Self-assembly of Polymer Fluids Under External Stimuli

Thesis submitted in fulfilment
for the Award of
Doctor of Philosophy
in
Physics

by
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Year of Submission
06 August 2024

To my loving parents and Nanaji.

Certificate

It is certified that the work in the thesis titled **Self-assembly of Polymer Fluids Under External Stimuli** by **Mr. Ashish Kumar Singh**, Roll Number **19171023**, has been carried out under my supervision, and this work has not been submitted elsewhere for a degree.

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Declaration

I, **Ashish Kumar Singh**, 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 06 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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Publications

1. Photo-induced bond breaking during phase separation kinetics of block copolymer melts- A dissipative particle dynamics study; Ashish Kumar Singh, Avinash Chauhan, Sanjay Puri, Awaneesh Singh; *Soft Matter*, 17 (7), 1802-1813 (2021).

2. Phase separation kinetics of block copolymer melts confined under moving parallel walls: A DPD study; Ashish Kumar Singh, Awaneesh Singh, Computational *Materials Science*, 226, 112224 (2023).

3. Growth kinetics and morphology characterization of binary polymeric fluid under random photo illumination; Ashish Kumar Singh, Avinash Chauhan, Awaneesh Singh; *Journal of Chemical Physics*, 160, 024907 (2024).

4. Photomodulated phase-separation kinetics of block copolymer melts: A DPD Simulation Study; Avinash Chauhan, Ashish Kumar Singh, Awaneesh Singh; *Molecular Simulation*, 50(5), 394-403 (2024).

5. DPD simulation study of segregation kinetics of binary polymer fluids: effect of external shear; Ashish Kumar Singh, Samiksha Shrivastav, Awaneesh Singh *(manuscript in preperation).*

6. Effect of random photo illumination on phase-separating dimers: A DPD simulation study; Ashish Kumar Singh, Awaneesh Singh *(work in progress).*

7. Insights into phase separation kinetics of fluids within polymer gel; Ashish Kumar Singh, Awaneesh Singh *(work in progress).*

8. Mixing and demixing of dimer melt system under the effect of alternate light cycles and shear: Ashish Kumar Singh, Vanshika Saini, Awaneesh Singh *(work in progress)*.

9. Phase separation kinetics of miktoarm star polymers in a solvent: Effect of size and number of arms; Devendra Kumar Verma, Ashish Kumar Singh, Avinash Chauhan, Awaneesh Singh *(work in progress)*.

Abstract

We have studied the phase separation kinetics of polymer fluids using the dissipative particle dynamics (DPD) simulation. In chapter 1, we have discussed the basic concepts on phase separating binary (AB) fluids, including the fundamental observables required to characterize the evolution morphology. We have explored mainly the following systems, simple binary fluid, polymer blend, and block copolymer (BCP) melt. The fundamental concepts of DPD simulation are also discussed, including the potential energies and details of simulation parameters used in further chapters.

In Chapter 2, we examine the phase segregation of a BCP melt system in $3d$ under external stimuli such as light. The bonds joining incompatible beads in BCP chains are considered photo-sensitive. We start with a homogeneous system and rapidly quench it to a temperature $T < T_c$, where T_c is the critical temperature. Simultaneously, we apply alternating on- and off-light cycles to the system. During the on-light cycles, bond-breaking reactions of the photo-sensitive bonds generates two corresponding active radicals. These active beads undergo recombination reactions in off-cycles, regenerating the original BCP chains. During the on-light cycles, macrophase separation occurs due to the breaking of stimuli-sensitive bonds, causing the two blocks to separate and behave as polymer blends. Conversely, off-light cycles result in microphase separation due to bond constraints between incompatible blocks. The study is divided into two sets: set 1 begins with an off-light cycle, while set 2 starts with an on-light cycle. We monitor domain evolution, scaling functions, and growth laws during each cycle. The characteristic length scale follows a power law growth $R(t) \sim t^{\phi}$, where ϕ is the growth exponent. Our simulation shows that the length scale follows all three regimes: diffusive ($\phi \sim 1/3$), viscous hydrodynamic ($\phi \sim 1$), and inertial hydrodynamic ($\phi \sim 2/3$) growth.

The time variation of the number of bonds broken and recombined demonstrates that our model accurately reproduces the first-order kinetics of photo-sensitive reactions.

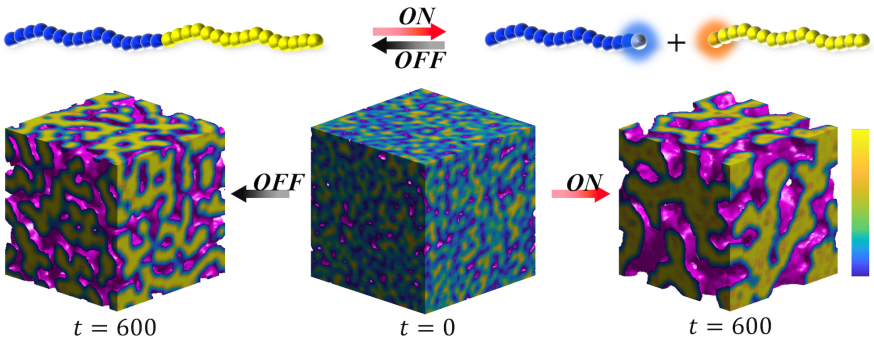

Fig. 1: Effect of on- and off-light cycles on the phase separation kinetics of BCP melt systems.

In chapter 3, we further explore the phase separation kinetics of polymer fluids using DPD simulations. We apply random photo-illumination to study its impact on the evolution of polymer blend and BCP melt systems. The polymer blend system has active radicals at one end of its each chain, while the BCP melt has light-sensitive bonds joining the incompatible blocks. The initial homogeneous mixture is quenched to a temperature below its critical value to induce phase separation. Simultaneously, the system is exposed to random photo-illumination, leading to two concurrent random events: (a) bond recombination reactions of the active radicals during the off-state of light and (b) breaking of photo-sensitive bonds in BCP chains when the light is on. The variation in the intensity of illuminated light is simulated by adjusting the bond-breaking probability P_b. The characteristic domain growth follows the typical power-law behavior $R(t) \sim t^{\phi}$. With varying P_b, the length scale transitions from microphase to macrophase separation at specific transition probabilities for both systems. The bond recombination probability is set to its maximum value $P_c = 1$, making microphase separation kinetics dominant at low P_b values. The excellent overlap in scaling function data indicates the formation of statistically similar domains across all probabilities. This study enhances

the understanding of phase separation kinetics in polymer fluids under external stimuli, affecting the fundamental properties of the system.

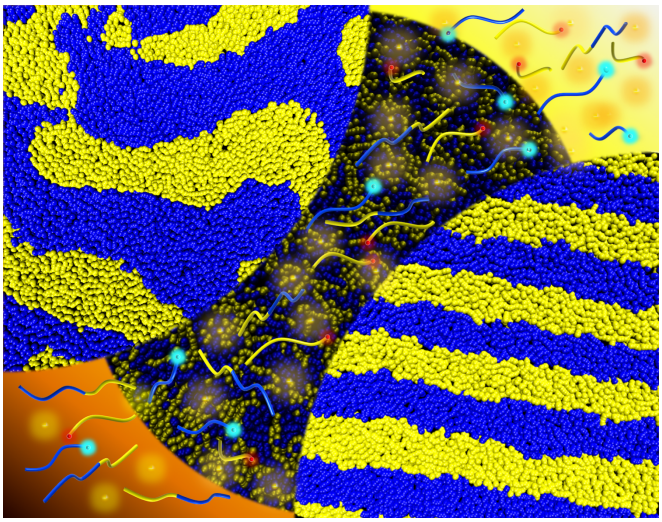

Fig. 2: Random photo-illumination on polymer blend systems.

In Chapter 4, we investigate the effect of external shear on the phase separation kinetics of BCP melt system. We consider a critical diblock copolymer melt system confined along the z-direction between two parallel solid walls at the top and bottom of the system. Initially, we quench the homogeneous mixture to a very low temperature and simultaneously apply external shear by moving the walls in specific directions. Our study is divided into four scenarios based on wall motion: (i) Both walls are fixed, (ii) Only the top wall moves with a constant velocity in x-direction, (iii) Both walls move in the same x-direction with the same velocity, (iv) The top wall moves in x-direction, while the bottom wall moves in opposite direction. We monitor the effect of external shear on domain coarsening, scaling functions, growth laws, anisotropy, and other relevant parameters. The characteristic length scale follows the usual power law behavior with diffusive growth at the early stage, which saturates at late times. However, with the application of shear, significant deviations are observed in the length scale data due to the formation of well-ordered structures. To minimize the effect of shear, domains rearrange themselves in a particular direction. Consequently, lamellar morphology forms much

earlier than in typical BCP melt systems, especially in scenario (iv), where a well-ordered lamellar structure is observed within specified time intervals. The viscosity plot shows shear-thinning behavior upon the application of shear for all cases. Overall, our study highlights the influence of shear rates on the microphase separation kinetics of BCP melts.

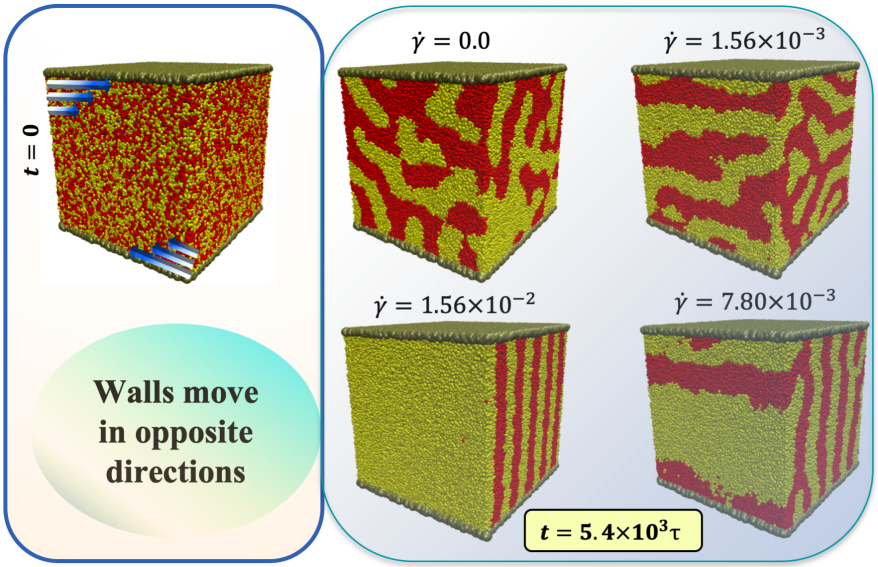

Fig. 3: Effect of external shear on the phase separation kinetics of BCP melts.

In Chapter 5, we examine the phase separation kinetics of a polymer blend system under the application of external shear. This study explores the effects of shear on both critical and off-critical polymer blend systems. Two rigid walls are placed at the top and bottom of the system, and shear is applied by moving these walls in specific directions. We again explored the four scenarios related to the shear generated by the wall motion, as expressed earlier for chapter 4. We monitor the effect of external shear on various properties such as morphological evolution, scaling functions, domain growth, radial distribution function, velocity profile, and viscosity. To counteract the effect of shear, the domains rearrange in a particular direction, forming organized structures. The characteristic length scale follows the typical power-law behavior: $R(t) \sim t^{\phi}$, where ϕ is the effective growth exponent. Initially, the length scale exhibits viscous hydrodynamic

growth ($\phi \sim 1$), transitioning to inertial hydrodynamic growth ($\phi \sim 2/3$) later on. At high shear rates, we observe anisotropy in the system due to domain flow in the direction of shear, resulting in more stable structures. As the shear rate increases, shear viscosity decreases, indicating shear-thinning behavior in all cases. In the off-critical mixture (case 4: when both walls are moving in opposite directions), cylindrical domains form at high shear rates, this is not observed in other cases within the same time interval. This study provides insights into how shear influences phase separation kinetics and domain organization in polymer blend systems.

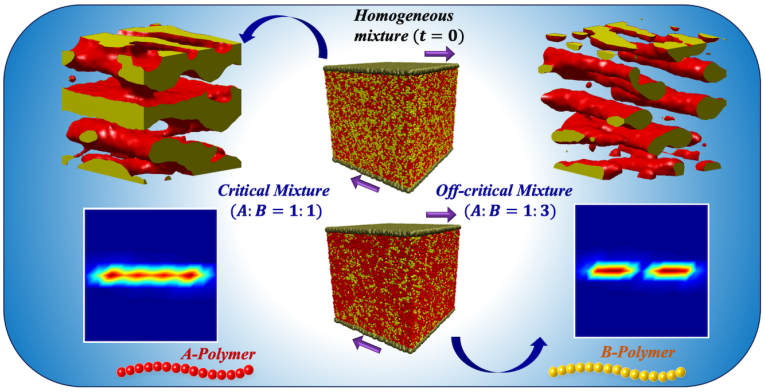

Fig. 4: Impact of external shear on critical and off-critical polymer blend systems.

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