to update the position and velocities of the fluid particles, whereas the positions and velocities of wall particles were never updated. Thus, the wall particles are fixed in spacetime and contribute only to the pairwise forces with the fluid. The temperature of the fluid is maintained via the Nosé-Hoover thermostat, which preserves the hydrodynamics [70, 71, 77].

We start recording trajectories of the fluid particles for $t > 0$. As time averaging was not possible for the nonequilibrium process of phase separation, we ran 20 independent simulations with different realizations of the initial configurations and thermostat noise. For morphological characterizations and computation of average domain size, the simulation box with atomic positions is mapped to a cubic lattice

using the majority-spin rule [46, 74, 78]. The mapping details are described in detail in the upcoming section.

4.3 Molecular Dynamics Results

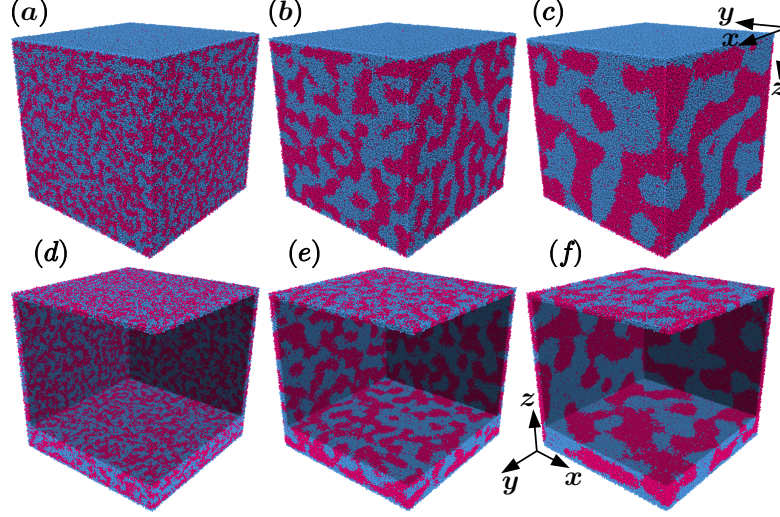


Figure 4.3.1: Upper panel: The time evolutionary snapshots of surface-directed spinodal decomposition in a simulation box of volume $L_x \times L_y \times L_D = 128\sigma \times 128\sigma \times 128\sigma$. Wetting occurs on the top wall located at $z = 0$. The two particle types in the binary mixture ($A+B$) are shown in blue (A -type) and pink (B -type) colors. The snapshots shown here are for the time $t > 0$ for a single quench to $T = 0.7T_c$ at $t = 0$, where $T_c (\simeq 1.423)$ is the bulk critical temperature. The snapshots belong to times (a) $t = 200$, (b) $t = 500$, and (c) $t = 3000$. Lower panel: An upside-down perspective of the 3d snapshots is shown in the upper panel. The cuts through the depletion region showcase the domain morphology prevalent for the different coarsening regimes.

This section contains qualitative illustrations of domain morphologies and the quantitative results of their coarsening in time. We begin with the illustrations of surface-directed spinodal decomposition (SDSD) presented as snapshots in Fig. 4.3.1. These snapshots belong to different growth regimes of $R_1(t)$ and exhibit the crucial morphological features required for a growth regime. Starting with the top wall at $z = 0$ getting coated with A -type particles for $t \geq 100$, the subsequent snapshots display the coarsening of the wetting layer and bulk domains together. Adjacent to the wetting layer, a region depleted in A -type particles is formed, hence denoted as a depletion layer. Notably, the average concentration of A -type particles in the depletion layer does not decay to zero with time, but its composition saturates at $A : B = 25 : 75$. Primarily, the depletion layer forms an impressive network of tubes connecting the bulk and the wetting layer. The existence of these tubes and

their length create a contrast between the diffusive growth of the wetting layer and the faster growth due to hydrodynamics [2, 52, 79–82]. The cuts in the lower panel of Fig. 4.3.1 efficiently display the interconnected domains perpendicular and parallel to the wetting wall for most of the simulation times, and we do not notice any asymmetrically shaped isolated droplets above the depletion layer. Further, the viscous-growth regime of hydrodynamics is possible only when long enough correlations (larger tube lengths) and well-defined interfaces have developed.

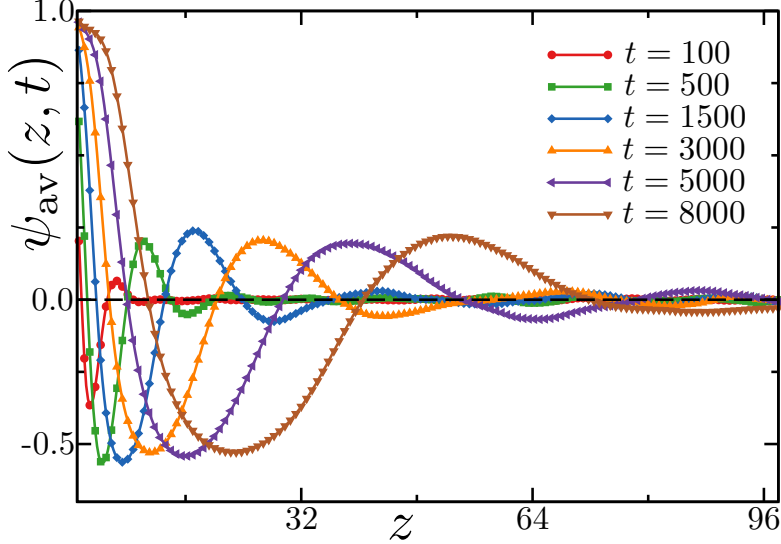


Figure 4.3.2: Laterally averaged order-parameter profiles, $\psi_{av}(z, t)$, with time specified. The profiles are constructed using a slab width of $\Delta z = 0.5$.

Our first quantitative analysis is highly credited to the depth-profiling techniques of the mixture compositions from the experiments [10, 83]. In a similar spirit and following our prior work on SDS [46, 62, 84], we present the laterally-averaged order-parameter profiles $\psi_{av}(z, t)$ as a function of depth z in Fig. 4.3.2. These profiles are computed as defined as

$$\psi_{av}(z, t) = \frac{1}{L_x \times L_y} \int_0^{L_x} \int_0^{L_y} \psi(x, y, z, t) dx dy. \quad (4.6)$$

The numerical adaptation of the above equation is straightforward and is done in the following manner. At first, the simulation box is partitioned into slabs of size $L_x \times L_y \times \Delta z$, where $\Delta z = 0.5\sigma$ is the slab width in the z -direction, positioned at depth z . Finally, $\psi_{av}(z, t)$ for each slab is equal to the composition obtained by the number difference of A -type and B -type particles.

The damped oscillatory profiles of Fig. 4.3.2 denote the multilayered morphology composed of alternate wetting and depletion layers. Such multilayered morphology stems strictly from the conservation of material ($\int_0^{L_z} \psi_{av}(z, t) dz = \psi_0 = 0$)

along the z -direction [59]. These composition waves, known as the SDSA waves [13], perform damped oscillations about the global composition ψ_0 and vanish while penetrating the bulk where it encounters the randomly oriented composition fluctuations.

4.3.1 The Growth of the Wetting Layer Thickness $R_1(t)$

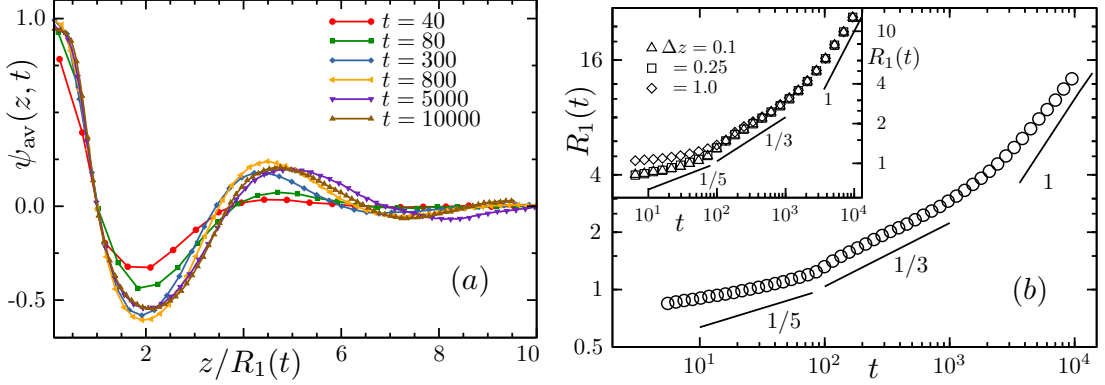


Figure 4.3.3: (a) Scaled version of the laterally-averaged order parameter $\psi_{av(z,t)}$ profiles shown in Fig. 4.3.2. The scaling factor is $R_1(t)$, which is calculated as the first-zero crossing of $\psi_{av(z,t)}$ along z . (b) The wetting layer thickness, $R_1(t)$, vs. time plotted on a log-log scale. The solid lines have slopes of 1/5, 1/3, and 1, depicting potential-dependent, diffusive, and viscous hydrodynamics growth. Inset: $R_1(t)$ growth for different slab widths denoting the different levels of precisions.

Next, in Fig. 4.3.3(a), we plot the scaling behavior of the SDSA profiles shown in Fig. 4.3.2. The scaling of the profiles is done using $R_1(t)$, which we compute from the *first-zero* crossing of the profiles of Fig. 4.3.2. The dynamical scaling hypothesis seems reasonable for two different time regimes, later than $t > 80$. Here, the sound data collapse for the small distances from the wall shows that $R_1(t)$ is the dominant length scale near the wetting wall. There is also a noticeable change in the scaling function form for times $t > 800$. However, such scaling is absent for $t < 100$ during the early-time kinetics of wetting layer formation when the characteristic oscillations (the SDSA waves) have not yet been established. Interestingly, the dynamic scaling hypothesis applies to cases with isotropic growth in all directions, such as in bulk. However, its extension to systems with a non-vanishing current in the scaling direction (concentration gradients due to the wall potential) is noteworthy [43]. The wavelength of the characteristic oscillations, we mentioned a moment ago, is extracted from the scaling plot and is about $\simeq 5$, which is not too far from the value of $\lambda_c = 2\pi/\xi_B \sim 6.28$ (where ξ_B is the bulk correlation length) derived from the linear theory of SDSA. The discrepancy may be due to the inappropriate use of bulk values with the surface effects. Moreover,

we plot the length scale $R_1(t)$ vs. time in Fig. 4.3.3(b), where $R_1(t)$ exhibits power-law growth for three different growth exponents. Solid lines with the growth exponents of $1/5$ and $1/3$ mark the potential-dependent and diffusive growth of the PB model. However, the exponent of 1 belongs to the viscous hydrodynamic regime present in hydrodynamic-enabled studies. Another aspect of the wetting layer growth to look out for is the crossover between different regimes. A sharp crossover happens between the early-time growth of $\alpha = 1/5$ and the diffusive growth with $\alpha = 1/3$. At the same time, the crossover from diffusion to the viscous hydrodynamic regime is broad and gradual, which signifies the relative dominance of the diffusion coefficient and the shear viscosity of the fluid for length scales in the proximity of $L(t) \approx (D\eta)^{1/2}$. Furthermore, the crossover time between diffusive and viscous hydrodynamic growth, $t_c \sim 2000$, is similar to the value obtained for bulk studies investigating SD [70, 71]. However, the length scale from the SD studies and our $R_1(t)$ do not match at the crossover, as they have different dimensionalities. Notably, no *fast-mode kinetics* ($\alpha = 3/2$) is observed in the wetting layer growth. The inset in Fig. 4.3.3(b) shows that changing the slab width (Δz) does not affect the $R_1(t)$ growth for the intermediate and late-time regimes; however, the accuracy is reduced if $\Delta z \sim \sigma$.

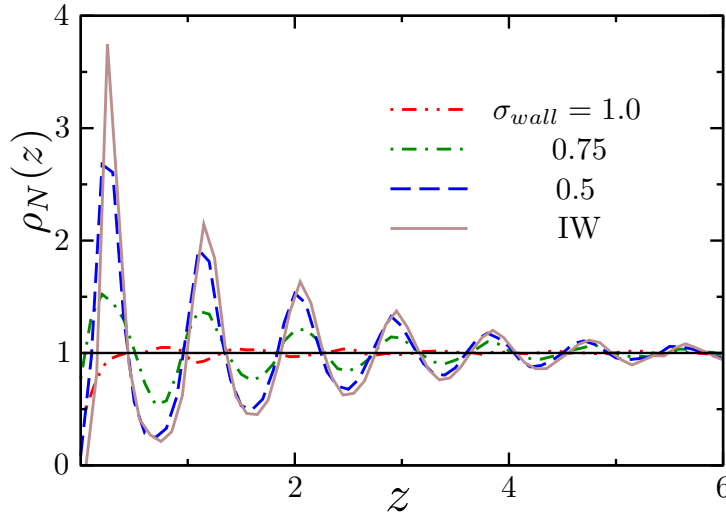


Figure 4.3.4: Reduced number density $\rho_N(z)$ plotted as a function of the depth z from the wetting wall. The profiles correspond to different walls made up of particles of size σ_{wall} . We chose a high packing fraction for $\sigma_{wall} = 0.75$ and 0.5 to reproduce the flat wall conditions. We have also included the density data from the integrated wall for comparison. The profile for $\sigma_{wall} = 1$ does not exhibit the non-uniform density oscillations near the wall, eliminating the wall-induced crystallization in the fluid mixture.

Before we continue the quantitative analysis of length scale growths, we briefly explore how the wall's roughness affects the fluid density next to the walls. In

our prior works on the SDSO [26, 46, 62], including the recent ones [26, 85] (see chapters 2 and 3), we took the integrated LJ potential (IW) potential to model the wall-fluid interaction, which is defined as:

$$u_w(z) = \frac{2\pi\rho_N\sigma^3}{3} \left[\frac{2\epsilon_r}{15} \left(\frac{\sigma}{z'} \right)^9 - \delta_\alpha \epsilon_a \left(\frac{\sigma}{z'} \right)^3 \right], \quad (4.7)$$

where $\alpha \in \{A, B\}$ and σ is the fluid-wall overlap distance. The attractive part of $u_w(z)$ is similar to $V(z) \sim z^{-n}$ of the PB model with $n = 3$. The preference of A -type particles by the wall materializes by setting $\delta_A = 1$ and $\delta_B = 0$. These unstructured walls (flat walls) cause the stacking of fluid particles into layers in their vicinity [49, 53, 63], which subsequently makes it difficult to measure $R_1(t)$ with microscopic precision. To produce similar effects in the amorphous walls, we recreate flat wall conditions by increasing the packing fraction of wall particles. To this end, we simulate smaller systems of size $(32\sigma)^3$ differing in the size of the wall atoms (σ_{wall}) and with highly packed walls. The resulting number densities appear in Fig. 4.3.4, where we have also shown the density profiles from the IW setup as a reference, which is a densely packed wall of infinite packing fraction [26]. Clearly, walls with higher volume fractions of interacting particles exhibit number densities closer to the integrated wall. Therefore, by keeping the wall density similar to the fluid density for $\sigma_{wall} = 1$, we avoided wall-induced particle layering and could access late-time growth regimes.

4.3.2 Parallel and Perpendicular Length Scales

We proceed further by characterizing SDSO in the conventional way of understanding the kinetics of characteristic concentration fluctuations using the two length scales ($L_{||}$ and $L_{\perp}$) introduced in Sec. 4.1. To investigate the length scale parallel to the wall, we define a depth-dependent two-point equal-time layerwise correlation function [13, 86]

$$C_{||}(\vec{\rho}, z, t) = \langle \psi(\vec{R}, z, t) \psi(\vec{R} + \vec{\rho}, z, t) \rangle - \langle \psi(\vec{R}, z, t) \rangle \langle \psi(\vec{R} + \vec{\rho}, z, t) \rangle, \quad (4.8)$$

the angular brackets denote the averaging over independent runs and integration over position vector $\vec{R}$ in layers parallel to the wall. A scalar correlation function $C_{||}(\rho, z, t)$ is obtained after we spherically average the isotropic contributions over $\vec{\rho}$ due to the semi-infinite geometry of the system in the xy -direction. Moreover, for perpendicular length scale, we have a special characterization where we correlate $\psi_{av}(z, t)$ along the z -direction, and the correlation is computed as:

$$C_{\perp}(Z, t) = \langle \psi_{av}(z, t) \psi_{av}(z + Z, t) \rangle - \langle \psi_{av}(z, t) \rangle \langle \psi_{av}(z + Z, t) \rangle. \quad (4.9)$$

Structure-function derived using ψ_{av} has the bulk structure factor ($\psi_{\text{av}} = 0$) deducted from the total structure factor. Thus, the length scale derived from this structure factor is associated solely with the multilayered structure along the SDS wave. This alternative approach could extract an equivalent of the wetting layer growth. The importance of this new approach over the conventional one for $R_1(t)$ is explained later in this section. In addition to $L_\perp(t)$ from the 1d correlation function, we also compute a length scale $L_\perp(y, t)$ from the 2d correlation function by replacing z in Eq. (4.8) by y . In this case, $L_\perp(y, t)$ corresponds to the growth of characteristic fluctuations in the cross sections normal to the wetting wall. Subsequently, we extract $L_\parallel(z, t)$, $L_\perp(t)$, and $L_\perp(y, t)$ from the respective correlation functions, as a distance over which the correlation values decay to zero [13, 86].

The correlation functions are calculated on a coarse-grained system, where the MD box is divided into volumes $\Delta x \times \Delta y \times \Delta z = \sigma^3$. Then we rectify $\psi(\vec{r}, t)$ of each lattice point at $\vec{r}$ using the majority spin rule, where we acknowledge the contributions of ψ from all its first neighbors. This method of coarse-grained mapping is similar to the numerical renormalization group technique described in Ref. [78]

Growth of the Perpendicular Length Scale $L_\perp(t)$

We begin with the correlation function of Eq. (4.9) and plot the results for different times in Fig. 4.3.5(a). The correlation curves show scaling for two different growth regimes for the distances in the wall's vicinity, which is analogous to $\psi_{\text{av}}(z, t)$ scaling shown in Fig. 4.3.3(a).

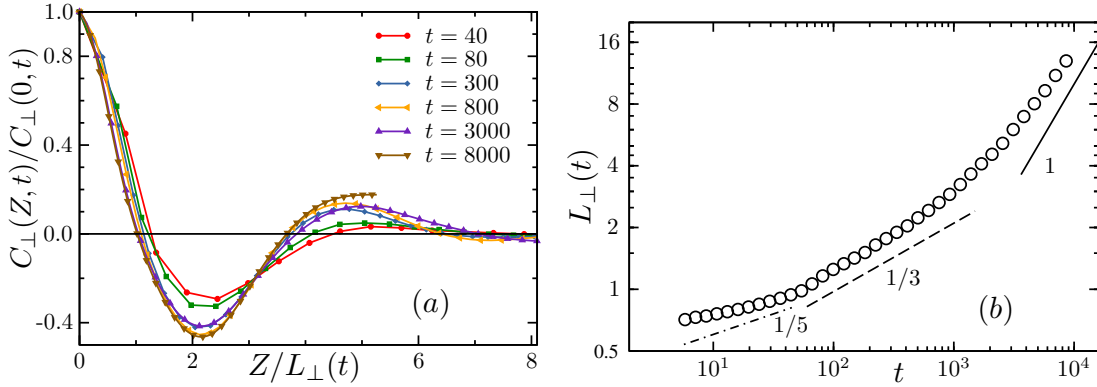


Figure 4.3.5: One-dimensional real-space correlation functions computed from the laterally averaged order parameters, $\psi_{\text{av}}(z, t)$, in z -direction. The characteristic length scale, $L_\perp(t)$, is computed as the distance where the correlation functions decay to zero. (a) The scaled data of $C_\perp(Z, t)/C_\perp(0, t)$ is superposed at reduced times specified as legends. (b) $L_\perp(z, t)$ vs. t on a log-log plot. The lines with slopes 1/5, 1/3, and 1 correspond to growth regimes of the potential-dependent, diffusion, and hydrodynamics, respectively.

Next, we extract the length scale and plot it vs. time on a log-log scale in Fig. 4.3.5(b). $L_{\perp}(t)$ exhibits power-law growth $\sim t^{\alpha}$ with crossovers between regimes. The intermediate times ($100 < t < 1000$), almost for a decade, mark the diffusive growth ($\alpha \sim 1/3$), which is followed by the viscous hydrodynamics for $t > 1000$. Moreover, the wetting layer thickness, $R_1(t)$ shows similar growth and a similar crossover in Fig. 4.3.3(b). $L_{\perp}(t)$ could also resolve the early-time growth, close to the potential-dependent growth from the PB model, which is also present for $t < 100$ in $R_1(t)$. No *fast-mode kinetics* occurs for this length scale, either.

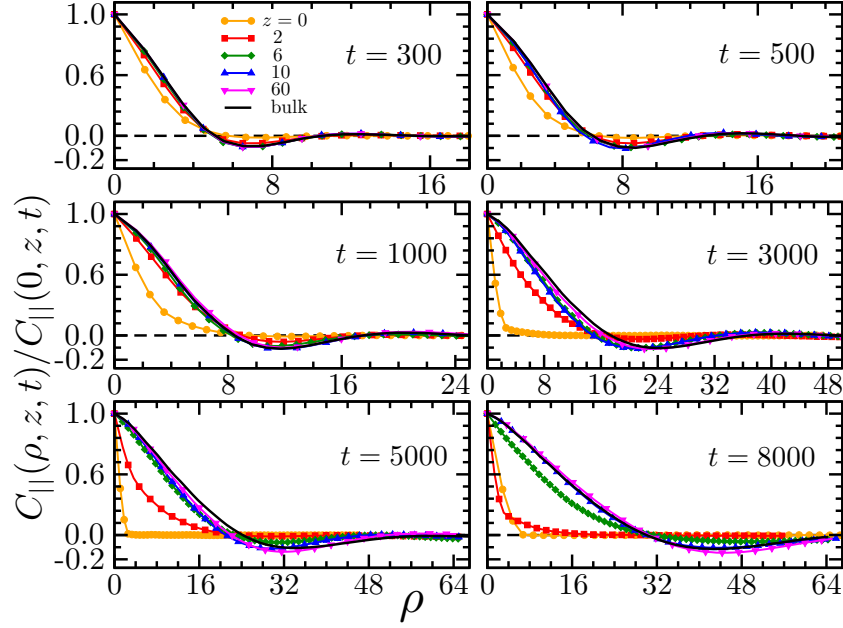


Figure 4.3.6: Plots of depth-dependent real-space correlation functions in the direction parallel to the wetting substrate. Each subplot corresponds to different layers placed at a depth z from the wetting surface. Different subplots contain data sets of $C_{\parallel}(\rho, z, t)/C_{\parallel}(0, z, t)$ at different reduced times specified.

Growth of Length Scales in the Cross-Sections Parallel and Perpendicular to the Wall

We examine $C_{\parallel}(z, t)$ at various depths along the composition wave. We further examine $C_{\parallel}(z, t)$ at multiple depths along the composition wave and compare it with the correlation values from the bulk (isotropic systems without walls). The results are shown in Figs. 4.3.6 and 4.3.6(a), where we have carefully chosen layers from the vicinity of the wetting layers, the depletion region, and the bulk. The correlation data corresponding to the bulk layers oscillate about zero, signifying the interconnected domain morphology for a critical composition ($\psi_0 = 0$).

Whereas, $C_{||}(z, t)$ in the wetting layers ($z = 0, 2$) show overdamped oscillations resulting from the off-critical domain morphologies, similar to spinodal decompositions in magnetic systems with non-conserved order parameter. The pinning of the correlation value in the layers at $z = 0$ for time $t > 1500$ corresponds to the saturation of $\psi_{av(z,t)} \simeq 1$ in the wetting layers ($z < R_1(t)$). The pinning is also present in the form of necking of $\psi_{av}(z, t)$ as seen in Fig. 4.3.2 for data close to the wall. Moreover, the underdamped correlations in layers lying above the wetting layers denote the presence of off-critical morphologies like droplets (tubes in our case) of one phase suspended in the sea of the second phase. Notably, there are disparities in the decay distances of $C_{||}(z, t)$, suggesting substantial morphological changes in the regions affected by the SDS waves. The disparities also occur when compared with the bulk correlations; however, they are associated only with the shifting morphologies in the region.

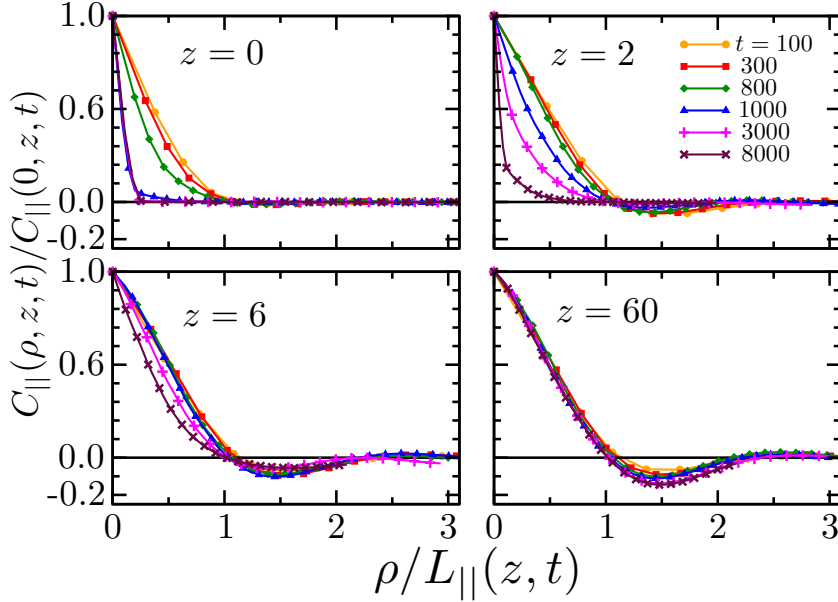


Figure 4.3.7: Plots of $C_{||}(\rho, z, t)/C_{||}(0, z, t)$ vs. scaled distances for layers in the vicinity of wetting surface and from bulk. Scaling in each subplot for different times is performed using characteristic length scales, $L_{||}(z, t)$, extracted as the decay distance of $C_{||}(\rho, z, t)/C_{||}(0, z, t)$ to 0.

In Fig. 4.3.7, we focus on the scaling behavior of the correlation data as a function of depth z from the surface. The distances, ρ , are rescaled by the length scale $L_{||}(z, t)$, where the latter is the distance at which $C_{||}(\rho, z, t)$ decays to zero. $C_{||}(\rho, z, t)$ exhibits good data collapse at all distances for two different growth regimes for the bulk layers. Furthermore, no reasonable scaling is seen for the layers lying inside the wetting layer ($z < R_1(t)$) at that time. In Fig. 4.3.8, we plot the scaling data of $C_{\perp}(y, t)$ for the xz cross-section at a fixed y . The correlation curve

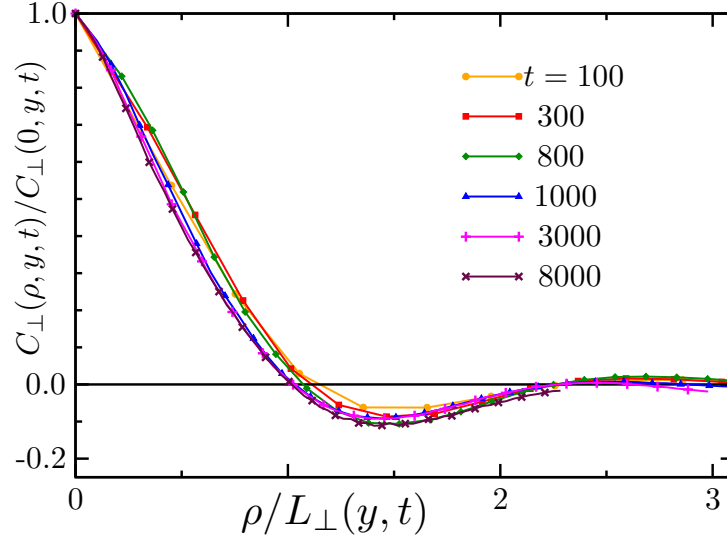


Figure 4.3.8: Plots of $C_{\perp}(\rho, y, t)/C_{\perp}(0, y, t)$ vs. scaled distances for the xz cross-section at a fixed y . Scaling in each subplot for different times is performed using the characteristic length scales, $L_{\perp}(y, t)$, extracted as the decay distance of $C_{\perp}(\rho, y, t)/C_{\perp}(0, y, t)$ to 0.

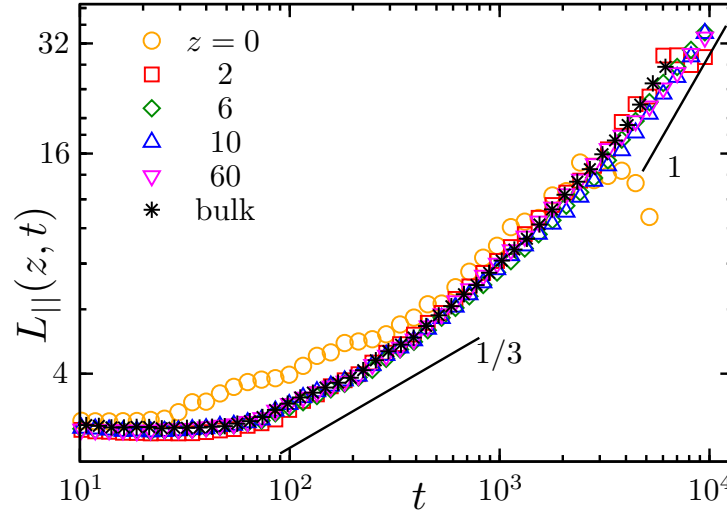


Figure 4.3.9: Time dependence of the parallel length scale $L_{\parallel}(z, t)$ at different depths from the wetting surface. The data correspond to growths in layers placed at $z = 0, 2, 6, 10$ (near the wetting surface) and $z = 60$ (away from the wetting surface). The bulk data corresponds to the length scale growth in a pure phase-separating system without walls. Solid lines shown here have slopes of $1/3$, $1/2$, and 1 .

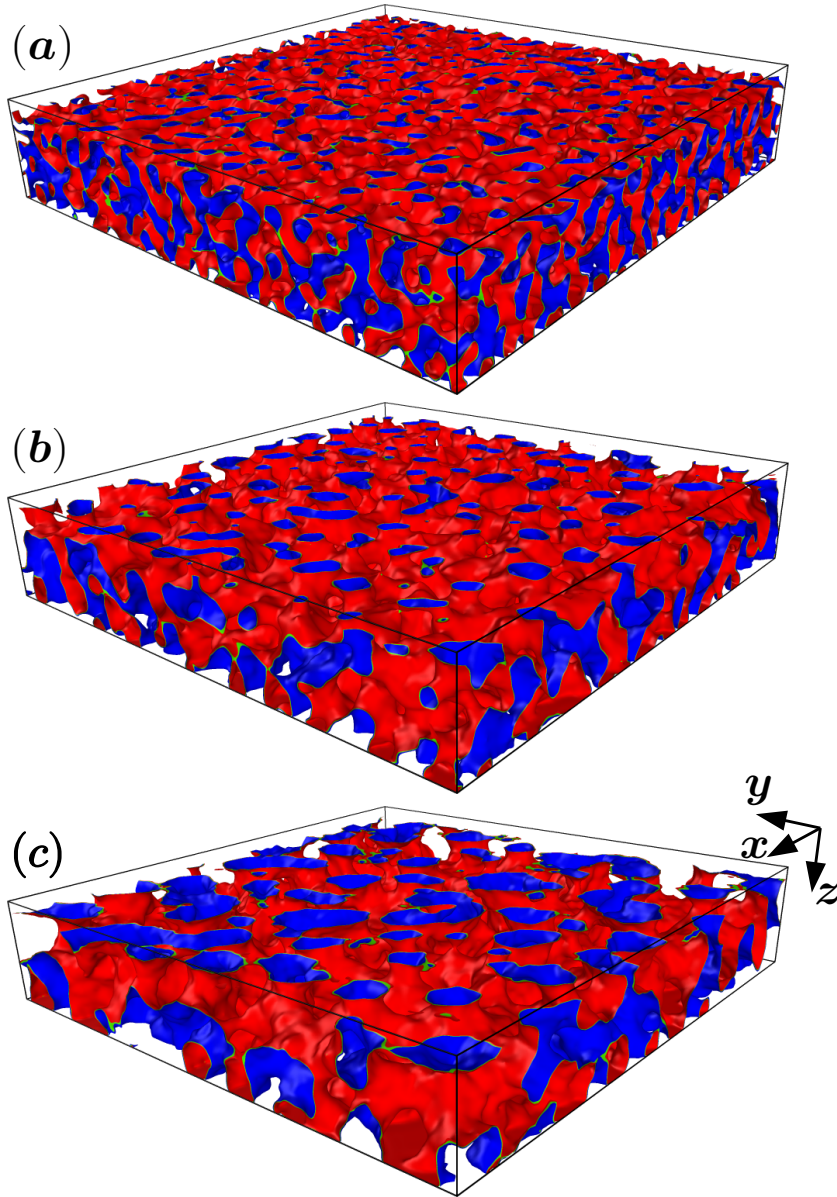


Figure 4.3.10: Time evolution of the morphology resulting from the wetting kinetics and phase separation interaction. The two phases in the binary mixture ($A + B$) undergoing SDSD are shown as blue and red isosurfaces, with their interfaces represented by a green isosurface. The isosurfaces are constructed on the noise-eliminated coarse-grained simulation box composed of the lattice structure (as discussed in the text). We only show the part of the lattice lying below the wetting layer ($z > R_1(t)$). The visualizations depict morphology at times equal to (a) 500, (b) 1500, and (c) 3000, ranging from diffusive growth regime to viscous hydrodynamics. The tubular structures are visible across the depletion region with openings toward the wetting layer, whereas no droplet morphology is present near the wetting layer.

shape and the minimum positions are similar to the scaling curves of $C_{||}(\rho, z, t)$ for $z = 6$ (for $t < 3000$) and $z = 60$ in Fig. 4.3.7 away from the wetting layer. This result, when compared with the depth-dependent correlations, suggests a single scaling function $[g(x = r/L_i)]$, where L_i can be $L_{\perp}(y, t)$ or $L_{||}(z, t)$ for the coarsening kinetics in either direction of the wall.

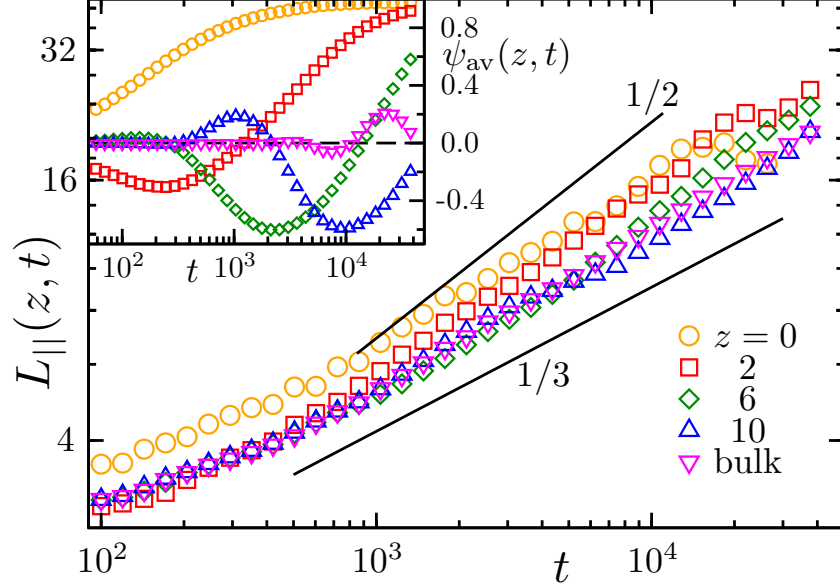


Figure 4.3.11: The time dependence of $L_{||}(z, t)$ is analogous to what is shown in Fig. 4.3.9, but for the simulations done with Andersen thermostat to avoid hydrodynamics. The length scale growth exhibits only diffusive growth with the growth exponent $\alpha = 1/3$ for layers above the wetting layer $z > 3$. Whereas the layers inside the wetting layer ($z = 0, 2$ for $t > 10^3$ and $z = 6$ for $t \geq 10^4$) gradually crossover to the accelerated growth with the growth exponent $\alpha = 1/2$. The accelerated growth emerges due to the fluctuation growth against the highly off-critical compositional background. The temporal evolution of compositions of the layers is shown in the *inset*.

We plot the extracted $L_{||}(z, t)$ vs. t on a log-log plot in Fig. 4.3.9. Not surprisingly, the bulk layers show length scale growing as $t^{1/3}$ and t^1 , corresponding to diffusion [6] and viscous hydrodynamics [2, 81]. Also, the layers affected by the SDS waves show similar growth regimes, except the layers with highly off-critical compositions ($z = 0$). Noticeably, the accelerated growth regime reported by Puri *et. al.* for long-range surface fields like ours is absent here. They advocated for accelerated growth with two possible explanations. Firstly, they considered it a transient regime, where the bicontinuous domain morphology breaks down into isolated elongated droplets of the wetting component, oriented parallel to the wetting layer on average. Such elongated droplets have a stronger tendency to compactify forming larger domains, which results in the accelerated growth of

$L_{||}(z, t) \sim t^{1/2}$, which resembles droplet growth via Brownian-Coagulation process for two-dimensional systems [5, 7, 8, 87]. Also, the layerwise effects were prominent and long-lived for a higher proximity to the wetting surface and are perpetually propagated into the bulk with the penetration of it by the SDSD waves. Secondly, a length scale associated with the fluctuations about a highly off-critical background ($\psi_0 \neq 0$) also results in $\alpha = 1/2$. Furthermore, their parallel length scale also showed depth-dependent orientational effects of the wetting layer, which was indicated by the increased growth magnitudes in $L_{||}(z, t)$ for z closer to the wetting wall. Similar elongation of the domains parallel to the wall was qualitatively reported by Brown and Chakrabarti [43] in their Monte Carlo simulations of SDSD. However, in our MD results, the data for the length scales $L_{\perp}(y, t)$ and $L_{||}(z, t)$ overlap comfortably for $z > R_1(t)$ (though the data for $L_{\perp}(y, t)$ not shown here), which signifies isotropic domains just above the depletion layers in contrast to the asymmetric fluctuations previously reported. Besides, these length scales do not exhibit the *fast-mode kinetics* as seen for the combined effects of hydrodynamics and long-range interactions in low-weight polymer mixtures.

Thus, our MD simulation results for the domain morphologies in the wetting layer's vicinity differ fundamentally from those of Puri *et. al.*. We do not encounter any elongated and isolated droplets above the depletion layer, which, upon coalescence, may give rise to the accelerated growth. Besides, we see wetting tubes connecting the bulk and the wetting layer, as seen in Fig. 4.3.1, together with the percolating domain morphology above the depletion layer. To further this claim, we present the domain morphology of the system below the wetting layer in Fig. 4.3.10 for a bigger system of size $L_x \times L_y \times L_z = 256 \times 256 \times 48$ with similar wetting parameters. The isosurfaces drawn exhibit the absence of droplets in any of the growth regimes, as visible from the snapshots of different simulation times. Notably, we do notice pinch-off events in the tubes during surface-tension-driven coarsening toward the top surface (the wetting wall) in Fig. 4.3.10(c). The spreading of the tubes is also seen at the top ($z = 0$) in the form of a large number of openings with blue-colored (A -rich phase) inner isosurfaces.

The accelerated growth observed by Puri *et. al.* was due to a diffusion-limited study. However, our MD simulations naturally incorporate hydrodynamics. Therefore, we perform simulations using the Andersen thermostat to eliminate any role of hydrodynamics in shaping the domain morphologies differently, in contrast to diffusive dynamics. The randomization of velocities at a fixed frequency in the Andersen thermostat truncates the system's trajectory in the phase space, and the resultant dynamics are purely diffusive. We show the length scale growth for this system in Fig. 4.3.11. We notice a gradual crossover from $\alpha = 1/3$ to the accelerated growth for layers affected by SDSD waves. Whereas the bulk layers exhibit the growth exponent $\alpha = 1/3$ throughout the simulation. However, the accelerated growth visible here for $z = 2, 3$ seems to emerge due to fluctuating growth against a highly off-critical background. This argument is supported by

$\psi_{\text{av}(z,t)}$ values in $z = 2$ and $z = 3$, which are above 0.8 for $t > 5000$. Moreover, the layers in or above the depletion region do not show a growth exponent of $1/2$ for the same period.

4.4 Summary

In the present work, we investigated the interaction of wetting kinetics and phase separation in a binary fluid mixture undergoing surface-directed spinodal decomposition over an amorphous wall. We focus on the characteristic length scales of the phase ordering obtained via morphological characterization in perpendicular and parallel directions of the wetting surface. These length scales include the wetting layer thickness $R_1(t)$, the perpendicular length scales of $L_\perp(t)$ (derived from laterally-averaged order parameter), $L_\perp(y, t)$ and the depth-dependent parallel length scale $L_\parallel(z, t)$.

The wall's roughness makes our setup stand out among the previous attempts regarding SDSD via molecular simulations. Due to the finite roughness of the amorphous wall in our system, we could avoid the layering effects seen for the flatter walls. The stacking of particles in the layers has caused crystallization of the fluid mixture once the wetting layer is 2σ to 3σ (where σ is the fluid particle diameter) wide. Therefore, with rough walls, we could access growths of the wetting layer and bulk domains during the late-time regime, which had not been previously achieved.

Our primary objective for this study was to report on the growth laws followed by the characteristic length scales during their interactions. Furthermore, we highlight the emerging domain morphology in the regions affected by the strong interactions of the wetting and phase separation kinetics. The investigated length scales follow a power-law growth $d_0 t^\alpha$, where α values correspond to a given coarsening regime and d_0 is the growth magnitude.

In the wall's vicinity, the wetting layer thickness $R_1(t)$ happens to be the dominant length scale, which, for the early-time regime, closely follows the potential-dependent growth [$\alpha = 1/(n+2)$] from the Puri-Binder model for a long-range Van der Waals interaction of the form $\sim 1/z^n$ (n being the range). $R_1(t)$ then crosses over to the diffusive growth of $\alpha = 1/3$ at intermediate times. Moreover, $L_\perp$ being analogous to $R_1(t)$, exhibits the similar trend. During the late-time regime, both show a common crossover to the surface-tension-driven growth ($\alpha = 1$). On the other hand, the parallel length scale $L_\parallel(z, t)$ shows variability with the depth z from the wetting wall, as the SDSD waves affect the domain morphologies in the layers it penetrates. No scaling is present in the layers enriched with wetting particles ($z < R_1(t)$). But, for the layers above the wetting layer ($z > R_1(t)$), $L_\parallel(z, t)$ exhibit the same sequence of growth exponents as seen for $R_1(t)$ and $L_\perp(t)$, and negligible variations in the growth magnitude d_0 with depth z . Also, the growth data for $L_\perp(y, t)$, which is analogous to $L_\parallel(z, t)$ but represents the cross-sections

normal to the wetting wall, show overlap with the parallel length scale data for $z > R_1(t)$, signifying no asymmetrical domain coarsening. These results are in contrast to the accelerated growth of $L_{||}(z, t) \sim t^{1/2}$ reported in the work by Puri *et. al.* for some layers above the first depletion region. They associate accelerated growth with the asymmetrical domain coarsening due to the orientational effects of the lateral structures formed. However, we do not encounter such asymmetrical domain coarsening, and we attribute this contrasting result to the weak lateral structures formed in our molecular simulations. Where the laterally-averaged values in the wetting and depletion layer in the cases of asymmetrical domains oscillate between $+1$ and -1 , the oscillations in our molecular simulations lie between $+1$ and -0.5 , with or without the hydrodynamics. The higher ratio of the wetting to non-wetting components in the depletion layer results from the tubular network spanning the region, which is absent from the cases of asymmetric domain coarsening.

Another surprise is the absence of the fast-mode kinetics for our simulation setup, which includes the critical elements (long-range attraction and hydrodynamics) responsible for it. Notably, no length scales exhibit the growth exponent of $\alpha = 3/2$, although we closely accessed the growth as early as the potential-dependent regime for all of them. The emphasis is on the early-time regime, where Wiltzius, Cumming, and others have reported the fast-mode kinetics.

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