Chapter 6

Conclusion and future plan

6.1 Conclusion

In this chapter, we briefly summarize all the chapters discussed in the thesis. We began with a basic introduction in Chapter 1. We explored the phase separation kinetics of polymer fluids under external stimuli such as light and shear. In the first chapter, we introduced the basic concept of phase separation, followed by the phase diagram of fluid mixtures. We also discussed the fundamental observables used to characterize domain evolution, such as RDF, scaling functions, and characteristic length scales. To provide a reference, we studied the phase separation kinetics of simple fluids, polymer blends, and BCP melt systems. Finally, we covered the DPD simulation method, including the essential potentials used to model polymer chains, the integration method, and parameter details.

In Chapter 2, we investigated the effect of on- and off-light cycles on the domain coarsening in a BCP melt system. We assumed that the bonds joining the incompatible blocks of BCP chains are photo-sensitive. During the on-cycle, these BCP chains undergo bond-breaking reactions, generating two active radicals that recombine during the off-cycles to regenerate the original BCP chains. These alternating light cycles alter the fundamental microphase separation properties of the BCP melt system. In the on-state of light, the system exhibits macrophase separation, and the length scale follows viscous and inertial hydrodynamic growth. Due to the reformation of BCP chains during the off-cycles, we observe microphase separation with a diffusive growth, followed by the characteristic length scale which saturates eventually. The first on-cycle determines the behavior of the scaling functions for subsequent cycles due to the occurrence of macrophase separation. By fitting the data on the number of bonds broken and recombined over time, we noted that our model accurately reproduces the results consistent with first-order kinetics of photo-sensitive reactions.

We extended the study from Chapter 2 to investigate the effect of random photo-illumination on the phase separation kinetics of polymer fluids (polymer blend and BCP melt) in Chapter 3. We fixed the bond-recombination probability at $P_c = 1.0$ and varied the bond-breaking probability $P_b \in (0, 1)$. The change in P_b simulates the variation in illuminated light intensity. From the reaction kinetics, we observed a power-law behavior in the number of bonds broken over time, where the growth exponent decreases with an increase in P_b. At lower probabilities and early time steps, the system exhibits microphase separation with diffusive growth in characteristic length scale. As the light intensity increases, the system transitions from microphase to macrophase separation at specific P_b values. Consequently, at high bond-breaking probabilities, the length scale transitions to inertial hydrodynamic growth at later time intervals. The transition probability from microphase separation to macrophase separation kinetics is observed to be 0.02 for the polymer blend and 0.2 for the BCP melt systems.

In Chapter 4, we study the phase separation kinetics of the BCP melt system under the influence of external shear. Shear is applied to the system by moving two rigid walls, one at the top and another at the bottom. When shear is applied, the domains begin to reorient along a particular direction to minimize its effect. Due to the bond constraint between incompatible beads, BCP chains organize themselves perpendicular to the flow direction, forming lamellar structures. At high shear rates, we achieve a well-ordered lamellar morphology much earlier than in usual BCP melt systems. From the length scale curve, we observe typical microphase separating behavior following an early time diffusive growth, which saturates later. However, at high shear rates, a significant deviation is noted due to the reorientation of the domains. The formation of ordered structures introduces anisotropy into the system. Additionally, we observe a decrease in shear viscosity with increasing shear rate in all cases, indicating shear thinning behavior.

Moreover, we study the effect of shear on domain evolution in a polymer blend system. We explored the phase separation kinetics of polymer blend systems with critical and off-critical mixtures in Chapter 5. External shear is applied to the system by moving two rigid walls, as in Chapter 4. Upon applying shear, the domains align along the shear direction, forming ordered structures. The system follows the usual macrophase separating behavior, where the length scale shows a crossover from viscous to inertial hydrodynamic growth. A significant deviation is noted at high shear rates. The development of anisotropy is represented by unidirectional length scale and structure factor curves, which show non-overlapping behavior along different directions under shear. As discussed previously, shear thinning behavior is observed in both systems, with a decrease in shear viscosity and an increase in shear rate. In the critical mixture, we notice the formation of distorted lamellar structures parallel to the solid walls, while in the off-critical mixture, distorted cylinders are formed at high shear rates and elongated along the flow direction.

6.2 Future Plan

For our future plans, we have initiated two new projects. The first project involves fully swollen hydrogels in a binary (AB) fluids in a cubic box: (i) AB binary simple fluid, (ii)

A polymer and B simple fluid mixture, and (iii) AB polymer blends. The hydrogel has certain affinity with fluid components. We aim to study the phase separation kinetics of this ternary system. By varying the gel density, solvent quality, and polymer chain lengths, we will monitor their effects on domain coarsening, scaling functions, and growth laws.

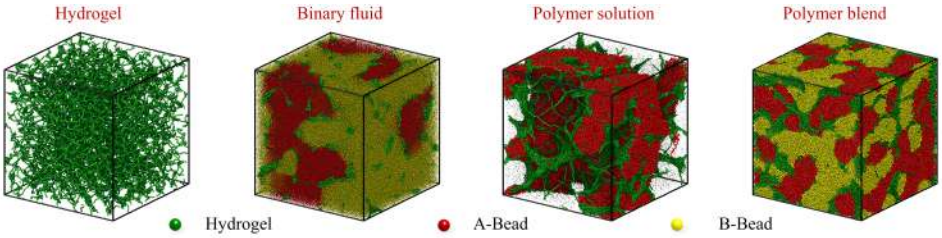
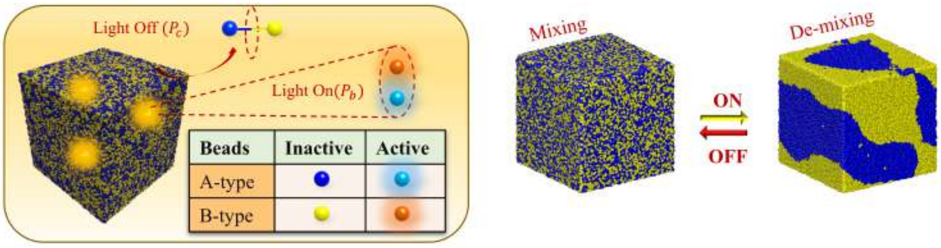


Fig. 6.1: Phase separation kinetics of different systems inside hydrogel.

Our second project focuses on dimers, where two different types of beads (e.g., A and B) are connected by a single light-sensitive covalent bond. We place a dimer system in a cubic box. Initially, we examine the phase separation in the bulk dimer system without any external influence. Then, we apply photo-illumination to the system, where the light on-state breaks the covalent bond, promoting the demixing of A and B type beads. When the light is off, recombination reactions occur between the incompatible beads, leading to mixing in the system. We will monitor the formation of secondary and tertiary structures after subsequent mixing and demixing cycles due to the light on- and off-states, respectively.



Beads	Inactive	Active
A-type	●	●
B-type	●	●

Fig. 6.2: Mixing and de-mixing in the dimer melt system on the application of alternate on-off light cycles.