Segregation kinetics and applications of brush-modified surfaces

Thesis submitted in partial fulfillment for the award of

DOCTOR OF PHILOSOPHY

in

PHYSICS

by

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DEPARTMENT OF PHYSICS

INDIAN INSTITUTE OF TECHNOLOGY

BANARAS HINDU UNIVERSITY

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YEAR OF SUBMISSION
06 August 2024

Dedicated to

My Family

and

My Grandfather

Lt. Dr. Radhey Shyam Yogi

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It is certified that the work contained in the thesis titled **Segregation kinetics and applications of brush-modified surfaces** by **Samiksha Shrivastav**, Roll Number **19171001**, has been carried out under my supervision and that this work has not been submitted elsewhere for a degree.

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I, **Samiksha Shrivastav**, certify that the work embodied in this thesis is my own bona-fide work and carried out by me under the supervision of **Dr. Awaneesh Singh** from 29 July 2019 to 6 August 2024 at the **Department of Physics**, Indian Institute of Technology (BHU), Varanasi. The matter embodied in this thesis has not been submitted for the award of any other degree/diploma. I declare that I have faithfully acknowledged and given credits to the research workers whenever and wherever their works have been cited in my work in this thesis. I further declare that I have not wilfully copied any others' work, paragraphs, text, data, results, etc., reported in journals, books, magazines, reports dissertations, theses, etc., or available at websites and have not included them in this thesis and have not cited as my own work.

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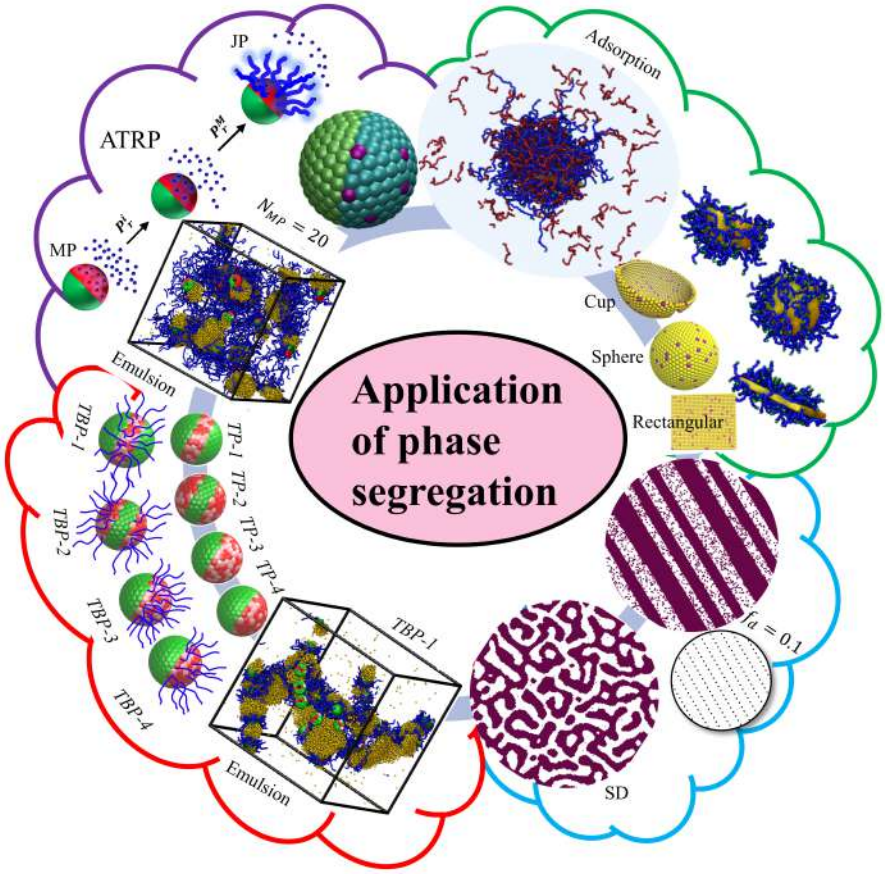
Abstract



My thesis explores various aspects of phase separation kinetics under external influences. Specifically, we studied the effect of polymer brush-modified macroparticle surfaces on biopolymer adsorption using dissipative particle dynamics (DPD) simulations. Our research analyzed the formation of oil-in-water emulsions and their stability with brush-modified Janus particles (JPs). We synthesized these polymer brushes using the atom transfer radical polymerization (ATRP) method. Additionally, in a separate work, we analyzed the impact of impurities on phase separation in $2d$ Ising model systems through Monte Carlo simulations.

Chapter 1 provides a comprehensive overview, delving into phase separation kinetics, domain growth, coarse-graining, quantifying various physical observables, and the simulation techniques utilized in the upcoming chapters.

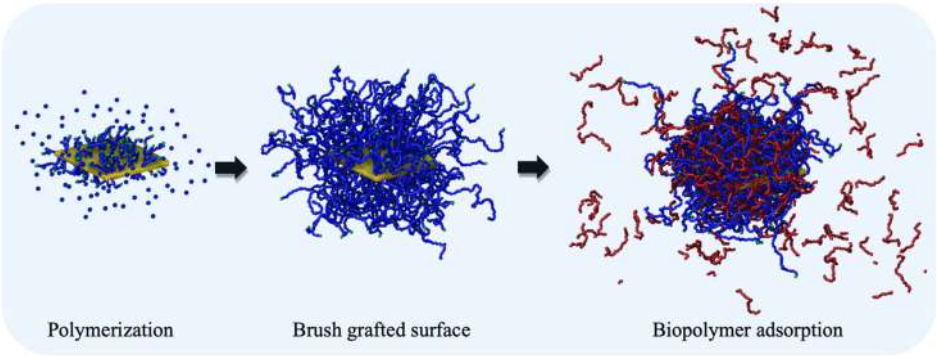


Fig. 1: Biopolymer adsorption on the brush-modified surface [1].

In Chapter 2, we examined the modification of microparticle (MPs) surfaces embedded with initiators through ATRP brush growth. This process led to the MPs acquiring a more spherical shape. We studied three types of surfaces: cup-shaped, spherical, and flat (rectangular/disc-shaped) and modified them with polymer brushes. Initially, we established the chemical kinetics of brush growth, including monomer conversion and reaction rates. Subsequently, we analyzed the structural changes during the brush modification by computing the spatial density distribution, radial distribution function, radius of gyration, hydrodynamic radius, and shape factor. We studied enzyme adsorption on ATRP-brush-modified particles, focusing on the effects of initiator concentration, polymer brush length, and biopolymer chain length, which can be used for enzyme immobilization. Our results showed that biopolymer adsorption increased with longer brush length, higher initiator concentration, and enhanced biopolymer concentration. The flat surfaces accommodated more biopolymers at saturation compared to cup-shaped or spherical surfaces. We validated these results experimentally. The table of contents of this work is shown in Fig. 1.

In Chapter 3, we numerically explore the stabilization of Pickering emulsions by brush-modified JPs using DPD simulations validated through experimental data. Each JP has a

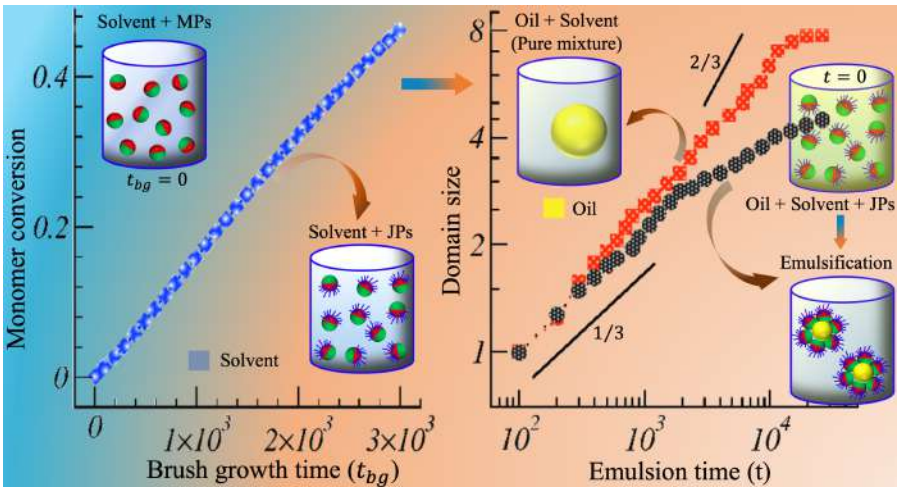


Fig. 2: Oil in water emulsion via brush-modified Janus Particle [2].

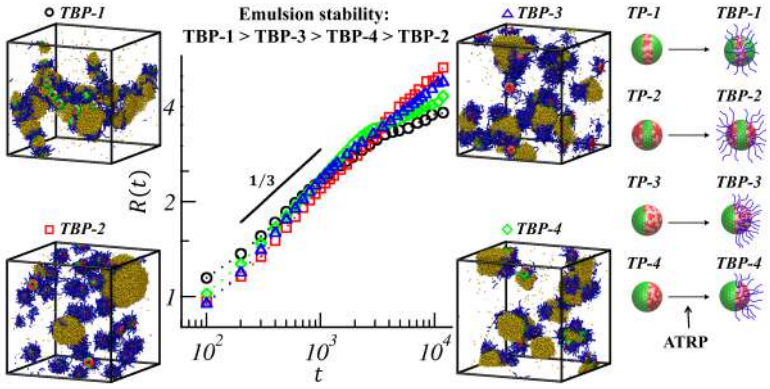


Fig. 3: Oil in water emulsification via tri-compartmental brush-modified Janus particle [3].

hydrophobic half (without brushes) and a hydrophilic half (brush-modified surface) with polymer brushes grown using ATRP. Initially, we analyzed the chemical kinetics of brush growth. We found that the number of JPs, grafted brush density, and brush length significantly influence the stability of oil-in-water emulsions. Furthermore, we examined the evolution kinetics and stability of emulsions by analyzing the growth of average domain size and scaling functions. This study elucidates the relationship between JP characteristics and Pickering emulsion stability. The table of contents for Chapter 3 is shown in Fig. 2.

In Chapter 4, an extension of Chapter 3, we investigate the formation of oil-in-water emulsions using brush-modified tricompartmental particles (TPs/JPs). Our objective was to

understand how the functionality of TPs influences the stability of Pickering emulsions by varying the brush length, grafting density, and types of JPs (TP-1 to TP-4) based on the polymer brush growth region on the microparticle surface. We examined stability and morphological changes using the radial distribution function, length scale growth, and scaling functions. The table of contents for Chapter 4 is shown in Fig. 3. Chapter 5 presents the segregation kinetics

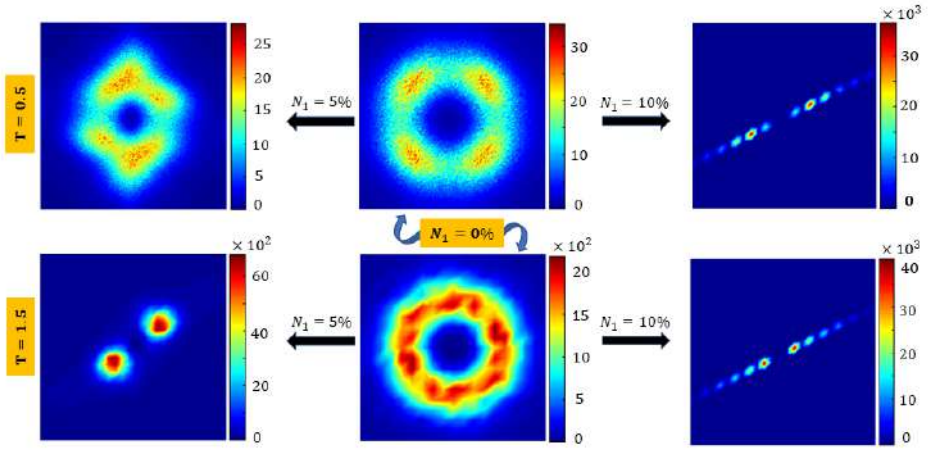


Fig. 4: Segregation kinetics under the influence of bond disorder [4].

of a $2d$ Ising system with varying bond disorders. We found that different quench temperatures affect the growth kinetics and scaling properties of the system. As the disorder increases, the morphologies transition from isotropic bicontinuous patterns to anisotropic strips and lamellae. At lower disorder levels, there is transient growth at deep quenches, while higher disorder levels lead to the formation of lamellar patterns. High disorder significantly alters scaling behavior, causing the length scale to freeze at finite sizes. In Fig. 4, we show the table of contents for Chapter 5.

Finally, in Chapter 6, we provide a comprehensive summary and conclusion of the research and findings presented in the thesis.

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