

Declaration

I hereby declare that the work presented in this thesis titled “*Kinetics of Phase Transitions in Multicomponent Fluid Mixtures using Computer Simulations: Role of Surface Potential and Mixture Composition*”, submitted to the Indian Institute of Technology Jodhpur in partial fulfillment of the requirements for the award of the degree of Ph.D. in Physics, is a bonafide record of the research work carried out under the supervision of **Dr. Prabhat K. Jaiswal**. The contents of this thesis in full or in parts, have not been submitted to, and will not be submitted by me to, any other Institute or University in India or abroad for the award of any degree or diploma.



Signature

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Certificate

This is to certify that the thesis titled “*Kinetics of Phase Transitions in Multicomponent Fluid Mixtures using Computer Simulations: Role of Surface Potential and Mixture Composition*”, submitted by Syed Shuja Hasan Zaidi (P19PH007) to the Indian Institute of Technology Jodhpur for the award of the degree of Ph.D. in Physics, is a bonafide record of the research work done by him under my supervision. To the best of my knowledge, the contents of this report, in full or in parts, have not been submitted to any other Institute or University for the award of any degree or diploma.



Signature

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Abstract

Phase transitions are transient processes in which a thermodynamically unstable or metastable state evolves to a stable state driven by minimizing the appropriate free energy. The instability or metastability occurs due to sudden changes in external parameters such as temperature, pressure, etc. Subsequently, the system undergoing phase transition finds itself in a *far-from-equilibrium* unstable state characterized by complex spatiotemporal pattern formation, where the patterns account for domains enriched in the preferred states. The phase transition dynamics are subject to the nonuniformities present in the form of defects, such as domain interfaces costing free energy, and the system proceeds by annealing these defects. Such an annealing process adopts nonequilibrium dynamics in the growth and coarsening of the domains, commonly referred to as *domain growth*, *coarsening kinetics*, and *phase-ordering kinetics*. The objectives of my thesis comprise systems that exhibit domain growth and coarsening kinetics in phase-separating binary mixtures (AB). In our studies, the quenched mixture is unstable to infinitesimal long-wavelength fluctuations and spontaneously decomposes into A -rich and B -rich domains demarcated by interfaces. This process is a widely used paradigm for the coarsening kinetics and is known as spinodal decomposition (SD). Phase separation is recurring in most *far-from-equilibrium* systems. One of the primary focuses of my work is to analyze the commonalities and distinctions in these systems.

The problems we address in our thesis emerge when we add surfaces to the phase-separating mixtures. The phase-separating mixture in contact with a surface is commonplace in metallurgy, chemical, and biological systems. For immiscible mixtures, if the surfaces preferentially attract one of the species, the surface becomes the origin of composition waves, known as surface-directed spinodal decomposition (SDSD) waves. These SDSD waves are composed of alternating segments of the wetting (rich in the preferred component) and depletion layers (lacking preferred particles). Using numerical simulations, we specifically study the wetting kinetics in the systems undergoing SDSD with functional surface properties. Our focus remains on elucidating the roles played by composition ratio ($A : B$), hydrodynamics in the system, and the chemical and physical heterogeneity of the surface in contact.

To begin with, we add a flat wall represented by an integrated wall potential $V(z)$ with an attractive part $\sim z^{-n}$, where z and n denote its depth below the horizontal fluid layer and its interaction range, respectively. We find that for critical compositions ($A : B = 50 : 50$), the wetting-layer thickness $R_1(t)$ at very early times exhibits a potential-dependent growth regime of $R_1(t) \sim t^\alpha$ with $\alpha = 1/(n + 2)$ being the growth exponent. The potential-dependent growth next crosses over to a universal *fast-mode* regime with $\alpha = 3/2$. In contrast, much slower logarithmic behavior in $R_1(t)$ is seen initially for a short-ranged surface potential ($n \rightarrow \infty$). Remarkably, a similar rapid growth with $\alpha = 3/2$ is seen in this case too. We invoked Siggia's arguments to explain the fast-mode kinetics, where novel long-range correlations develop in the early phase separation stage, resulting in *coating mechanism*. Secondly, we investigate the role of the composition ratio in the binary mixture for a similar attractive long-range potential $V(z)$. We show that

$R_1(t)$ in early times slows down if the minority component (minority wetting) wets the surface. However, the potential-dependent growth of $R_1(t) \sim t^{1/(n+2)}$ is obtained when the majority component (majority wetting) wets the surface. The contrasting results corroborate a local barrier of thickness greater than the thermal correlation length above the wetting layer for minority wetting. In this case, the probability of particles crossing the barrier to feed the wetting layer is lower. We also report the recovery of the potential-dependent growth for the minority wetting by weakening the local barrier.

Furthermore, we replace the flat walls with amorphous ones to investigate the late-time growth regimes of $R_1(t)$. By choosing the amorphous walls, we could avoid surface-induced crystallization in the mixture and examine the wetting kinetics in SDSD for times much later than previously reported by molecular simulation. 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 scales show widely accepted growth exponents of $\alpha = 1/3$ (Lifshitz-Slyozov (LS) law) and 1 (Siggia's mechanism), which are also universal. However, we could not observe the *fast-mode* as the *coating mechanism* was absent due to the roughness of the amorphous wall. Furthermore, we highlight the possible orientational effects of the multilayered structures on domain coarsening near the surface.

In the end, we replaced chemically homogeneous surfaces with chemically patterned substrates. By setting the pattern's periodicity commensurate with the mixture's inherent length scale, we notice the transposition of surface patterns to the fluid mixture in contact. The emerging patterns are denoted as a transient surface-registry regime exhibiting a dynamical crossover from surface-driven to other universal coarsening regimes. Moreover, we provide details of the scaling behavior for the *registry* formation and melting times as a function of the pattern size M_x . We further assess lateral domain morphologies and examine the crossover using correlation functions, structure factors, and domain length scales.

The kinetics of SDSD are of great technological and scientific importance, offering a pathway to curate and design functional materials by enabling precise control over their domain morphologies. Given the above, acquiring a detailed understanding of the process is beneficial.

Acknowledgements

To begin with, I am profoundly grateful to my parents and my sister for their unwavering support and prayers, whose encouragement has empowered me throughout my academics. Secondly, I thank Samapika, from the chemistry department, whose passionate cooking and admirable recipes nourished and amused me. I want to thank her for the companionship, research discussions, coffee breaks, and evening cycling excursions over the past 4 years. Thirdly, I thank my lab members from my institute, Vijay, Hema, and Saumya from BIT Mesra, Ranchi, for the insightful discussions and meetings concerning the group's research theme. Also, I give big cheers to all my people for all the random musings and their efforts to put up with me on a day-to-day basis. Fourthly, I would like to express my heartfelt gratitude to my institution, the Indian Institute of Technology Jodhpur (IITJ), for accepting me into a PhD program and providing the essential resources for conducting the research that shaped this thesis. I would also like to thank Professor Sanjay Puri at JNU, Delhi, and Dr. Madhu Priya at BIT Mesra, Ranchi, for their early mentoring and collaboration, which have paved the way for my current endeavor. I also extend my heartfelt thanks to Professor Ananya Debnath at IITJ and Dr. Krishna Kanti Dey at IITGN for their collaborations and for introducing me to biophysics and colloidal sciences, which have upgraded my capabilities beyond the scope of this thesis. Thanks to my Student Research Committee members, Professor Ananya Debnath, Dr. Shahab Ahmad, and Dr. Santosh Mogurameplly, for their timely interventions in analyzing my progress and providing valuable feedback and support along this journey. Lastly, I save my most profound appreciation for my PhD supervisor, Dr. Prabhat K. Jaiswal, to whom I am indebted for his constant academic support and guidance throughout my PhD journey. Our extended research discussions are a special mention, which helped address my intermittent doubts and fostered my curiosity. His valuable suggestions and feedback have been instrumental in finalizing the research work that will culminate in this thesis. I am incredibly grateful for the freedom he provided, which allowed me to grow professionally.

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To those with whom I share unconditional love.

List of Publications

1. **S. S. H. Zaidi**, P. K. Jaiswal, M. Priya, and S. Puri, “Universal fast mode regime in wetting kinetics”, Phys. Rev. E **106**, L052801 (2022).
2. **S. S. H. Zaidi**, S. Suvarna, M. Priya, S. Puri, and P. K. Jaiswal, “Early time wetting kinetics in surface-directed spinodal decomposition for off-critical quenches: A molecular dynamics study”, J. Chem. Phys. **161**, 154703 (2024).
3. **S. S. H. Zaidi**, M. Priya, S. Puri, and P. K. Jaiswal, “Interaction of wetting kinetics and spinodal decomposition of binary mixtures on an amorphous wall”, Manuscript under preparation.
4. **S. S. H. Zaidi**, H. Teherpuria, S. Mogurampelly, and P. K. Jaiswal, “Surface-directed spinodal decomposition on chemically patterned substrate: A molecular dynamics study”, Manuscript under preparation.

***Publication not included in the thesis**

5. **S. S. H. Zaidi**, M. Priya, and P. K. Jaiswal, “Late-time wetting kinetics in off-critical quenches”, Manuscript under preparation.
6. A. Maiti, **S. S. H. Zaidi**, P. K. Jaiswal, and K. K. Dey, “Effects of crowding and enzyme-driven active fluctuations on particle correlations in colloidal suspensions”, Under review in Phys. Rev. E (2025).
7. **S. S. H. Zaidi**, P. K. Jaiswal, and A. Debnath, “Polymer translocation into active Medium”, Manuscript under preparation.

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