Chapter 6

Conclusion and Outlook

In this chapter, we recapitulate the original research statements presented in the Introduction. We highlight the key findings and conclusions of this thesis. Finally, we discuss the study's limitations, explore potential advancements of the research presented in this thesis, and provide suggestions for future investigations and follow-up studies.

The core objectives of this thesis revolve around our primary goal of understanding the dynamic interplay between wetting kinetics and spinodal decomposition in binary mixtures under a hydrodynamic background. The objectives are in the context of structural evolution and are investigated through computer simulations. From a technological perspective, the insights developed are relevant for the design and fabrication strategies of optical and electrical devices (films) such as organic photovoltaics, transistors, etc [1–3]. Also, the acquired microscopic understanding facilitates uncovering the debated growth mechanism reported by the experiments, such as the fast-mode growth [4–6]. We employed molecular dynamics simulation to investigate the interplay in a symmetric binary mixture undergoing spinodal decomposition on a substrate preferentially wetted by one of the components. We found a profound impact of substrate characteristics, such as roughness and interaction with fluid particles, on the formation of the wetting layer, its coarsening, and thickness. The wetting layer thickness was limited for the flat walls with vanishing roughness and power-law interaction due to surface-induced crystallization. However, its growth exhibited potential-dependent power-law growth at a very early time. In contrast, with amorphous walls of finite roughness, we recovered the early to late universal coarsening regimes of the wetting-layer growth, where the crossovers between the different growth regimes matched the ones from the bulk phase-separating mixtures. We also reported the transposition of the chemically distinct patterns of the substrate as a registry in the fluid layers when the pattern periodicity was larger than the mixture's inherent length scale. We found that the registry formation and melting time in fluid layers at some depth show scaling with the pattern length scale for times earlier than when the hydrodynamics sets in. In the next section, we revisit the research questions explored in this thesis and comment on them on the basis of our main conclusions, which are also summarized here. Lastly, we address possible advancements in the research presented in this thesis and suggest further studies.

6.1 Conclusion

This thesis presents an in-depth investigation of surface-directed spinodal decomposition (SDSD) in symmetric binary fluid mixtures through molecular dynamics simulations, providing significant insights into the interplay between wetting kinetics and phase separation via spinodal decomposition, which shapes the domain morphologies in the substrate vicinity and the bulk. The study traverses a wide range of surface potentials, wall characteristics, and compositional variations of the mixture, revealing universal growth behaviors, distinctive dynamical regimes, and the effects of substrate properties on SDSD. Our specific focus was on the role of hydrodynamics in the various stages of domain coarsening in SDSD.

Universal Growth Regimes and Fast-Mode Kinetics: Our simulations on the flat walls captured the complete set of growth regimes for the wetting layer thickness $R_1(t)$ under both long-range and short-range surface potentials. These regimes include potential-dependent, fast mode, diffusive, and hydrodynamic dynamics, qualitatively elucidating (via snapshots and videos) the mechanisms underlying each stage of wetting layer growth.

A major focus of this work was to address the long-standing controversy surrounding the universal fast-mode kinetics, with growth exponents of 3/2. By analyzing time-dependent snapshots and material transport mechanisms, we confirmed the fast mode as a short-lived transient regime following the early-time potential-dependent growth regime, characterized by the rapid growth of droplets preceding the formation of the wetting layer. We notice the building up of tubes of the preferred phase as long-range correlations, characteristic of hydrodynamics, at the very early phase separation stage. The tubes connect the bulk to the wetting layer and flush its material on the surface in a pseudo-two-dimensional way, resulting in the coating of the surface with the preferred phase. This we refer to as *coating mechanism*, as the fast-mode regime is truncated as soon as the first particle layer transforms into the wetting layer. Consistent across surface potentials, this behavior reconciles theoretical predictions and experimental results observed in polymer blends and fluid mixtures. For long-range surface potentials of the form $V(z) \sim z^{-n}$, $R_1(t)$ demonstrated early-time growth $t^{1/(n+2)}$, aligning with the potential-dependent growth of the Puri-Binder (PB) phenomenological model. Short-range potentials exhibited logarithmic early growth, followed by transitions through fast-mode growth, diffusive, and hydrodynamic regimes. These findings mark the first atomistic simulations to resolve all growth regimes of wetting kinetics, offering critical validation of the phenomenological theory by PB.

Composition Effects and Phenomenological Theory: The role of compositional variations in SDSD was thoroughly examined, revealing the contrasting dynamics based on the relative abundance of wetting particles. Systems with surplus wetting components adhered to theoretical predictions, with the first term of the Puri-Binder phenomenological current accurately describing the early-time dynamics. In contrast, systems deficient in wetting particles exhibited slower growth, with equilibrium constraints in the wetting layer causing shifts in the depletion layer toward the nucleation regime. By reducing the surface-field strength, we relaxed these constraints and recovered potential-dependent growth, highlighting the intricate coupling between surface forces and phase separation dynamics.

This investigation demonstrates how field strength and composition influence fluctuation growth, identifying avenues for future studies to better understand the underlying mechanisms driving these behaviors.

Wall Effects and Domain Morphology: Another significant contribution of this work is the exploration of wall roughness and chemical patterning on SDSD. For amorphous walls, the absence of layering effects allowed us to access the late stages of domain growth. Unlike flat-wall systems prone to particle crystallization due to the layering near the surface, rough amorphous walls enabled the continuous evolution of wetting layers and bulk domains into the hydrodynamic regime. This setup provided new insights into the role of surface roughness in mitigating the artificial effects and achieving realistic SDSD dynamics with the thicker wetting layer.

Chemical patterning of the substrate introduced registry formation in the fluid layers, influenced by the patch periodicity and interaction strength. We observed rapid registry development in contact layers, followed by its weakening with depth due to destructive interference from diametrically opposite SDSD waves originating at the contrasting patches. The scaling laws governing registry formation and dissolution were identified, revealing how pattern dimensions and transportation mechanisms shape these scaling processes.

Absence of Fast-Mode Kinetics and Domain Symmetry: In contrast to our studies with flat walls reporting the accelerated growth regime ($\alpha = 3/2$) in systems with the two critical components of long-range interactions and hydrodynamics, our simulations on amorphous walls did not exhibit such fast-mode kinetics under similar conditions. Furthermore, no evidence of asymmetric domain coarsening was observed, and all layers demonstrated consistent growth exponents at different depths. We attributed the absent asymmetry to the weak multilayered lateral structures formed in our MD simulations, which contrast with the numerical results PB obtained. Moreover, the absence of the fast mode is due to the surface roughness, which does not facilitate the coating mechanism. The absence of these phenomena highlights the sensitivity of SDSD dynamics to surface properties and interaction parameters, underscoring the need for further investigation into these discrepancies.

The findings presented in this thesis bridge the gaps between phenomenological theories, experimental results, and atomistic simulations, significantly advancing the understanding of SDSD and wetting phenomena. The elucidation of universal growth behaviors, substrate effects, and compositional influences provides a robust framework for studying phase transitions in confined systems and surface-dominated processes.

6.2 Outlook

Before listing the future directions envisaged as a result of this thesis, let us understand the broader sense made by the results of this thesis. The standard model

of LJ fluid used in this thesis emphasizes that the realistic chemistry between the two species and the walls does not alter the intermediate to late stages of domain growth and even thermodynamical phase behavior to significant extents. Therefore, it was safe to ignore the minute details of the systems, as overall, chemical specificity will adjust the phase boundaries and layer morphologies. At the same time, any form of activity will generate richer, nonequilibrium wetting behaviors and new coarsening kinetics beyond those captured by simple LJ simulations.

Based on our findings, we propose here some plans for further research. In Chapter 2, we reported the fast-mode regime due to the coating mechanism over a flat wall. A natural step is to extend the investigation for the quench to different temperatures, as we know of experimental results on how the prefactor of the fast-mode kinetics varies with the decreasing depth of the quench [4–6]. Further, the role of fluctuations could be examined for the early stages of growth of the wetting layer thickness [7, 8]. We plan to use Lattice-Boltzmann methods to simulate the early-time wetting layer growth by implementing the Shan-Chen multicomponent model [9], which incorporates the intermolecular forces similar to our MD simulations.

In Chapter 4, we analyze the late-time stages of wetting-layer growth for critical mixtures, where the thickness could reach the system size with no wall-affiliated artificial effects. For our upcoming works, we have extended the analysis to slightly- and highly off-critical mixtures and can now examine the role of bulk phase separation on wetting kinetics. We intend to compare these results with existing phenomenological theories. We will be the first to present the late-time growth results from the atomistic simulations of SDSD, which will help validate the current numerical results and phenomenological theories. Furthermore, we plan to expand the study of SDSD on amorphous walls to wetting and phase separation in porous materials. The initial investigation was carried out by Tanaka *et. al.* [10] using diffusion-limited phase field modeling, it was emphasized that the emerging domain morphology and domain sizes are not similar to conventional belief, which can be inferred from the behavior in a simple cylindrical pore [11]. Our results on the wetting kinetics and domain morphology are based on a simple MD setup without any complex topography, and it would be naive to speculate; however, the setup could be extended in a very straightforward way with inherent hydrodynamics, which is lacking in the works of Tanaka [10].

In Chapter 5, we address the role of surface inhomogeneity on pattern selection by the fluid undergoing spinodal decomposition. We have started with the system where the checkerboard pattern is commensurate with the composition of the binary mixture (50 : 50); the natural question arises: What will happen when commensuration is not followed? Such questions are addressed by the numerical simulations qualitatively at a larger length and time scales [12, 13]. MD simulations with inherent hydrodynamics will provide equally important quantitative results, and a microscopic understanding will help validate the established