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Mesoscale Computational Studies of Thin-film Bijels

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Mesoscale Computational Studies of Thin-film Bijels

A dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Engineering

by

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Bachelors of Science in Physics, 2013

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This dissertation is approved for recommendation to the Graduate Council.

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Abstract

Bijels are a relatively new class of soft materials that have many potential applications in the technology areas of energy, medicine, and environmental sustainability. They are formed by the arrest of binary liquid spinodal decomposition by a dispersion of solid colloidal nanoparticles. This dissertation presents an in-depth simulation study of Bijels constrained to thin-film geometries and in the presence of electric fields. We validate the computational model by comparing simulation results with previous computational modeling and experimental research. In the absence of suspended particles, we demonstrate that the model accurately captures the rich kinetics associated with diffusion-based surface-directed spinodal decomposition. When chemically-neutral particles are included in the films, the simulations capture surface-modified Bijel formation, with stabilized domain structures comparable with the experimental observations of Composto and coworkers. Next, the Bijel morphology space is explored. Key parameters varied are the Bijel liquid phase composition and the Bijel film thickness. Simulations reveal a broad spectrum of structurally unique morphologies that have yet to be observed in experiments and which could have interesting applications in membrane science and other domains. Lastly, the tunability of thin-film Bijels using applied external electric fields is explored. To accomplish this the coupled Cahn-Hilliard Particle Dynamics computational model is modified to include the effects of liquid domain alignment and particle dipole-dipole interactions in the presence of an electric field. Dielectric contrast between liquid domains governs liquid domain alignment and dielectric contrast between colloidal particles and liquid matrix governs particle polarizability. Both were varied in simulations and the study reveals unique internal morphologies including those with through-thickness liquid channels. Results include identification of electric field effects on phase evolution and final morphology as well as relevant mechanisms. It was also found that particle chains act as nucleation sites for phase separation. Electric field effects and mechanisms on morphology are identified and compared with other morphology-tuning parameters such as particle loading and liquid-liquid composition. For the simulations in this dissertation,
extensive analyses of surface-to-volume ratios, interfacial particle attachment statistics, and topological interfacial curvatures within the Bijels are presented for a complete characterization of their morphological structure.
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Chapter 1
Introduction

1.1 Motivation

In the last few decades science has witnessed important advances in nanotechnology and its ubiquitous applications such as medicine, energy conversion and storage, computing, manufacturing, food, cosmetics, and textiles, just to name a few. Nanotechnology is based on material structures with length scales on the order of 1-100s of nanometers, or collections of tens-to-millions of atoms, for example, nanoparticles of varying shapes such as spheres, cylinders, cones, etc. About a decade ago, man’s ability to manipulate the ultra small into functional materials brought promises of a scientific revolution that would solve many of societies challenging problems. However, like most things, science over promised and today we still haven’t cured cancer, solved the energy crisis, or created artificial life. This begs the question, “WHY?” Some might wonder if nanotechnology overpromised. But if you take a close look at the research going on today one will find that nanotechnology is still very much a hot topic of research; however, there is now a focus on making it more practical. It is not that nanotechnology has not lost its promise of delivering incredible new technologies, but making it useful has been more difficult than was expected.

Why has making it useful been so difficult? Many examples of nanotechnology have been inspired by nature, such as nano textured surfaces found on the iris leaf [1], shark skin [2], and gecko feet [3]. How do nanostructures in nature come about? This question is at the heart of one of the main difficulties in making nanosized materials useful—that is, how do we efficiently distribute nano structures into macroscale systems that we can then use to create new technologies? It is crucial that the distribution process does not alter the nano structures thereby preserving their superior size and shape dependent properties which we wish to exploit. Additionally, there exists a large gap in length scale between the nano and macroscales which begs the question of how are we going to distribute the nanostructures? Nature seems to have figured out how to do this part too. What we find
in nature is that there is a whole hierarchy of structures [4] from the nanoscale all the way up to the macroscale [5]. The structures between the nano and macroscale can be thought of as mesoscale structures (meso means middle). By having a hierarchical structure from the nano-to-macroscale the unique properties of the nanostructures are preserved and their functionality delivered at the macroscale. It is also important that the processes is scalable and efficient in order to be able to achieve mass production at a economic costs. These three issues of distribution, hierarchical structure, and efficiency are very difficult challenges facing scientists and engineers working to bring nanotechnology to market.

Initially, top-down material synthesis and processing techniques were employed in efforts to create nanostructures and distribute them into material systems. Top-down approaches are analogous to traditional manufacturing and processing which carve or cut bulk material into the desired shape and use some mechanism to physically place the structure in its desired location. Top-down processing techniques for nanoscale structures are called nanofabrication techniques in the literature [6]. Some examples include nano-lithography methods and vapor deposition methods. Unfortunately top-down approaches have all the wrong problems. They are notoriously energy expensive and difficult to scale up.

In contrast, bottom-up material synthesis and processing techniques focus on harnessing the natural interactions of atoms and nanostructures to allow them to self-assemble into useful conformations and hierarchical distributions. They are hallmarked by the need for low energy input and process in parallel which promotes scalability [7]. Life itself is the quintessential example of bottom up synthesis and processing—single celled organisms are built of self-assembled structures such as proteins, bi-lipid membranes, and DNA [8]. The challenge with such bottom-up self-assembly processes is that, in order to use them, they require an in-depth understanding of the interactions between constituents and the right environment to take place.

Soft materials such as liquids, colloids, gels, foams, and biological materials are some of the most promising material systems in terms of potential for utilizing bottom-up synthesis and processing techniques [8, 9]. They often have a rich mesoscopic structure.
Mesoscale structures are those on the order of nanometer-to-micrometers [10]. Soft materials are characterized by distinct mesoscale physics which means that their properties are best predicted by the interactions between their nano-to-microscale structures. Understanding the rich, complex, and vast set of interactions at the mesoscale is an incredible challenge and cutting-edge area of research [11]. Part of this challenge comes from the overwhelming sizes of parameter spaces that need to be explored. Another part of the challenge is that our intuition about mesoscale systems often fails us. This is because of the complexity that arises out of coupled mesostructure behavior [10]. Another way of saying this is that the sum of the parts does not equal the whole [12]. Studying nano-to-mesostructures and their behavior in isolation does not translate into an understanding of their behavior in heterogenous collections or groups.

Mesoscale modeling and simulation techniques of soft material systems has therefore also become increasingly important because they provide the in-depth understanding of constituent interactions necessary in mesoscale self-assembly processes. At the mesoscale, computer modeling and simulation has progressed beyond simply explaining experimental results and is now being used as a primary tool to explore and discover novel material systems that have never been realized in the laboratory. Modeling and simulation has the advantage of being able to explore the massive parameter spaces in mesoscale systems in a more efficient and cost effective way relative to experimental techniques. Of course the simulation models must be validated against experimental work to ensure their accuracy. However, once this is accomplished, it much easier to develop an understanding of the coupled mechanisms in complex systems using computational modeling and simulation techniques because one can almost effortlessly turn on and off different components of the model influencing some emergent behavior.

The research work presented in this dissertation has several motivations in the area of mesoscale materials science and computational modeling of soft materials. First, it seeks to advance the state-of-the-art in mesoscale materials modeling tools and techniques. It also applies those computational modeling techniques to explore the creation of novel soft materials enhanced by nanostructures. In particular, it aims to explore a class of soft
materials that is rich in its potential technological applications and utilizes bottom-up, self-assembly processes, exhibits hierarchical structure, and can be efficiently scaled up via roll-to-roll manufacturing—namely thin-filmed Bijels. Finally, it also strives to further develop our fundamental understanding of mesoscale physics in soft material systems.

1.2 Thin-film Bijels: A Versatile Class of Soft Materials

A good example of versatile soft material [13], one actually discovered via simulation before being created in the lab, is the Bijel. The term “Bijel” is an acronym that stands for \textit{B}i\textit{c}ontinuous \textit{I}nterfacially \textit{J}ammed \textit{Emulsion Gel}. Discovered in 2005 [14], A Bijel is a soft material composed of two phase separating liquids, often a polar and non-polar mixture such as oil and water, which is stabilized by a distribution of nano-micron sized particles also known as colloidal particles. The term “phase” is used to delineate between two materials of differing state (liquid, solid, gaseous) or composition (oil and water etc). Phase separation is the thermodynamically driven process of a single phase material separating into two distinct material phases. Oil and water is a classic example of liquid phase separation. Most people have had the experience with Italian salad dressing, where after giving the bottle a vigorous shaking to mix the dressing constituents, the oil and vinegar-water phases spontaneously begin to separate. If left for a long enough time, the two liquid phases will phase separate until there is a large oil domain floating atop a large vinegar-water domain. Although this process can be driven by the flow of the two liquids, it is primarily a thermodynamic process governed by the free energy of the system. The mutual interactions of the two immiscible (non-mixing) liquids are such that they naturally prefer to be separated, thereby minimizing how much they must remain in contact with one another. Essentially, the two-phase system has a lower total free energy in this separated state. In liquid systems, the phase separation from a mixed single phase state to a separated two phase state is initiated by a thermal quench (either down in temperature or up in temperature, according to the phase diagram of the binary mixture). Depending on the composition of the system, phase separation will proceed via spinodal decomposition or nucleation and growth.

To Form a Bijel, the binary mixture starts out in the single phase state and is quenched
into the two-phase region of the phase diagram. Typically a composition close to the critical composition is used so that phase separation proceeds via spinodal decomposition. The phase separation continues until stabilized by the colloidal particles. The phase separating liquids are stabilized in the sense that the particles get trapped on the interfaces between the two phase separating liquid domains and jam the phase separation process (see Figure 1.1 (a)-(b)).

Figure 1.1: (a)-(b) Bijel simulation renderings. Yellow and blue volumes represent two immiscible liquid phases and the green spheres represent colloidal particles. In (a) the two liquid phases are well mixed and colloidal particles are randomly distributed throughout the liquids. (a) represents the state of the system before the onset of phase separation. (b) represents the system after particles have collected on the liquid-liquid interfaces and jammed the phase separation process. (c) is a rendering of a gyroid surface.

Bijels are also characterized by the jammed domains being bicontinuous, meaning, that a continuous line could be drawn from any point in one phase to any other point in that phase without ever crossing a liquid phase boundary. This bicontinuous morphology is very similar to the minimal surface geometry of the gyroid and shares similar geometric properties (Figure 1.1 (c)). In particular, the domain sizes are typically very uniform, lacking constrictions or pinched off droplets. The average domain size is also simple to tune by varying parameters such as the colloidal particle loading, quench rate, and annealing time.

One way for making the Bijel practical is to solidify one of the liquid phases and remove the other. When this is done, a highly porous soft solid is left behind. Not only that, but the internal surfaces of the porous solid are lined with embedded colloidal particles giving it a hierarchical structure. In this way, Bijels become an attractive bottom-up, self-assembly route for delivering a wide array of nanoparticles to functionalize porous
soft solids. Additionally, if these bijels could be made in thin-films, they could be easily mass produced using a roll-to-roll manufacturing system.

Figure 1.2: BD/CH simulations by Millett [15] of electric field alignment in thin films of (a-c) a 50-50 polymer blend resulting in a columnar bijel structure, and (d-g) a 35-65 blend resulting in through membrane channels. Both cases lead to close-packed particle layers on the interfaces. Particles are not shown in the middle column for clarity. Light blue and dark blue colors denote the two liquid phases.

A few early experimental studies using phase separating homopolymer blends and nanoparticles demonstrated the creation and first analysis of thin-film bijels [16–18]. These studies showed that the thin film morphology is heavily influenced by surface effects on the liquid-liquid phase separation [19, 20] and supported a diverse range of morphologies. These morphologies included those that were three-dimensional and bi-continuous as well as those that were two-dimensional and discrete. These preliminary studies left several parameters lacking sufficient exploration and did not address others. Of particular interest are parameters such as the binary mixtures composition, film thickness, particle loading, and the role of surface directed spinodal decomposition. Until this dissertation, these early studies are all that have been done to study thin-film Bijels.

In addition to the already large and unexplored parameter space in thin-film Bijels, preliminary work by Millett [15], illustrated how thin-filmed Bijels could have their morphologies further tuned by the application of an electric field to align polymer domains in the out-of-plane direction (see Figure 1.2). This work demonstrated how thin-film bijels
could potentially be used to create soft polymer membranes, with through membrane channels and channel interfaces decorated with jamming nanoparticles.

The significance of this dissertation will be to achieve an in-depth understanding of the mesoscale structures and interactions in thin-film Bijels via computational modeling. In particular, it will develop a computational approach that directly couples grid-based phase-field models of liquid phase separation to particle dynamics models of colloidal distributions. This computational approach will capture the self-assembly of the nanoparticles onto the liquid-liquid interfaces and their jamming effect. It will also capture the surface-directed spinodal decomposition effects on the phase separation of the liquids. This hybrid computational model will be validated against the early preliminary work described above. It will then be used to probe and study the thin-film bijel parameter space, thereby exploring Bijel systems never before created in the laboratory. The computational approach will also be extended to model the effects of an applied electric field on thin-film Bijels in order to explore and study the coupled effects of liquid domain alignment and induced electric dipole interactions. The computational modeling and simulation work will provide a fundamental understanding of thin-film Bijels which will guide the creation of new experimental processes for creating Bijel membranes with highly tunable morphologies. This will accelerate the design cycle as well as inspire the eventual creation of new bijel derived membrane technologies.

1.3 Dissertation Objectives

The main objective of this dissertation is to develop and validate a computational method for modeling thin-film Bijels and then utilize it to study the their kinetic pathways and jammed morphologies. The model will capture both surface directed effects on phase separation and the effects of applied electric fields. The specific objects include:

1. Validate the hybrid Phase-field particle dynamics computational approach by reproducing the few experimental and computational results on thin-film polymer Bijels. Specifically, reproduce the computational work of Hore and Laradji [20] and the experimental results of Composto [17].

2. Study the effects of surface-directed spinodal decomposition (SDSD) on the thin-
film Bijel morphology. Specifically study these effects by varying the film thickness, thermal noise strength, and particle loading.

3. Explore the thin-film bijel parameter space to discover the range of morphologies that exist. Specifically vary the binary liquid mixture composition and film thickness.

4. Analyze the simulated Bijel films in terms of particle attachment to liquid-liquid interfaces, interfacial surface area to volume ratio, and interfacial curvatures to identify trends and correlations.

5. Extend the computational approach first developed in [15] to include the alignment effect of external electric fields on the liquid domains as well as the induced electric dipole interactions of colloidal particles.

6. Study and analyze the coupled effects of liquid domain alignment and particle chain formation produced by an applied electric field to thin-film bijel membranes. Specifically vary the dielectric contrast between liquids and particle polarizability. Analyze their effect on channel size and distribution, particle attachment to liquid-liquid interfaces, and the interfacial surface area to volume ratio.

1.4 Dissertation Structure

This dissertation contains three articles. The first article was published in the *Journal of Chemical Physics*. The second article was published in the soft materials technical journal *Soft Matter*. The third article has been submitted to the same journal, *Soft Matter*, and is currently under review. The first paper is titled, “Numerical simulations of bijel morphology in thin films with complete surface wetting” [21]. This paper addresses objectives 1 and 2 and is presented as chapter 4 of this dissertation. The second paper is titled, “Diverse morphologies in thin-film bijels by varying film thickness and composition” [22]. It addresses objectives 2–4 and is presented as chapter 5 of this dissertation. The last paper is titled “Tuning Thin-film Bijels with Applied External Electric Fields” and is presented in chapter 6 and addresses objectives 5 and 6.
Due to the concise nature of these articles, only the most relevant information with regards to corresponding literature and computational methods is included as an introduction to each article. Therefore chapters that give a more expansive and thorough discussion of these topics have been included in this dissertation. Chapter 2 titled \textit{Scientific Background}, includes an introductory discussion with relevant literature citations for the topics of: thermodynamic driven phase-separation of liquids, colloidal particles and their Brownian motion, Bijel formation, surface-directed spinodal decomposition, electric field induced polymer domain alignment, and electric dipole interactions between colloidal particles. Chapter 3 is titled \textit{Computational Methods} and includes a discussion with relevant literature citations on the topics of: Cahn-Hilliard phase-field modeling of liquid-liquid phase separation, Brownian and Langevin particle dynamics modeling, the coupling of these models, modifying the hybrid phase-field particle dynamics model to account for electric field effects, numerical solvers employed for solving the governing equations, and simulation analysis techniques and algorithms.

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Chapter 2
Scientific Background

As mentioned in Chapter 1, this dissertation is primarily concerned with the computational modeling of thin-film Bijels. The first three sections are largely a review of the recent scientific literature on Bijels, surface directed spinodal decomposition, and electric field effects on phase separating liquids and colloidal particle distributions. Most of the content from these first four sections is presented again in Chapters 4-6 with much less discussion. Bijels being composed of phase separating liquids and a distribution of colloidal particles, the last two sections of this chapter will discuss the basic thermodynamics of liquid-liquid phase separation and the motions of colloidal particles. These sections include information scattered throughout a number of textbooks which has been aggregated here for the convenience of the reader.

2.1 Bijels

As was mentioned in the introduction chapter, Bijels are a soft material system that was discovered via simulation in 2005 by Cates’ group [1]. Cates’ group specializes in theoretical studies of soft materials such as emulsions, colloids, polymers, and surfactant solutions. They had been using Lattice Boltzmann computations to simulate liquid-liquid phase separation via spinodal decomposition (i.e. starting from the single phase region of the phase diagram and quenching into the binary phase region below the spinodal line, see Figure 2.9). Figure 2.1 shows the time evolution of a simulated binary mixture at the critical composition undergoing spinodal decomposition. Also for comparison, a system with composition inside the metastable region is shown undergoing droplet nucleation and growth. The images show the system starting from a uniformly mixed single phase state (far left images in Figure 2.1) and its phase separation, or evolution through time, in successive images to the right. In spinodal decomposition, phase separation proceeds uniformly throughout the entire domain via diffusion and is hallmark by its bicontinuous morphology. Cates’ group wondered if it would be possible to freeze in the morphology of the binary mixture undergoing spinodal decomposition during its intermediate stages
using solid particles that segregated to the liquid interfaces. They developed a Lattice Boltzmann model to simulate the physics and began exploring its parameter space. Their results were astonishing and ultimately inspired the creation of a new class of soft materials, which they named Bijels, standing for bicontinuous jammed emulsion gels. Figure 2.2 shows some of these early simulations and experimental Bijel results.

In Cates’ seminal simulation paper the Bijel’s formation process is outlined [1]. The basic requirements are to have a binary liquid mixture that is miscible (i.e. single phase) and can be quenched, typically by decreasing the temperature, into an immiscible two phase state where phase separation occurs via spinodal decomposition. Included in the single phase mixture, before the quench, is a dispersion of colloidal nanoparticles with the key characteristic of having no affinity for either of the two liquid phases which develop during phase separation. This condition is referred to as neutral wetting and corresponds to a liquid-liquid-particle contact angle of approximately 90 degrees. When the binary liquid and particle mixture is quenched into the two-phase region, phase separation of the single liquid phase into two phases proceeds creating interfaces between the two phases. This interface has a surface tension $\gamma$.

As phase separation proceeds, the interface moves and begins to collect the colloidal particles dispersed throughout the domain which get adsorbed to the interface and re-
mained attached due to surface tension induced capillary forces. Initially this particle adsorption to the interface does not alter the phase separation; however, as the interface shrinks, eventually particles form a dense monolayer. At this point the two phase separating liquids must either halt in their coarsening or expel particles from the interface to continue. The energy cost for particle expulsion from the interface is proportional to the interfacial tension and the area of the interface covered by a particle. For a particle contact angle of 90 degrees this area is approximately the cross sectional area of the spherical particle. Thus the energy cost for particle expulsion is \( \epsilon = \gamma \pi r^2 p \). For particles with a 3 nm radius, a typical surface tension of \( \gamma = 0.01 Nm^{-1} \), and at room temperature \( T = 300K \), the detachment energy is roughly ten times the particles thermal energy, \( k_b T \). Thus particles are very unlikely to detach from the interface due to their own thermal motion. For particles larger than 3 nm this energy cost only increases [1]. Hence, the particle laden interface jams the phase separation and freezes in the intermediate spinodal structure.

After the Bijel’s initial discovery via simulation, Clegg’s group [3] established a reproducible experimental protocol for creating bijels in bulk using a 2,6 lutidine-water
mixture and surface treated silica nanoparticles (Figure 2.2 on right). In this study, they also established the Bijel’s average domain size dependence on particle loading, conducted the first measurements of its rheological properties, as well as explored off-critical compositions in the 2,6 lutidine-water phase diagram. One of the largest challenges with this and other early attempts to realize a three-dimensional Bijel in the lab, was the strict requirement for the particles to neutrally wet both liquid phases. This required delicate surface treatment of the nanoparticles. Later, techniques were explored for creating Bijels that did not require these delicate particle surface treatments [4].

After these two initial studies, more in depth fundamental studies were conducted which focused on studying the Bijel’s rheological properties [3, 5-10], particle adsorption and desorption to liquid-liquid interfaces and thermodynamic stability [1, 11-14], particle wetting properties such as the particle/liquid/liquid contact angle [13, 15-17], varying the shape and type of colloidal particles [18-20], the different morphologies that can be induced by varying different parameters [7, 15, 21], using high molecular weight liquids [22, 23], and characterization techniques [24]. Important findings from these studies include the following:

• The average domain size of the Bijel, that is from interface-to-interface, is inversely proportional to the particle loading and proportional to the particle size $L \sim r_p/\phi_p$, where $L$ denotes the average size of liquid domains, $r_p$ is the average radius of the colloidal particles, and $\phi_p$ is the volume fraction of particles.

• Bijels are a metastable thermodynamic state. They may possibly be made thermodynamically stable if particles have attractive forces or chemical bonding while jamming the interface.

• The monolayer of jamming colloidal particles can remain stabilized even after phase separated liquids remix, imparting mechanical stability to the gel.

• Particle wetting properties such as contact angle can induce a preferential interfacial curvature that influences jammed morphology.
• Bijels can be made from two non-polar liquids. They may also be made using higher molecular weight liquids such as polymer blends.

• Jammed particles on the liquid-liquid interface remain dynamic after jamming which allows them to reorganize in response to stress from compression or shearing.

In addition to these fundamental studies, another method for creating Bijels has also been introduced which utilizes a process known as “Solvent Transfer Induced Phase Separation” or STRIPS for short [25, 26]. STRIPS utilizes a ternary mixture with two immiscible components in solution along with nanoparticles. The ternary mixture is jetted into an aqueous phase where the solvent then diffuses out of the ternary mixture and induces phase separation via spinodal decomposition of the two immiscible components. It is a fairly new technique and can be used for creating bijel fibers, particles, and thin-films. Yet another method for creating Bijels from purely immiscible liquid mixtures (i.e. there is no single phase region in the mixtures phase diagram) being developed by other groups [27, 28]. This method utilizes a direct mixing approach of the two immiscible liquids and combines a surfactant with the dispersed colloidal particles. In [27] the nanoparticles and surfactant are mixed in separate phases and then combine at the interface to stabilize droplets which are then mechanically mixed. In [28], the surfactant and particles are kept together in one of the phases and a two step mixing process is used that first forms droplets and then transforms to a bicontinuous morphology.

Many other Bijel studies have focused on Bijel applications for the energy and biomedical industries. In most of these applications they have been used as templates for creating hierarchically porous metals, ceramics, and other materials [29–34]. The general approach begins by forming a bijel with the desired morphology and domain sizes. Next, one or both liquid phases are solidified and one of the phases is removed. This leaves a porous soft-solid which can then be used as the template for the metallic, ceramic, or other material. After coating the template with the desired material, the Bijel template can be removed chemically or burned away. In addition to being used as templates, Bijels have also been used to create capsules [35] for controlled release applications as well as edible bijels for the food industry [36].
Figure 2.3: Figures adapted from [21], illustrating the thin-film polymer bijel morphologies that resulted from changing film thickness and particle loading. Left is a cartoon illustrating top-down and side views of a discrete morphology in (a) and bicontinuous morphology in (b). Right, shows a morphology map based on film thickness and particle loading.

2.2 Bijels in Thin-film Geometries

With the exception of two studies by Composto’s group [21, 22] and the work done with STRIPS [25, 26], all the Bijel studies have focused on bulk geometries. The limited work done in confined thin-film geometries, which is solely experimental studies, illustrates that the confining surfaces has a large impact on the Bijel morphology. Composto’s group demonstrated that simply varying the film thickness and particle loading in Bijel thin-films leads to two very different morphologies. Figure 2.3 shows a cartoon schematic of the two morphologies resulting from the thin-film Bijels made with PMMA-SAN polymer blend and silica nanoparticles. It also depicts a morphology map for these thin-films based on the film thickness and particle loading.

One of the main contributing factors to the morphologies seen in Composto’s experimental work [21] is the influence of surface directed spinodal decomposition (SDSD). For phase separation happening near a surface, it is common for one of the equilibrium liquid phases to preferentially wet the surface. This wetting phenomenon influences the kinetics of phase separation in the local region to the surface. When there are two confining surfaces in close proximity, such as in the case of a thin film (usually a substrate and air interface), these wetting effects are compounded.

Surface directed phase-separation has been studied extensively both experimentally
and computationally. Most of these studies were done with single surface geometries. A few addressed the case where there are two confining surfaces for thin-film geometries [37-41]. A thorough review, covering both single surface and two-surface geometries, is presented by Puri [42]. One computational modeling study of SDSD by Hore and Laradji [43] gives an excellent description of the SDSD effects on phase separation kinetics and morphology. Figure 2.4 shows their dissipative particle dynamics simulation renderings for a thin film undergoing SDSD. The morphology starts out bicontinuous in the early stages. In the intermediate stages wetting layers form at the top and bottom of the film and the bicontinuous morphology starts to break up into discrete columns that span the entire thickness of the thin film. During the late stages the columns grow in diameter by depleting the wetting layers at the top and bottom of the film.

These studies demonstrated that SDSD was capable of inducing rich morphological transitions resulting in thin films with both two and three-dimensional structure. At the start of the Authors PhD studies, Composto’s group was the only one to have conducted a thin-film Bijel study [21]. As shown in Figure 2.3, that work demonstrated that thin-film Bijels retained some of the morphological features that occur in SDSD systems without particles. Furthermore, it showed that loading and film thickness could be used to select which SDSD morphology, either two-dimensionally discrete or three-dimensionally bicontinuous, was acquired by the Bijel thin-film. The rich dynamics of SDSD combined with the stabilizing effect of particles and its potential to create diverse thin-film Bijel morphologies was a strong motivating aspect for the Author’s computational work presented in this dissertation. The paper presented in Chapter 4 utilizes the computational work of Hore and Laradji [43] as well as Composto’s experimental work [21] to validate a computational model for studying thin-film Bijels. The paper presented in Chapter 5 expands on this work and represents the first major research thrust to study thin-film Bijels since Composto’s first experimental investigation [21]. It explores other morphologies that can be stabilized in thin-film Bijels by varying liquid composition and film thickness.
Figure 2.4: Figures from [43], illustrating the early, intermediate, and late stages of surface directed spinodal decomposition in thin-film geometries. For each simulation time stamp a side-view and top-view of a cross-section through the center of the film are shown.
2.3 Electric Field Alignment in Polymer Mixtures and Colloidal Particle Induced Electric Dipole Interactions

Another attractive feature of Bijels in thin-film geometries is their potential to be further tuned by the alignment of liquid domains by electric fields. Preliminary research in this area by Millett [44] demonstrated the potential of using electric fields to transform thin-film polymer Bijel morphologies to those with through membrane channels and channel interfaces functionalized by adsorbed nanoparticles. Figure 1.2 features simulation renderings from [44] illustrating the electric field alignment of thin-film bijels. Using electric fields to direct self-assembly and control particle motions is currently a major theme being explored in the scientific community [45-51]. In this section we review relevant literature to the alignment of liquid polymer domains and the influence of electric fields on dispersions of colloidal particles.

2.3.1 Alignment of Binary Liquid Mixtures by an Electric Field

When a binary mixture is subjected to an external electric field, electric dipoles are induced in the liquid molecules which adds electrostatic energy to the system. The electrostatic energy contribution to the system’s free energy is given by [52],

\[ F_{es} = -\frac{1}{2} \int \epsilon(r)E^2(r)dr \]  

where \( \epsilon(r) \) is the dielectric constant at position \( r \) and \( E(r) \) is the electric field at the same position. If the binary mixture is immiscible and two liquid phases are present, then both the dielectric constant and the electric field are functions of the liquid-liquid compositions \( \phi_A \) and \( \phi_B \), where \( A \) and \( B \) denote the two liquid phases. Thermodynamically, the system will undergo spontaneous changes in the composition in order to minimize its overall free energy which will include changes that minimize the electrostatic energy contribution.

Early studies of applying electric fields to binary liquid mixtures studied the elongation of droplets [53-56]. In these works it was shown that the electrostatic contribution to the free energy in immiscible mixtures favored alignment of the domains with the electric field and hence the elongation of the droplets; however, this effect usually creates more
Figure 2.5: Examples of electric field alignment in (a) diblock copolymers [59], (b) a homopolymer blend [58], (c) colloidal particles in a liquid, leading to a particle cell structure [65], (d) simulations of the same phenomenon shown in (c) [66].

interface and consequently competes with interfacial free energy contributions of surface tension [53]. Interestingly it was found that for low viscosity immiscible liquids, higher field strengths burst the droplets, whereas for high viscosity liquids the droplets would be continuously elongated into threadlike domains [54]. Further studies where done on phase separating polymer and block copolymer blends [57–63]. The immiscible block copolymer blend study was done for thin-film geometries and demonstrated that electric field alignment was able to overcome preferential wetting of the substrate surface [59]. Another study illustrated how electric fields can even be used to induce remixing of phase separated liquids near the critical point of the phase diagram [64]. The parts of these studies most relevant to this work are that two-phase binary mixtures may be aligned by electric fields (see Figure 2.5a,b) and that higher viscosity mixtures, such as polymer blends, tend to continuously deform in order to align with the electric field as opposed to bursting.
2.3.2 Colloidal Suspensions in Electric Fields

When electrically neutral colloidal particles are subjected to an electric field, the electric field will induce an electric dipole moment in the particles. Because the particles are free to rotate about in their suspended medium, these dipoles will align in the direction of the electric field. A particle with an electric dipole experiences dipole-dipole interactions with its surrounding neighbors such as attractions or repulsions based on the local configuration of neighboring particles. Based on these interactions and in concert with non-dipolar forces, particles can assemble into chains [67–69], chain aggregates [70], or crystal structures [69, 71, 72].

The classic example of a colloidal dispersion in an electric field is that of an electrorheological fluid [69]. In these materials, high concentrations of colloidal particles are dispersed in a non-polarizable liquid (i.e. has a very small dielectric constant). When the electric field is applied, particles align in chains with strong attractive forces between chained particles. As the electric field strength is increased the viscosity of the electric field increases until, after crossing a critical value, the liquid solidifies. This phase
transformation is completely reversible but has a longer relaxation time. When the concentration of colloids is curtailed to very low densities ($c < 0.1$), particle chains begin to aggregate and form walls and networks of walls surrounding regions devoid of particles [65, 66, 73] (see Figure 2.5c,d).

This literature on electric fields applied to lower colloidal particle concentrations is most relevant to our work presented in chapter 6. For that work, we utilized the experimental and modeling work in [65, 66] to validate our model of electric-field induced dipole interactions of colloids. Although not included in that paper, we were able to qualitatively reproduce the results achieved in [66] using our particle dynamics model. For a comparison see the colloidal particle network formation in Figure 2.5c,d with our results shown in Figure 2.6.

2.4 The Cahn-Hilliard Equation

The goal of this section is to introduce the reader to the Cahn-Hilliard equation and the thermodynamics on which it is based. There are journal articles that introduce and derive the Cahn-Hilliard equation [74–76]; however, these papers lack sufficient background information connecting the Cahn-Hilliard equation to thermodynamic free energy models for polymer systems used in this dissertation. This section includes relevant descriptions of thermodynamic free energy models and a derivation of the Cahn-Hilliard equation.

To begin, the Cahn-Hilliard (CH) equation was introduced by John Cahn and John Hilliard [77–80] to describe the time evolution of a binary alloy’s microstructure in terms of its free energy derived chemical potential. Since then it has been used to model many phenomena including phase separation of binary and ternary liquids [81, 82], tumor growth [83–85], grain growth [86, 87], powder sintering [88, 89], pore migration in a thermal gradient [90, 91], and multiphase fluid flows [92–95], just to name a few.

The CH equation is commonly expressed as:

$$\frac{\partial \phi}{\partial t} = \nabla \cdot \left( M \nabla \frac{\delta F}{\delta \phi} \right)$$  \hspace{1cm} (2.2)

In this equation $\phi$ is known as an order parameter which represents a conserved value in
the system being modeled and fully characterizes the phase transformation. Examples in binary component systems undergoing second order phase transformations include component concentrations such as a component in a binary alloy or liquid mixture. \( \phi \) itself is a function of space and time, \( \phi(x, y, z, t) \), meaning that it can vary depending on physical location in the system and according to what time is being referenced. The typical range for values of \( \phi \) are from \([0, 1]\) if representing a concentration or from \([-1, 1]\) when representing something like the difference between two concentrations \( c_A - c_B \) in a binary mixture. \( M \) in equation 2.2 is the mobility of the order parameter and is related to the diffusive kinetics of the order parameter. It can also be a function of space and time, temperature, other thermodynamic variables, or \( \phi \) depending on the nature of the system. \( F \) in equation 2.2 is the free energy of the system and is typically a function of both \( \phi \) and its gradient and temperature, \( F(\phi, \nabla \phi, T) \). \( F \) is said to be a functional, because it takes other functions as its inputs.

For phase separating liquids, \( \frac{\delta F}{\delta \phi} \) is the chemical potential \( \mu \) and is derived from the free energy of the system by,

\[
\mu = \frac{\delta F}{\delta \phi} \tag{2.3}
\]

where the right-hand side of equation 2.3 is the variational derivative of the free energy functional. This free energy functional is usually the Gibbs free energy or Helmholtz free energy. The nature of the system, whether it be phase separating liquids, cancerous growths, metal alloys, or pores in a matrix, determines the number of order parameters and functional forms of \( M \) and \( F \) needed to model the system with equation 2.2. The way equation 2.2 is shown above, it may seem it is limited to having a single order parameter \( \phi \) with corresponding mobility, \( M \), and free energy, \( F \), but this is not the case. A set of CH equations can be used that evolve any number of order parameters with associated mobilities all of which will correspond to a single and free energy functional.

The solution to the CH equation is the time evolution of the systems order parameters over some specified time domain. The time evolution is always towards thermodynamic equilibrium in terms of minimizing the specified free energy \( F \). For simple systems, analytical solutions exist for this partial differential equation which is typically fourth
order due to gradient terms included in $F$; however, most complex systems must be numerically approximated [96]. This topic will be covered in depth in the next chapter.

We now turn our attention to how the free energy of systems of phase separating liquids can be represented and used to model the chemical potential required in the CH equation.

2.4.1 Thermodynamics of Binary Mixtures

Thermal physics is concerned with the equilibrium state of natural systems [97]. It describes such systems in terms of their constituents and mutual interactions by defining the energy of the system. The free energy of a system is a framework for understanding the spontaneous changes which happen in systems under constant temperature and pressure or volume conditions. The Gibbs free energy is used to describe systems in constant pressure and temperature environments. The mathematical expression for the Gibbs free energy is,

$$G = H - TS$$

(2.4)

where $H$ is the systems enthalpy, $T$ is the absolute temperature, and $S$ is the systems entropy. The enthalpy of the system, $H = U + PV$, is composed of the systems internal energy $U$ and the atmospheric work required to create the system $PV$, where $P$ is the pressure and $V$ the volume of the system.

The Helmholtz free energy is used to describe systems in constant volume and temperature environments. The Helmholtz Free energy is given by,

$$F = U - TS$$

(2.5)

and is the same as the Gibbs free energy without the inclusion of the atmospheric work term $PV$.

The second law of thermodynamics states that all natural systems will undergo spontaneous change in order to maximize their entropy $S$ [97]. Another way of saying this is that the system’s constituents and their energy will spontaneously change in order to occupy the system state with highest statistical probability. By virtue of the definitions of the free energy given in equations 2.4 and 2.5, this implies the equilibrium state of a
system is the one which minimizes its free energy. For a binary liquid mixture, its final equilibrium state will be the one that minimizes its total Gibbs or Helmholtz free energy. The miscibility of the mixture is dependent on the interplay between the internal energy and entropy of the mixture. Mixing always increases entropy and thereby favors mixing of the two liquids because of the subtractive relationship of the entropy in equations 2.4 and 2.5. That means that immiscibility of a binary mixture requires the enthalpy to favor separation instead of mixing.

![Diagram of A B Mixture](image)

Figure 2.7: Left Top, binary liquids unmixed. Left bottom, binary liquids after mixing. Right, Gibbs free energy trend before mixing as a function of $\phi_B$.

### 2.4.2 Mean Field Theory Approximations for the Free Energy of Binary Mixtures

To make this more precise in mathematical terms, let us consider a binary system of liquids (labeled $A$ and $B$) and formulate their free energy in terms of their volume fractions $\phi_A$ and $\phi_B$ at a fixed temperature $T$. We will use the Gibbs free energy for this example. Assuming that we keep the liquids unmixed at first (see top-left schematic of Figure 2.7), the Gibbs free energy can be written as,

$$G_0 = \phi_A G_A + \phi_B G_B = (1 - \phi_B)G_A + \phi_B G_A$$

(2.6)
where $G_A$ and $G_B$ are the Gibbs free energy of the system when made up entirely of liquid $A$ or liquid $B$. The plot on the right side of Figure 2.7 illustrates how the free energy of the unmixed system varies linearly in terms of liquid volume fraction.

Now assume the liquids are isothermally mixed as depicted on the bottom left side in Figure 2.7. In this mixed state the Gibbs free energy can be expressed as the sum of the unmixed free energy $G_0$ and the change in free energy due to mixing $\Delta G_{mix}$:

$$G_{mix} = G_0 + \Delta G_{mix}$$

(2.7)

The change in free energy due to mixing can be further broken down into enthalpic and entropic terms:

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix}$$

(2.8)

The entropic term $\Delta S_{mix}$ is always positive because there are always more ways to arrange the interaction energy and liquid molecules after mixing. Depending on the interactions between liquid molecules, the enthalpic term may be positive or negative depending on the type of interactions between the two liquids.

Now let us employ the commonly used mean-field model that assigns liquid molecules to lattice sites and only accounts for the interactions with molecules occupying nearest neighbor lattice sites. This allows calculation of $\Delta H_{mix}$ and $\Delta S_{mix}$ in terms of liquid volume fractions. It also assumes that liquid molecules are roughly of the same size and of low molecular weight. The right side of Figure 2.8 shows a schematic of such a lattice with a mixture of liquid molecules of species $A$ and $B$. The entropy of mixing, $\Delta S_{mix}$, can be calculated using the Boltzmann equation,

$$\Delta S_{mix} = k_b \ln \left( \frac{\Omega}{\Omega_0} \right)$$

(2.9)

where $k_b$ is Boltzmann's constant and $\Omega$ is the multiplicity function representing the total number of ways the species $A$ and $B$ molecules can be uniquely arranged on the lattice. $\Omega_0$ is the multiplicity function for the unmixed state and is equal to one because there is
only one unique configuration of molecules in the unmixed state. In terms of the number of molecules of different liquid species $N_A$ and $N_B$, the multiplicity function for the mixed state is given by,

$$\Omega = \frac{N_a!}{N_A!N_B!}$$

(2.10)

where $N_a = N_A + N_B$ is the total number of molecules in the system, which, for the sake of convenience, we are choosing to be one mole of molecules, or Avogadro’s number $N_a$. Note that this mean field model ignores any non-combinatorial contributions to the entropy of mixing.

Next, by applying Stirling’s approximation for very large numbers (i.e. $\ln(N!) = N \ln(N) - N$) to equation 2.10 yields,

$$\Omega = N_a \ln(N_a) - N_a - (N_A \ln(N_A) - N_A + N_B \ln(N_B) - N_B)$$

(2.11)

$$= -N_A \ln(\phi_A) - N_B \ln(\phi_B)$$

(2.12)

with $\phi_A = N_A/N_a$ and $\phi_B = N_B/N_a$ as the volume fractions of liquid species $A$ and $B$. Multiplying equation 2.12 by $N_a/N_a$ and substituting it into equation 2.9 we get the entropy of mixing in terms of the molar volume fractions of the two species.

$$\Delta S_{mix} = -R (\phi_A \ln \phi_A + \phi_B \ln \phi_B)$$

(2.13)

where $R = k_b * N_a$ is the universal gas constant.

Now we will address the enthalpy (heat) of mixing $\Delta H_{mix}$. If we assume there is no change in the volume of the system upon mixing (i.e. $\Delta V_{mix} = 0$), then the only contribution to the enthalpy of mixing is the change in internal energy $\Delta U_{mix}$ which can be assumed to depend on the interaction energies of the liquid molecules with their nearest neighbors on the lattice. There are three types of interactions between liquids: $A - A$ interactions, $B - B$ interactions, and $A - B$ interactions. The interaction energies for these three types will be denoted $\epsilon_{AA}$, $\epsilon_{BB}$, and $\epsilon_{AB}$. The internal energy of the mixed
Figure 2.8: Left, schematic of liquid molecules on a lattice. Right, regular solution model for the Gibbs free energy of a binary liquid mixture, fixed temperature $T$, and function of liquid composition.

The system is simply the sum of all the interaction energies in the system,

$$U_{\text{mix}} = n_{AA}\epsilon_{AA} + n_{BB}\epsilon_{BB} + n_{AB}\epsilon_{AB}$$  \hspace{1cm} (2.14)$$

where $n_{AA}$, $n_{BB}$, and $n_{AB}$ are the number of corresponding interactions in the binary mixture. If each molecule on the lattice has $z$ nearest neighbors, then the relationship for the number of $A$ and $B$ molecules $N_A$ and $N_B$ with the number of pairwise nearest neighbor interactions, can be expressed as $zN_A = n_{AB} + 2n_{AA}$ and $zN_B = n_{AB} + 2n_{BB}$ respectively [74]. These two equations may be solved to for $n_{AA}$ and $n_{BB}$ resulting in,

$$n_{AA} = \frac{1}{2}(zN_A - n_{AB})$$  \hspace{1cm} (2.15)$$
$$n_{BB} = \frac{1}{2}(zN_B - n_{AB})$$  \hspace{1cm} (2.16)$$

These relations can be further substituted into the equation for the internal energy of the mixed system in (equation 2.14) to get the following result [74]:

$$U_{\text{mix}} = \left[ \frac{zN_A}{2}\epsilon_{AA} + \frac{zN_B}{2}\epsilon_{BB} \right] + n_{AB}\left[ \epsilon_{AB} - \frac{1}{2}(\epsilon_{AA} + \epsilon_{BB}) \right]$$  \hspace{1cm} (2.17)$$
The first term inside the first set of square brackets in equation 2.17 is clearly the internal energy of the liquids in the unmixed state, which means that the remaining term corresponds to the mixing energy $\Delta U_{\text{mix}}$.

If the molecules on the lattice were randomly mixed then the probability of an empty lattice site getting occupied by an $A$ or $B$ molecule would be $\phi_A$ or $\phi_B$. There are also $zN_a/2$ pairwise interactions, the probability of one of these being an $A-B$ interaction is $2\phi_A\phi_B$; therefore, the number of $A-B$ interactions can be calculated as $n_{AB} = \phi_A\phi_B zN_a$. Substituting this into our result for the energy of mixing (second term in equation 2.17), we get the following expression for the enthalpy of mixing [74]:

$$\Delta H_{\text{mix}} = \phi_A\phi_B zN_a \epsilon_{AB} - \frac{1}{2} (\epsilon_{AA} + \epsilon_{BB}) = \chi \phi_A\phi_B \quad (2.18)$$

The parameter $\chi = zN_a [\epsilon_{AB} - \frac{1}{2} (\epsilon_{AA} + \epsilon_{BB})]$ is called the regular solution constant and represents the strength of molecular interactions. It is positive when $\epsilon_{AB}$ interaction energies are stronger than the mean of $\epsilon_{AA}$ and $\epsilon_{BB}$ interaction energies and negative otherwise.

Now we may combine the results for entropy and enthalpy of mixing to get the Gibbs (or Helmholtz) free energy of mixing in terms of absolute temperature and the volume fractions of the liquid species. Using the relation $\phi_A = 1 - \phi_B$ we get:

$$\Delta G_{\text{mix}} = \chi \phi_B(1 - \phi_B) + RT [(1 - \phi_B) \ln(1 - \phi_B) + \phi_B \ln \phi_B] \quad (2.19)$$

Note that at $\phi_B$ values of 0 or 1 the free energy of mixing goes to zero as expected. Equation 2.19 is known as the regular solution model [98]. It assumes ideal mixing (no volume changes and no non-combinatorial contributions to entropy) and does not account for liquid-liquid interfacial energy. Because it does not appropriately account for interfacial energy, when used with the Cahn-Hilliard equation to model phase separation it does not produce correct kinetics such as the experimentally observed spinodal decomposition or nucleation and growth. The work of Cahn and Hilliard [77–80] was to formulate a free energy representation that accomplished this and will be discussed later in this section.
Figure 2.9: Hypothetical phase diagram for a binary liquid mixture with miscibility gap. Binodal curves are solid black and spinodal curves are dashed black. A system usually has a upper critical solution temperature (UCST) or an lower critical solution temperature (LCST), but not both which are shown in the phase diagram.

A plot of equation 2.19 is shown on the right side of Figure 2.8 for a fixed temperature and several values of $\chi$. The red curve illustrates a system with an immiscible equilibrium state, meaning two equilibrium phases. The double well nature of this curve has two minima which correspond to the compositions of the two separate phases—an $\alpha$ phase that is rich in the $A$ species, and a $\beta$ phase that is rich in the $B$ liquid species. The blue curve in the plot shows the case when the $\Delta H_{mix}$ exactly balances with $T\Delta S_{mix}$. It corresponds to a state with exactly one free energy minima, thus it has a single phase equilibrium state (i.e. liquids are miscible). The green curve is the case when the enthalpy of mixing is zero and also corresponds to a miscible equilibrium state.

2.4.3 Miscibility of Low and High Molecular Weight Liquids

Figure 2.9 shows a hypothetical phase diagram for a binary liquid mixture. For low molecular weight liquids, for example oil and water, it is common for there to be some point in the composition temperature space where both liquids mix and form a single phase (this is called partial miscibility). In Figure 2.9, single phase regions are colored light gray while regions with two distinct phases are colored darker gray. There are also blue regions labeled metastable regions. Critical solution temperature and composition
points are labeled as well. The thick dark lines are binodal line and separate single and binary phase regions of the phase diagram. The dashed dark line is the spinodal line and separates the metastable two phase region from the spinodal two phase region. In metastable regions, phase separation happens via the nucleation and growth mechanism (nucleation of droplets which then grow by coalescence or Ostwald ripening). In the metastable regions there is an energy barrier that must be overcome in order to nucleate a second phase. In the spinodal regions, there is no energy barrier to phase separation and phase separation happens everywhere simultaneously. This kind of phase separation is known as spinodal decomposition.

Depending on the system, it may have either a lower critical solution temperature (LCST) or an upper critical solution temperature (UCST), but typically not both. Lower molecular weight liquids more commonly have a UCST while higher molecular weight melts, such as polymer blends or solutions, more commonly have an LCST [99]. In general, lower molecular weight liquids increase in miscibility as temperature increases; however, due to non-combinatorial contributions to $\Delta S_{\text{mix}}$ and temperature dependence of $\Delta H_{\text{mix}}$ this behavior is often reversed for polymer blends. Most polymer blend phase diagrams don’t even have a single phase region on their phase diagram; however, many shorter chain versions (oligomers) of their longer chain polymer counterparts do [99].

2.4.4 Flory-Huggins Theory: Thermodynamics of Polymers

Flory and Huggins utilized the mean field approach to extend the regular solution model to polymers in solution and later to polymer blends [100, 101]. Their work modifies the free energy of mixing in equation 2.19 to account for the combinatorial affects of polymer chains to the entropy of mixing, as well as modifying the enthalpy of mixing to include relevant polymer interactions and temperature effects. The resulting free energy model is slightly more complex:

$$\Delta G_{\text{mix}} = RTV \left[ \frac{\chi_{12}}{v_r} \phi_B (1 - \phi_B) + \frac{(1 - \phi_B)}{v_A} \ln(1 - \phi_B) + \frac{\phi_B}{v_B} \ln \phi_B \right]$$

(2.20)

Here, $V$ is the systems volume, $v_A$ and $v_B$ are the molar volumes of a species $A$ and $B$ polymer chain, and $v_r = \sqrt{v_A v_B}$. $\chi_{AB}$ is called the Flory-Huggins interaction parameter.
The definitions of $\phi_A$ and $\phi_B$ are also altered to be:

$$\phi_A = \frac{v_A N_A}{V}; \quad \phi_B = \frac{v_B N_B}{V} \quad \text{and} \quad V = v_A N_A + v_B N_B$$

(2.21)

Just as with the regular solution theory, the Flory-Huggins model for the free energy of mixing does not account for liquid-liquid interfacial energy. Both regular solution and Flory-Huggins theory lack the ability to quantitatively capture the thermodynamics of specific experimental conditions [99]. Despite these limitations, they provide a qualitative description of the thermodynamics of low and high molecular weight liquids that is useful for understanding general trends and phenomenal relationships.

### 2.4.5 Accounting for Interfacial Energy

Cahn and Hilliard recognized the deficiency in binary mixture regular solution theory with respect to accounting for interfacial energy. In their early work [77–80] they showed how the addition of a gradient term to the free energy could properly account for this missing interfacial energy contribution. The main result is the expression for the free energy and is given by,

$$F = N_v \int_V \left[ f_0(\phi) + \frac{\kappa}{2} (\nabla \phi)^2 \right] dV$$

(2.22)

Where $N_v$ is the number of molecules per unit volume, $f_0(\phi)$ is the bulk free energy density, and the integral is over the volume of the system. $f_0$ can be approximated using the regular solution model’s free energy of mixing or the Flory-Huggins model for polymers by letting $f_0(\phi) = \frac{\Delta G_{\text{mix}}}{V}$. The gradient term $\kappa (\nabla \phi)^2$ accounts for the interface’s contribution to the free energy. The $\kappa$ parameter is used to scale the interfacial energy contribution to the total free energy and is directly related to the interfacial width of the interface.

The Cahn-Hilliard equation as expressed in equation 2.2 comes about by connecting the free energy expressed in 2.22 to the continuity equation which is given by,

$$\frac{\partial \phi}{\partial t} = -\nabla \cdot \mathbf{J}$$

(2.23)
where \( J \) is the flux and is related to chemical potential of the system by \( J = -M \nabla \mu \). Note that the chemical potential \( \mu \) is simply the variational derivative of the free energy \( \mu = \delta F/\delta \phi \). The variational derivative of the Cahn-Hilliard free energy functional is given by \cite{96},

\[
\frac{\delta F}{\delta \phi} = \frac{\partial f_0}{\partial \phi} - \kappa \nabla^2 \phi
\]  

(2.24)

Combining the continuity relation in equation 2.23, with these other relations results in the Cahn-Hilliard equation as shown below.

\[
\frac{\partial \phi}{\partial t} = -\nabla \cdot J
\]

\[
= -\nabla \cdot (-M \nabla \mu)
\]

\[
= \nabla \cdot \left( M \nabla \frac{\delta F}{\delta \phi} \right)
\]

\[
\frac{\partial \phi}{\partial t} = \nabla \cdot \left( M \nabla \left( \frac{\partial f_0}{\partial \phi} - \kappa \nabla^2 \phi \right) \right)
\]

(2.25)

This is the most common form of the Cahn-Hilliard equation that is used in this work.

### 2.4.6 Ginzburg-Landau Free Energy Functional

As was just mentioned in the previous discussion of the Cahn-Hilliard equation, the regular solution model or Flory-Huggins model for bulk free energy of mixing can be used as the bulk free energy \( f_0 \). However another formulation pioneered by Ginzburg and Landau is more commonly used in computational modeling due to its convenience. The Ginzburg-Landau free energy is given as a power series expansion in terms of the order parameter \( \phi \):

\[
F = \int_V \left[ a_0(T) + a_1(T) \phi + \frac{a_2}{2} \phi^2 + \frac{a_3}{3} \phi^3 + \frac{a_4}{4} \phi^4 + \frac{a_5}{5} \phi^5 + O(\phi^6) \right] dV
\]

(2.26)

where the coefficients \( a_i(T) \) depend on temperature and possibly other thermodynamic variables. For binary mixtures undergoing continuous second order phase transformations, the free energy potential is symmetric (see plot of regular solution model in Figure
2.8), and only even terms are needed in the expansion.

\[
F = \int_V \left[ a_0(T) + \frac{a_2}{2} \phi^2 + \frac{a_4}{4} \phi^4 \right] dV \tag{2.27}
\]

Figure 2.10 shows a plot of a Flory-Huggins model for phase separating polymers of similar size (equation 2.20) and the corresponding Ginzburg-Landau model (equation 2.27). Note that in this plot \(a_2 < 0\) and \(a_4 > 0\) which is necessary to get the symmetric double well shape. All the computational modeling presented in this dissertation uses a Ginzburg-Landau free energy functional in the Cahn-Hilliard equation. This concludes the discussion of the thermodynamics of liquid phase separation which is an important process in the formation of Bijels. We now turn our attention to the theoretical description of dispersions of colloidal particles which are responsible for stabilizing the liquid phase separation by interfacial jamming.

2.5 Colloidal Particle Distributions and Their Motion

A colloidal dispersion is a microscopic insoluble mixture of one substance (or phase) in another. Examples include microscopic particulate phases dispersed in liquids or gases such as blood (solid particulate dispersed in a liquid) and dust (solid particulate dispersed in a gas). In general, the dispersed and medium phases can be solid, liquid, or gas, the one
exception being a gas phase dispersed in a gas medium. This is because, under almost all conditions, gases are always miscible with one another. Therefore, other examples of colloidal dispersions include fog or clouds (liquid dispersed in a gas), whipped cream (gas dispersed in a liquid), milk (liquid dispersed in a liquid), styrofoam (gas dispersed in a solid), gelatin (liquid dispersed in a solid), and some alloys (solid dispersed in a solid). The dispersed phase can have particles with sizes ranging from the nanometer to micrometer scale [102].

2.5.1 Colloidal Stability

Colloids are considered stable if the dispersed phase remains mixed in the other phase at equilibrium. Aggregation and sedimentation of the dispersed phase happen for unstable colloidal dispersions. Aggregation happens when there are attractive forces between particles. Sedimentation occurs when particles are either too large or form large aggregates such that gravitational forces dominate their motion and they fall out of suspension [102].

In this research, we will only be considering solid particle dispersions in highly viscous multiphase liquids. We also assume such particles are surface treated to neutrally wet both liquid phases that make up the dispersion medium. Such surface treatments create steric repulsions between colloidal particles which reinforces stability of the colloidal suspension. Additionally, we assume particle sizes are on the smaller end of the colloidal particle size spectrum (50 nm - 1 \( \mu \)m in diameter) where gravitational effects can be neglected. Consequently, colloidal stability is ensured for the systems of interest in this work. We now turn our attention to describing the Brownian motion of colloidal dispersions.

2.5.2 Brownian Motion of Colloidal Particles

Stable dispersions of colloidal particles in viscous liquids undergo Brownian motion in their liquid medium. This Brownian motion may be described by the stochastic equations of motion for Brownian dynamics or the equations of motion for overdamped Langevin dynamics. The main difference between the pure Brownian description and overdamped Langevin description is that of inertial effects. For pure Brownian motion, damping
forces in the medium are so high that particles have zero average acceleration (no inertia) and particle velocity is directly proportional to the net force. In contrast, Langevin dynamics preserve inertial effects by assuming there is a non-zero average acceleration which is directly proportional to the net force. However when the damping or drag force in the Langevin dynamics model is high, average accelerations are very close to zero and approximate Brownian motion very well. The research work in this dissertation utilizes both models, Brownian and Langevin dynamics; therefore a description of both is given here. We start with the more general Langevin dynamics followed by Brownian dynamics.

**Langevin Dynamics**

The Langevin equations of motion for a particle \( i \) in a colloidal dispersion are:

\[
m_i \mathbf{a}_i = \mathbf{F}_{pp}^i - \mathbf{F}_{d}^i + \mathbf{F}_{s}^i \quad (2.28)
\]

where on the left-hand side, \( m_i \) and \( \mathbf{a}_i \) are the mass and acceleration of particle \( i \). On the right hand side is the sum of the forces on the \( i^{th} \) particle. There are three main force contributions. First, there are particle-particle interaction forces denoted \( \mathbf{F}_{pp}^i \). It is typically derived from a potential energy function describing the particle particle interactions and may include steric repulsive forces, Van der Waals forces, and when present, dipolar interactions. Second, there is the dissipative force from the dispersion medium denoted \( \mathbf{F}_{d}^i \). This force is directly proportional to the particles velocity (linear drag). Lastly, there is the stochastic force denoted \( \mathbf{F}_{s}^i \) which accounts for the random forces on the particle from the thermal motion of the medium. The strength of this force is non-linearly proportional to the systems temperature and viscosity.

Overdamped Langevin dynamics are used to describe the colloidal particle motion for the journal article presented in Chapter 6. The overdamping is accomplished by having a very strong damping or drag force (i.e. \( \mathbf{F}_{d}^i \)). Precise details of the model are given Chapter 6. The other two journal articles constituting Chapters 4 and 5 utilize a Brownian dynamics model.
Brownian Dynamics

The Brownian equations of motion for a particle $i$ in a colloidal dispersion are:

$$v_i = \eta_i (F_i^{pp} + F_i^s)$$  \hspace{1cm} (2.29)

where $v_i$ and $\eta_i$ are the particles velocity and mobility, and the force contributions are the same as those for Langevin dynamics in equation 2.28 without the dissipative force from the medium. The distinctive feature of these equations is the lack of acceleration and assumption of a highly viscous dispersion medium. The equations of motion, whether overdamped Langevin 2.28 or Brownian 2.29, can be solved analytically, but are much more conveniently solved numerically. Details of the numerical solution techniques will be given in Chapter 3.

Capillary Forces at Liquid-Liquid Interfaces

When colloidal particles are dispersed in multiphase liquids, colloidal particle wetting properties become important. If the colloidal particle surfaces are not specifically treated to make the particles neutrally wet multiple liquid phases then they typically favor complete wetting of one liquid phase over another which results in particles segregating to one phase. In bijel formation, having colloidal particles neutrally wet both liquid phases of the binary-phase mixture is typically required. Neutral wetting of particles (i.e. a contact angle of approximately 90 degrees) leads to particles experiencing capillary forces from liquid-phase boundary interfaces. It is these capillary forces which are responsible for particles remaining attached to the phase boundary interface. These capillary forces have to be added into the equations of motion represented in equations 2.28 and 2.29 above.

Kaptay [103], gives a general derivation for capillary forces on particles of any shape at phase boundary interfaces. For spherical particles at a flat liquid-liquid phase boundaries and a 90 degree contact angle, the capillary force on the particle perpendicular to the interface is expressed by,

$$F^{\text{cap}} = 2\pi r \sin(\phi_c) \left[ -\sigma_{12} \sin(\phi_c + \theta) \right]$$  \hspace{1cm} (2.30)
Figure 2.11: Diagram illustrating the quantities used in equation 2.30. This figure is borrowed from [2].

where $r$ is the particle radius, $\theta$ is the contact angle, $\sigma_{12}$ is energy associated with the phase boundary interface between the two liquid phases, and $\phi_c$ is an angle relating the particles center-of-mass to the interface contact line on the particle surface (see Figure 2.11). Millett and Wang [2] developed a computational approach for calculating this capillary force for diffuse interface models. This approach is used to model capillary forces for the papers presented in Chapters 4 and 5. A slight variation of the same method is used to model capillary forces in Chapter 6. The algorithmic details are given in each of those respective chapters.

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Chapter 3

Computational Methods

This chapter will give an overview of the computational methods used to accomplish the research presented in the next three chapters. It will begin with a broad overview of the Phase-field modeling approach and how it is used in this research. It will build off of the description of the Cahn-Hilliard equation discussed in section 2.4 of the previous chapter. A discussion of how the Phase-field approach is coupled to the particle dynamics model will then be given next. This is followed by a description of the numerical solution techniques to solve the governing equations followed by a discussion of simulation length and time scales. Lastly, a section which covers the algorithms and quantities used to analyze the simulation results is presented.

3.1 Phase-field Modeling

Phase-field modeling is a mesoscale simulation approach that is based on thermodynamics. It is used to model phase changes and the time evolution of material microstructures [1]. Material phases such as solid, liquid, or gas phases are represented by an order parameter, typically denoted as a concentration $C(r, t)$ or abstract parameter $\phi(r, t)$ which can represent a solid, liquid, or gas depending on its numerical value. Phase changes from solid to liquid, liquid to gas, liquid to solid, etc are first order phase transitions. For these kinds of phase changes the amounts of any given phase are not conserved over time. For example, in a solidification phase change, initially the system is entirely liquid with no solid ($\phi = 1$ might denote the liquid phase). At the completion of the phase change the system will be completely solid ($\phi = -1$ could represent this solid phase). During the phase change process the fraction of liquid to solid phase decreases. Thus the amount of liquid phase in the system is not conserved through time. For second order phase transitions, such as phase separation of a binary mixture, the order parameter is conserved through time. For example, in a binary alloy with a set composition of type $A$ metal and type $B$ metal, the order parameter might be the concentration of type $A$ metal (i.e. $C = 1$ corresponds to a composition of 100% metal $A$). As phase separation
proceeds, the amount of metal $A$ in the system does not change with time and is thus said to be conserved.

The governing equation for the time evolution for non-conserved order parameters is the Allen-Cahn equation [1]. For conserved order parameters it is the Cahn-Hilliard equation. These equations are given in relations 3.1 and 3.2.

$$\frac{\partial \phi_i}{\partial t} = -L_{\phi_i} \frac{\delta F}{\delta \phi_i} \quad \text{Allen-Cahn}$$

$$\frac{\partial \phi_i}{\partial t} = \nabla \cdot \left( M_{\phi_i} \nabla \frac{\delta F}{\delta \phi} \right) \quad \text{Cahn-Hilliard}$$

Both the Allen-Cahn and Cahn-Hilliard equations depend on a thermodynamic free energy functional $F(\phi_i, \nabla \phi_i)$, where $\phi_i$ are the order parameters of the system, $\nabla \phi_i$ are their gradients, and both are functions of time and space. The operation $\delta F/\delta \phi_i$ is the functional or variational derivative of the free energy with respect to the order parameter $\phi_i$. This is due to the fact that $F$ is a functional, meaning that it takes functions as inputs. The order parameters may be a mixture of conserved and non-conserved types, each of which is evolved by its own corresponding Allen-Cahn or Cahn-Hilliard equation. For the Allen-Cahn equation, $L_{\phi_i}$ is usually a constant; however, $M_{\phi_i}$ in the Cahn-Hilliard equation is the mobility of a conserved species and can be a function of other thermodynamic variables such as $\phi_i$ and temperature $T$. The parameters $L$ and $M$ set the time scales associated with the system.

Another important feature of Phase-field models is the smooth transition between phases at their boundaries. It is said that boundaries in Phase-field models are diffuse as opposed to sharp. Although this is not always physically realistic, it allows for the model to not explicitly track the phase boundary interface. This brings great flexibility to Phase-field methods in contrast to the family of sharp interface methods which are required to track the interface, usually in a very ad-hoc fashion. For a comprehensive overview of Phase-field methods applied to materials science with a comparison to sharp interface models see [2]. Due to their flexibility, Phase-field models are continually being extended and expanded upon by researchers to model new phenomena. Some recent
examples include their use in modeling crack nucleation and growth [3], nanowire growth [4], capacitance switching [5], and phase inversion in polymer solvent systems [6] which demonstrates their broad use and application.

In this dissertation, the Phase-field method is used to model the phase-separation of high viscosity liquids such as polymer blend melts. As mentioned above, phase separation is a second order phase transition and therefore only involves conserved order parameters; consequently, only the Cahn-Hilliard equation is used in our Phase-field models and not the Allen-Cahn equation. This Phase-field model is also directly coupled to a Brownian or Langevin particle dynamics model in order to simulate bijel formation in thin films. This coupling is discussed in the following section.

When modeling phase separation with the Cahn-Hilliard equation it is also common to use the modified Cahn-Hilliard-Cook equation instead (presented in section 3.2.1 below). Cook added an additional term to the Cahn-Hilliard equation that injects thermal noise which corrects the Cahn-Hilliard equation’s prediction of spinodal decomposition in its very early stages [7]. This thermal noise was found to be absolutely necessary to reproduce the early thin-film Bijel results presented in Chapter 4 [8]. Without it, the surface directed spinodal decomposition effects were incorrect.

3.2 Coupled Phase-field and Particle Dynamics Modeling

The papers presented as Chapters 4-6 of this dissertation all utilize a three order Parameter Phase-field method in order to model the Bijel formation process in confined thin-film geometries. The three order parameters are all conserved and are denoted by $\phi_1$, $\phi_2$, and $\psi_i$. The order parameters $\phi_1$ and $\phi_2$ represent the concentrations of the two phase-separating liquids of the Bijel and are each evolved by their own Cahn-Hilliard equation with associated free energy functional $F(\phi_1, \phi_2, \psi_i)$. The third order parameter $\psi_i$ represents the solid particle phase of the $i^{th}$ particle and is not evolved by a Cahn-Hilliard equation, but is instead evolved by the equations of motion for Brownian or overdamped Langevin dynamics. Despite being evolved by a different set of governing equations, it still directly influences the free energy of the binary liquid mixture $F(\phi_1, \phi_2, \psi_i)$ and provides the coupling link for the colloidal particles to effect the liquid-liquid phase sep-
Figure 3.1: Schematic (top) showing binary mixture (yellow and blue) with particle (green) at the liquid-liquid interface. Plot (bottom) shows numerical values of the three order parameters, $\phi_1$, $\phi_2$, and $\psi$ along the thick black dashed line that intersects the particle at the interface. Note that the order parameters transition smoothly as opposed to sharply at the interfaces. This graphic was borrowed from [9].

Separation and induce interfacial jamming. The particles are influenced by the liquid-liquid interfaces by capillary forces which are calculated using information from the three order parameters $\phi_1$, $\phi_2$, and $\psi$. The capillary force provides the coupling link which allows the liquid-liquid phase separation to effect the particles. Hence, there is a direct two-way coupling between the particles and the liquids that is controlled and specified in the Phase-field free energy model $F(\phi_1, \phi_2, \psi)$ and the particles capillary forces, $F^{\text{cap}}$.

Figure 3.1 illustrates the relationship between the Phase-field order parameters $\phi_1$, $\phi_2$, and $\psi$. Each takes on a value between zero and one and represents a concentration of a liquid or a particle. In regions of the system occupied by liquid purely composed of liquid 1, $\phi_1 = 1.0$. For regions where there is no presence of liquid 1, $\phi_1 = 0$. This relationship is the same for the other two order parameters $\phi_2$ and $\psi$. At the interface between liquids or liquid and particle, these order parameters transition smoothly from a value of one to zero.

3.2.1 Applied Electric Fields

The last paper presented as Chapter 6 of this dissertation modifies the Cahn-Hilliard equation and particle dynamics models to account for the presence of an applied external electric field. This is accomplished by including another term in the Cahn-Hilliard-Cook
equation and adding an induced dipole-dipole interaction to the particle dynamics governing equations. The modified Cahn-Hilliard equation is given in equation 3.3.

\[
\frac{\partial \phi_i}{\partial t} = M_i \nabla^2 \frac{\delta F}{\delta \phi_i} + k_z \frac{\partial^2 \phi_i}{\partial z^2} + \zeta
\]  

(3.3)

When compared with equation 3.2 one sees the inclusion of the Cook term \( \zeta \) which accounts for thermal noise and the electric field term \( k_z \frac{\partial^2 \phi_i}{\partial z^2} \) which accounts for the electrostatic free energy contribution to the system and approximates equation 2.1 in section 2.3.1. Here the electric field is applied in the z-direction, which is the out-of-plane direction for the thin-film Bijel. The constant \( k_z \) is related to the dielectric properties of the binary liquid mixture and the strength of the applied electric field. This method for modeling the electric field alignment of the binary liquid mixture is derived in [10]. The derivation assumes that the dielectric term in equation 2.1 can be expanded in a Taylor series of the liquid composition and neglects all but the linear terms. The explicit details are given in Chapter 4.

For particles, the electric field induced dipole interactions are modeled using the point dipole approximation [11]. They also have a soft steric repulsion that is modeled using a Lennard-Jones like potential. Consequently, the particle interactions are very similar to those of a Stockmayer fluid which is defined as particle-particle interactions using the Lennard-Jones potential with a point electric dipole moment [12].

### 3.3 Numerical Solution Techniques

In order to simulate the formation of a Bijel using the above computational model, the governing equations must be solved numerically over some length and time domain. A discussion of the characteristic length and time scales is given in the next section. To solve the Cahn-Hilliard equation and coupled particle equations of motion, a discrete Cartesian grid is used for the simulation domain. The grid is three-dimensional with \( nx \), \( ny \), and \( nz \) nodes in the xyz-directions. The distance between grid nodes is uniform and constant for all three directions and is represented by the symbol \( \delta \). The continuous order parameters \( \phi_1, \phi_2, \) and \( \psi \) are discretized such that their values are stored at the discrete nodes of this grid. For the models used in Chapters 4 and 5, a finite difference method is
used to solve the Cahn-Hilliard equation on this grid. In the Chapter 6 a Fourier Spectral method is used to solve the Cahn-Hilliard equation on the grid. The particle positions are numerically integrated using a simple Euler update for the Brownian equations of motion used in Chapters 4 and 5, and a velocity-verlet solver is used for the overdamped Langevin equations of motion in Chapter 6. An overview of each of these numerical integration techniques will be given below.

### 3.3.1 Cahn-Hilliard Equation Finite Difference Solver

To solve the Cahn-Hilliard equation an explicit time marching finite difference stencil is utilized. The free energy models \( F(\phi_1, \phi_2, \psi) \) employed in the Cahn-Hilliard equation in Chapters 4-6 are designed in the spirit of Ginzburg-Landau free energy functionals discussed in section 2.4.6. For the sake of introducing the finite difference approach we will use a simpler Ginzburg-Landau free energy functional which is given in equation 3.4.

\[
F(\phi, \nabla \phi) = \int_V \left[ \frac{a_2}{2} \phi^2 + \frac{a_4}{4} \phi^4 + \frac{\kappa}{2} (\nabla \phi)^2 \right] dV \tag{3.4}
\]

Values for the coefficients of \( a_2 = -1 \) and \( a_4 = 1 \) will give a double well free energy with minima at \( \phi = -1, 1 \) which would be appropriate for a phase separating binary mixture with order parameter \( \phi = \phi_1 - \phi_2 \). The variational derivative of equation 3.4 with respect to \( \phi \) is the chemical potential \( \mu = \frac{\delta F}{\delta \phi} \) and is given by,

\[
\mu = a_2 \phi + a_4 \phi^3 - \kappa \nabla^2 \phi \tag{3.5}
\]

Inserting this into the Cahn-Hilliard equation shown in 3.2 yields,

\[
\frac{\partial \phi}{\partial t} = M \nabla^2 \left( a_2 \phi + a_4 \phi^3 - \kappa \nabla^2 \phi \right) \tag{3.6}
\]

where the mobility \( M \) is being treated as constant and \( \nabla^2 \) is the Laplacian operation.

The Laplacian operation in three dimensions is \( \nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \). To formulate the finite difference stencil, a second order central finite difference approximation can be used for each of the second derivative terms in the Laplacian operator. Let \( \phi_{ijk} \) indicate the
value of the order parameter stored at grid node \(i, j, k\) where \(1 \leq i \leq nx\), \(1 \leq j \leq ny\), and \(1 \leq k \leq nz\). Then the central finite difference approximation for the Laplacian of \(\phi_{ijk}\) is given by equation 3.7.

\[
\nabla^2 \phi_{ijk} \approx \frac{\phi_{i+1jk} + \phi_{i-1jk} + \phi_{ij+1k} + \phi_{ij-1k} + \phi_{ijk+1} + \phi_{ijk-1} - 6\phi_{ijk}}{\delta^2}
\]

(3.7)

In equation 3.7, \(\delta\) is the simulation grid spacing.

Now let \(\mu_{ijk}\) be the value of the chemical potential stored on the grid at node \(i, j, k\). Employing the finite difference approximation in equation 3.7, \(\mu_{ijk}\) can be approximated by equation 3.8.

\[
\mu_{ijk} = a_2 \phi_{ijk} + a_4 \phi_{ijk}^3
- \kappa \left( \frac{\phi_{i+1jk} + \phi_{i-1jk} + \phi_{ij+1k} + \phi_{ij-1k} + \phi_{ijk+1} + \phi_{ijk-1} - 6\phi_{ijk}}{\delta^2} \right)
\]

(3.8)

Next, the entire right-hand side of the Cahn-Hilliard equation shown in 3.6 at the \(i, j, k\) node can be approximated as equation 3.9 by applying the central finite difference approximation for the Laplacian in 3.7 to \(\mu_{ijk}\).

\[
\frac{\partial \phi_{ijk}}{\partial t} = M \left( \frac{\mu_{i+1jk} + \mu_{i-1jk} + \mu_{ij+1k} + \mu_{ij-1k} + \mu_{ijk+1} + \mu_{ijk-1} - 6\mu_{ijk}}{\delta^2} \right)
\]

(3.9)

It should be noted that equation 3.8 should be applied to every single node in the system before applying equation 3.9 to every node. To complete the time marching scheme, a forward finite difference approximation can be applied to the time derivative of \(\phi_{ijk}\) on the left-hand side of equation 3.9. Letting the discrete time be denoted as a superscript this yields the final time marching finite difference scheme for updating the values of \(\phi_{ijk}\) stored on the simulation grid:

\[
\phi_{ijk}^{t+1} = \phi_{ijk}^t + M \Delta t \left( \frac{\mu_{i+1jk} + \mu_{i-1jk} + \mu_{ij+1k} + \mu_{ij-1k} + \mu_{ijk+1} + \mu_{ijk-1} - 6\mu_{ijk}}{\delta^2} \right)
\]

(3.10)

In equation 3.10, \(\Delta t\) is the discrete time step. Equation 3.10 is an explicit finite difference
scheme and consequently has a numerical stability criterion based on the values of $M$, $\delta$, and $\kappa$ which restrict the discrete time step size $\Delta t$ in order to maintain numerical stability.

In the simulations employed for this dissertation, periodic boundary conditions are used in the xy-directions which represent the lateral directions of the Bijel thin-film. For the z-direction, a no-flux boundary condition is employed. The finite difference approximations employed here have local and global truncation errors which means the time marching scheme will not give exact solutions. This is not a concern because even exact solutions would not be expected to quantitatively correlate to a physical system, but rather only represent qualitative predictions that allow the discovery of correlations between model parameters. For a comprehensive introduction to these finite difference methods the Author recommends the following text by Sauer [13].

3.3.2 Cahn-Hilliard Equation Fourier Spectral Solver

In Chapter 6, a semi-implicit Fourier spectral (SIFS) method [14] is employed to solve the Cahn-Hilliard equation instead of a finite difference method. The SIFS method transforms the spatial components of the order parameter $\phi(x,y,z,t)$ into Fourier space using the three-dimensional Fourier transform:

$$\tilde{\phi}(k,t) = \iiint \phi(r,t) e^{i \mathbf{r} \cdot \mathbf{k}} d\mathbf{k} = \int \int \int \phi(r,t) e^{i r \cdot k} dk_x dk_y dk_z$$  \hspace{1cm} (3.11)

where $\mathbf{r} = (x,y,z)$ and $\mathbf{k} = (k_x, k_y, k_z)$ are the system position vector and spatial frequency vector. Denoting the Fourier transform of the order parameter by $\tilde{\phi}(k,t)$, the Cahn-Hilliard equation in 3.6 can be written in Fourier space as equation 3.12.

$$\frac{\partial \tilde{\phi}(k,t)}{\partial t} = M \nabla^2 \left( \tilde{f}_0 - \kappa \nabla^2 \tilde{\phi}(k,t) \right)$$  \hspace{1cm} (3.12)

In equation 3.12, $\tilde{f}$ is the Fourier transform of the $[a_2 \phi + a_4 \phi]$ part of the Ginzburg-Landau free energy and $\mathbf{k}$ is the Fourier space vector with magnitude $k = \sqrt{k_x^2 + k_y^2 + k_z^2}$.

In Fourier space, the discrete Laplacian operation on $\tilde{\phi}_{ijk}$ is given by $\nabla^2 \tilde{\phi}_{ijk} = -\mathbf{k} \cdot \mathbf{k} \tilde{\phi}_{ijk} = -k^2 \tilde{\phi}_{ijk}$. Applying a forward finite difference approximation for the time
derivative in 3.12 and a ̃φ^{t+1}_{ijk} for the κ term, equation 3.12 for grid node i, j, k becomes:

\[
\frac{\tilde{\phi}^{t+1}_{ijk} - \tilde{\phi}^{t}_{ijk}}{\Delta t} = -Mk^2\tilde{f}^{t}_{ijk} - Mk^4\kappa\tilde{\phi}^{t+1}_{ijk}
\]  

(3.13)

Equation 3.13 can then be solved for ̃φ^{t+1}_{ijk} to get the following semi-implicit time marching scheme:

\[
\tilde{\phi}^{t+1}_{ijk} = \tilde{\phi}^{t}_{ijk} - \frac{Mk^2\Delta t\tilde{f}^{t}_{ijk}}{1 + Mk^4\Delta t}
\]  

(3.14)

To apply the SIFS time marching scheme in equation 3.14 to the order parameter φ on the discrete Cartesian grid, a discrete version of the three-dimensional Fourier transform given by equation 3.11 is needed. In simulations presented in Chapter 6, the “Fastest Fourier Transform in the West”[15] implementation of the discrete Fourier transform was used. The SIFS method has a convergence rate that is almost three orders of magnitude higher than the finite difference method introduced in the last section. This means that it allows much larger sizes of the discrete time step Δt in comparison to explicit finite difference methods. A thorough overview of the SIFS method can be found in [14, 16].

The SIFS method only works with periodic boundary conditions in all three-dimensions. Consequently, in order to get a no-flux like boundary at the top and bottom of the Bijel membrane’s simulation domain, a physics based boundary is defined using the Ginzburg-Landau free energy functional. To do this, the grid nodes at the top and bottom xy-planes of the system (i.e. grid nodes with z = 0 and z = nx · δ), the free energy \( F(\phi, \nabla \phi) \) is modified to represent only particle material. This essentially drives all components of the liquid concentrations \( \phi_1 \) and \( \phi_2 \) out of these regions in order to minimize the free energy.

### 3.3.3 Particle Dynamics Solvers

The equations of motion for pure Brownian dynamics which were defined and discussed in section 2.5.2 are easily integrated with a simple Euler integration scheme. This scheme has a large truncation error, but due to the stochastic nature of the particles Brownian motion and the fact that there is no preservation of inertia from time-step to time-step the impact is negligible. Thus particle positions can be updated with the relation in
equation 3.15.

\[ r^{t+1}_i = r^t_i + v^t_i \Delta t \]  

(3.15)

where \( r_i \) and \( v_i \) are the position and velocity vector of the \( i^{th} \) particle. The velocity is \( v_i \) is derived from the net force on the particle by equation 2.29.

For the overdamped Langevin equations of motion defined and discussed in section 2.5.2, accelerations are non-zero and consequently the Euler time integration scheme is not appropriate. Instead, a velocity-verlet integrate scheme is used, which is the de facto time integration method in molecular dynamics simulations [17] and has third order accuracy. The velocity-verlet update for particle positions is a four step process:

1. Calculate \( v^{t+1/2}_i \) for all particles using:

\[ v^{t+1/2}_i = v^t_i + \frac{\Delta t}{2} a^t_i \]

2. Calculate \( r^{t+1}_i \) for all particles using:

\[ r^{t+1}_i = r^t_i + \Delta t v^{t+1/2}_i \]

3. Derive \( a^{t+1}_i \) from the net force on particle \( i \) divided by the particles mass using \( r^{t+1}_i \) for all particles.

4. Calculate \( v^{t+1}_i \) for all particles using:

\[ v^{t+1}_i = v^{t+1/2}_i + \frac{\Delta t}{2} a^{t+1}_i \]

In the above steps, \( r_i \), \( v_i \), and \( a_i \) are the position, velocity, and acceleration vectors of the \( i^{th} \) particle and \( \Delta t \) is the discrete time-step.

3.4 Simulation Length and Time Scales

In this computational model the width of the diffuse interface can be directly related to the interfacial width of polymer-polymer interfaces. Figure 3.2b shows experimental measurements of interfacial widths in binary polymer blends which are typically 5-20
nm. In the simulations presented in the next three chapters, the interfaces roughly span four simulation grid nodes (see Figure 3.2a) which gives a length scale of approximately 2-5 nm as the distance between simulation nodes and is the characteristic length $L_0$ for the polymer phase separation. This length scale can also then be applied to the colloidal particles which have diameters from 6-10 grid spaces which translates to 30-50 nm diameters.

Figure 3.2: (a) Coupled Phase-field and particle dynamics model in which the polymer domains and the nanoparticle are represented by $\phi_1$, $\phi_2$, and $\psi_i$ variables, which transition from values of 1 to 0 across diffuse interfaces. (b) Experimental measurement of polymer-polymer interface widths [18], which are typically 5-20 nm.

The length of the time domain is arbitrary and no particular time units are attached for the simulations presented in chapters 4-6; however, they are expected to resolve the two important time scales associated with the Brownian motion of the colloidal particles and diffusion of polymer chains. Polymer chains diffusing in thin-films with thicknesses above 50 nm typically have diffusion coefficients on the order of $10^{-12} \text{ cm}^2\text{s}^{-1}$ [19], which corresponds to a timescale of,

$$
\tau_{\text{pol}} = \frac{L_0^2}{D} \approx \frac{(3 \text{ nm})^2}{10^{-12} \text{ cm}^2\text{s}^{-1}} = 8 \times 10^{-5} \text{ s}
$$

(3.16)

where $L_0 = 3 \text{ nm}$ is the assumed simulation grid spacing. The time scale for the Brownian motion of the colloidal particles is given by $\tau = \frac{6\pi \eta r_p^3}{k_B T}$ [20] where $\eta$ is the viscosity of the medium, $r_p$ is the particle radius, $k_B$ is Boltzmann’s constant and $T$ is the absolute temperature. For particles with diameters in the range of 30 – 50 nm and polymer melt
viscosities in the range of $10^{-2} - 10^0 \, Pa \, s$ \[21\] at temperatures above the typical glass transition temperatures of about 500 $K$ \[21\], this time scale is estimated to be,

$$
\tau_{\text{part}} = 6\pi \eta r^3 / k_B T = 6\pi \times (10^{-1} \, Pa \, s) \times (20 \, nm)^3 / k_b \cdot (500 \, K) \approx 5 \times 10^{-4} \, s \quad (3.17)
$$

The ratio of the two time scales $\tau_{\text{part}}/\tau_{\text{pol}} \approx 5$ but could be even larger in some systems. In order to handle these time-scale differences particle positions were only updated after completing 5-20 Cahn-Hilliard equation updates. In the work presented in chapters 4 and 5, twenty Cahn-Hilliard updates per particle update were used. In Chapter 6, five Cahn-Hilliard updates per particle update were used. This allows the liquids to equilibrate in accordance with updated particle positions. The different offsets between the first two papers and the last is due to the fact that the simulations in the last paper utilized the spectral method discussed above instead of the finite difference method. This method allows the use of much larger time steps when doing Cahn-Hilliard updates and therefore reduces the number of intermediate Cahn-Hilliard updates needed between particle updates.

3.5 Simulation Analysis and Post-processing

In Chapters 4-6 several quantities are calculated from the simulation data generated by numerically solving the equations of motion for $\phi_1$, $\phi_2$, and $\psi$. A brief description of these quantities and the methods for calculating them is given in this section.

3.5.1 Channel Diameters and Number Densities

![Figure 3.3: Schematic of Bijel membrane with through membrane channels.](image)

In many of the thin-film Bijel morphologies encountered in Chapters 4-6, cylindrical channels extend from the bottom to the top of the thin-film as illustrated in Figure
3.3. The number and diameter of these channels is of interest. The Hoshen-Kopelman algorithm on a two-dimensional slice in the xy-plane in the center of the thin-film is used to calculate the number of channels and their average diameter. The Hoshen-Kopelman algorithm loops over the grid nodes of the slice sampling an order parameter (for example $\phi_1$) and marks contiguous regions occupied by that order parameter. These contiguous regions can then be counted and a diameter estimated by assuming they are spherical in shape by using equation 3.18.

$$d_{\text{chan}} \approx \sqrt{\frac{4A_{\text{chan}}}{\pi}}$$  \hspace{1cm} (3.18)

In equation 3.18, $A_{\text{chan}}$ is the cross sectional area of the channel estimated by the Hoshen-Kopelman algorithm.

The Hoshen-Kopelman algorithm can also be used in the full three-dimensions of the grid to count clusters and estimate their volume. If the channels are distinct domains that span the thickness of the film, the diameter can also be estimated by assuming they have a cylindrical geometry and then using the equation for the volume of a cylinder to back out the channel diameter:

$$d_{\text{chan}} \approx \sqrt{\frac{4V_{\text{chan}}}{\pi h}}$$  \hspace{1cm} (3.19)

where $h$ is the thickness of the film. An overview of the Hoshen-Kopelman algorithm is given in [22].

The channel number density is a measure of the number of channels per unit area of the Bijel thin-film. Here this density is denoted as $\rho_c$. It is calculated by dividing the total number of channels in the film by the cross-sectional area of the film in the lateral directions (xy-dimensions):

$$\rho_c = \frac{nx \cdot ny \cdot \delta^2}{N_{\text{chan}}}$$

where $nx$ and $ny$ are the number of grid nodes in the xy-dimensions, $\delta$ is the grid node spacing, and $N_{\text{chan}}$ is the number of channels calculated by the Hoshen-Kopelman algorithm.
3.5.2 Fraction of Particles Attached to the Interface

During the Bijel formation dynamics, the fraction of particles attached to the interface at any given time is a useful metric for understanding how particle interactions coupled with interfacial dynamics influence the overall Bijel morphology. In order to count the number of particles attached to the interface an algorithm that loops over the region of simulation grid occupied by each particle is utilized. While looping over this section of the grid local to each particle, a particle attached to an interface can be detected when the all three order parameters \( \phi_1, \phi_2, \) and \( \psi \) have non-zero values above some threshold. When this condition is true, it means there is a triple-junction where the particle touches a liquid-liquid interface (see Figure 3.2a and note that there is a small square in the center of the graph right next to the particle that denotes this triple junction). As soon as this condition is detected to be true, the algorithm counts the particle as attached to the interface, breaks from scanning the local grid to that particle and moves on to scan the next particle. By doing this operation for all particles, the count of particles on the interface is obtained and then divided by the total number of particles in the system to get the fraction of particles attached.

3.5.3 Paraview

A software package named Paraview [23] is used in this dissertation to create high fidelity renderings of the simulated Bijels, track the liquid-liquid Bijel interface, estimate its surface area, and calculate interfacial curvatures. It is a powerful and versatile tool for conducting simulation post-processing. Each of these quantities will be described below.

3.5.4 Surface Area to Volume Ratios

During the Bijel formation process, phase separation creates an interface between the two liquid phases. As the liquid domains coarsen, this surface area decreases until particle jamming halts the phase separation. By measuring the interfaces surface area and normalizing it by the Bijel membranes volume, one can track the effect of particle jamming and discern other features effecting the overall interfacial surface area. This surface area normalized by the thin-films volume is denoted here as \( S/V \). It is calculated using Paraview’s isosurface feature which is used to track the Bijels interface and estimate
its surface area. This surface area estimate is then divided by the Bijel membrane’s volume, \( V = nx \cdot ny \cdot nz \cdot \delta^3 \), to get \( S/V \).

### 3.5.5 Interfacial Curvatures

![Schematic illustrating the principle curvatures of a two-dimensional surface. Image taken from [24]](image)

As demonstrated by Reeves and coworkers [25], the Bijel morphology is better characterized by considering the curvature of its liquid-liquid interface. Figure 3.4 shows a schematic of a two-dimensional surface that is characterized by two principle curvatures \( \kappa_1 \) and \( \kappa_2 \). From these principle curvatures, two useful quantities may be calculated, namely the Mean curvature expressed in equation 3.20 and the Gaussian curvature expressed in equation 3.21.

\[
H = \frac{\kappa_1 + \kappa_2}{2} \quad (3.20)
\]

\[
K = \kappa_1 \cdot \kappa_2 \quad (3.21)
\]

In Chapter 6, the methodology of Reeves and coworkers [25] is followed to calculate area averaged Mean and Gaussian curvatures of the Bijel interface. This is done using the Paraview software package. The details of this method are presented in the supplementary material of Chapter 6.

### Bibliography


Chapter 4

Paper 1: Numerical simulation of bijel morphology in thin films with complete surface wetting

4.1 Abstract

Bijels are a relatively new class of soft materials that have many potential energy and environmental applications. In this work, simulation results of bijel evolution confined within thin films with preferential surface wetting are presented. The computational approach used is a hybrid Cahn-Hilliard/Brownian Dynamics method. In the absence of suspended particles, we demonstrate that the model accurately captures the rich kinetics associated with diffusion-based surface-directed spinodal decomposition (SDSD), as evidenced by comparison with previous theoretical and simulation-based studies. When chemically-neutral particles are included in the films, the simulations capture surface-modified bijel formation, with stabilized domain structures comparable with the experimental observations of Composto and coworkers. Namely, two basic morphologies - bicontinuous or discrete - are seen to emerge, with direct dependence on the film thickness, particle volume fraction, and particle radius.

4.2 Introduction

A growing area of research in the broad field of materials science and engineering is
the creation of new materials with self-assembled nanoscale or mesoscale architectures
with desirable functionality for specific applications [1]. Bijels (or bicontinuous jammed
emulsion gels) are a relatively new class of materials that exhibit a unique microstructure
consisting of two interpenetrating fluid domains that are stabilized by a two-dimensional
arrangement of solid colloidal particles segregated to the internal fluid-fluid interfaces [2].
This interfacial particle segregation is best facilitated when the particles have relatively
equal wettability with both fluids (i.e., a contact angle of 90°, although non-90° contact
angles have been shown to alter the fluid domain morphology [3]).

A bijel is created by quenching a uniformly-mixed solution with dispersed particles
below a critical point where phase separation via spinodal decomposition initiates. Once

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established fluid domains develop, the suspended solid particles attach themselves to the fluid-fluid interfaces and form a jamming monolayer that slows, and eventually halts, the phase separation. This results in a freezing of the system in a metastable state where the two fluid phases form bicontinuous domains. Stabilization is achieved because the interfacially-attached colloids reduce the fluid-fluid interfacial area and therefore the interfacial energy of the system [4]. This concept of interfacial stabilization is similar to other approaches that utilize segregating components including surfactant-stabilized emulsions and vacancy-stabilized alloys [5–7]. There are many possible applications for bijels, such as microreactors, scaffolds for creating continuous porous networks, filtration materials, and polymeric solar cells and/or electrodes for batteries or supercapacitors [2, 4, 8–12].

Our understanding of the processes governing bijel formation in bulk samples is fairly well established [2, 4, 13–15]. On the other hand, the kinetics and morphology of bijels within confined regions, for example thin films, is much less understood. Within a thin film, in the absence of colloids, the spinodal decomposition of a binary system is altered by the confining boundaries and undergoes what is known as surface-directed spinodal decomposition (SDSD) [16]. Experiments and simulations have shown that fluids undergoing SDSD form bicontinuous morphologies early on, which then transform into discrete morphologies [16–34]. For the case of SDSD bound by a lower and upper substrate, the early-stage bicontinuous morphology consists of two outer wetting layers separated by an inner bicontinuous region. As time progresses, the bicontinuous domains break down and vertical cylindrical domains form that bridge between the top and bottom substrates. This marks the onset of the transition to the discrete morphology. The late stages of phase separation are characterized by growth in the diameter of the stable cylindrical domains which gradually, but not completely, deplete the wetting layers at the top and bottom substrates. This final stage is referred to as the discrete morphology. All three stages are well described by the work of Hore and Laradji [33].

The behavior of a bijel within a thin film should be expected to retain some SDSD characteristics, however the stabilizing effect of the colloids may alter the emerging struc-
ture. Indeed, experiments by Composto and coworkers [35, 36] demonstrated the emergence of both discrete and bicontinuous morphologies in thin-film polymer-based bijels stabilized with nanoparticles. They established that the stabilized bijel morphology, discrete or bicontinuous, could be controlled by varying the thickness of the film, as well as the nanoparticle volume fraction [35, 36]. Using a simple geometric model they were able to create a morphology map based on film thickness and nanoparticle volume fraction [35, 36].

To date, the experimental work conducted by Composto represents the first and only investigation of bijel morphology in thin film confinement. Considering the many potential applications of thin film bijels, it would be beneficial to have a computational model that accurately captures the rich interplay between SDSD and bijel formation. Additionally, the vast parameter space that governs these systems has not been fully explored.

This paper presents a numerical simulation study of bijel formation within thin films in which the top and bottom surfaces are preferentially wetted by one of the fluids. We employ a hybrid Cahn-Hilliard/Brownian Dynamics (CH/BD) computational method that aims to fill the above-mentioned computational gap. The CH/BD model here simultaneously evolves a phase-separating binary mixture containing chemically-neutral colloidal particles that segregate to the fluid-fluid interfaces. The phase separation is diffusion-governed and does not account for convective transport, hence the model is restricted to highly viscous fluids, such as the polymer melts investigated by Composto et al. [35, 36]. We are able to reproduce these experimental results, and demonstrate that the computational model can predict the important processes governing bijel morphology in thin-film confinement.

4.3 Modeling Approach

The CH/BD computational approach used here simultaneously captures the stochastic Brownian motion of colloidal particles co-evolving within a phase-separating binary fluid mixture. The colloids are assumed to be hard spheres with a defined radius and equal wettability for both fluid types. Their trajectories are evolved in space and time using a
standard particle dynamics algorithm (very similar to Molecular Dynamics, for example).

The binary fluid is represented by (continuous) volume fraction variables on a grid that are evolved in space and time according to a Cahn-Hilliard model. A direct coupling between the particles and the fluids is maintained via interfacial capillary forces. All numerical computations were performed with standard finite differencing schemes. The simulation approach used is largely similar to a previous paper by our group [37].

The phase-separating binary fluid is modeled by solving the Cahn-Hilliard equation for two conserved variables on a three-dimensional Cartesian grid. The Cahn-Hilliard equation is given by:

$$\frac{\partial \phi_i}{\partial t} = M_i \nabla^2 \frac{\delta F}{\delta \phi_i}$$

(4.1)

where $M_i$ and $\phi_i$ are the mobility and volume fractions of fluid $i$, and $F$ is the free energy density functional of the binary phase mixture. $M_i$ is dependent on temperature and is a representation of the viscosity of fluid $i$. The free energy density functional, $F$, is dependent on $\phi_1$, $\phi_2$, and a local particle volume fraction, $\psi$, according to:

$$F = \int [f(\phi_1, \phi_2, \psi) + \kappa (\nabla \phi_1)^2 + \kappa (\nabla \phi_2)^2] dV.$$  

(4.2)

$f(\phi_1, \phi_2, \psi,)$ is the bulk free energy, and the gradient terms (the second and third terms in Eq. (2)) further define the interfacial energy. In this model all interfaces are diffuse, whereby volume fraction variables smoothly transition across phase boundaries from values of zero to one (or vice-versa). $\kappa$ is an interfacial energy coefficient. We numerically approximate the spatial gradients in Eqs. (1) and (2) using a central finite difference (seven point stencil in 3-dimensions) and the time gradient in Eq. (1) with a forward Euler finite difference.

The bulk free energy density functional is given by:

$$f = w(f_{FF} + f_{FP} + f_{FS}),$$

(4.3)

where $f_{FF}$ accounts for fluid-fluid interactions, $f_{FP}$ for fluid-particle interactions, and $f_{FS}$

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for fluid-substrate interactions. Each of these terms is given by the following equations:

\[ f_{FF} = (3\phi_1^4 - 4\phi_1^3) + (3\phi_2^4 - 4\phi_2^3) + 6\phi_1^2\phi_2^2 \]  
\[ (4.4) \]

\[ f_{FP} = 6\psi(\phi_1^2 + \phi_2^2) \]  
\[ (4.5) \]

\[ f_{FS} = \beta(z)[(\phi_1 - 1)^2 + \phi_2^2] \]  
\[ (4.6) \]

Equation 4.3 takes on three distinct energy landscapes depending on the local conditions, as illustrated in Figure 1. When considering a section within the center of the film, not inside a particle, \( f \) assumes a double-well function typical of an immiscible binary system. Figure 4.1a illustrates this bulk energy landscape where the dotted red line is associated with the physical constraint that \( \phi_1 + \phi_2 = 1 \). This double-well polynomial can be an approximation for the Flory-Huggins energy, if melted polymer blends are assumed [37]. The particle volume fraction, \( \psi \), is stored on the grid and has a value of 1 inside any particle and a value of zero elsewhere (particle diameters are necessarily one order of magnitude larger than the grid resolution). Consequently, the term in \( f \) associated with \( \psi \) is only activated within a particle and changes the bulk free energy landscape to have a single minima at the point \( \phi_1 = \phi_2 = 0 \) as depicted in Figure 4.1c. This serves to drive both fluid fractions to zero within particles.

We assume the film is bounded by solid surfaces on the top and bottom planes of the domain. It is typical in experimental settings for one of the fluids to preferentially wet such external surfaces. The \( \beta(z) \) function captures this preferential wetting:

\[
\beta(z) = \begin{cases} 
\frac{\beta_{\text{max}}(5\delta-z)}{4\delta} & 1\delta \leq z \leq 5\delta \\
0 & 5\delta < z < \delta(n_z - 5) \\
\frac{\beta_{\text{max}}(z-(n_z-4)\delta)}{4\delta} & \delta(n_z - 5) \leq z \leq n_z\delta 
\end{cases}
\]  
\[ (4.7) \]

Essentially, \( \beta(z) \) includes two linear functions equal to \( \beta_{\text{max}} \) at the top and bottom boundaries that linearly decrease to zero over a distance of \( 4\delta \) moving into the domain. The parameter \( \delta \) is the discrete spacial step size in the three coordinate directions, and
Figure 4.1: (a) Free energy density landscape for an immiscible binary fluid as a function of the two fluid volume fractions, $\phi_1$ and $\phi_2$, with energy minima at ($\phi_1 = 1, \phi_2 = 0$) and ($\phi_1 = 0, \phi_2 = 1$). The dotted red line corresponds to the free energy under the constraint $\phi_1 + \phi_2 = 1$. (b) Free energy density landscape adjacent to the substrates illustrating preferential wetting with a minimum point at ($\phi_1 = 1, \phi_2 = 0$). (c) The free energy density landscape inside a particle with a minimum point at ($\phi_1 = 0, \phi_2 = 0$). (d) Illustration showing relationship between different free energy density landscapes and where they correspond spatially on the simulation grid.

$n_z$ is the grid size in the $z$-direction. Hence, the top and bottom wetting substrates are diffuse. The bulk free energy density landscape adjacent to the substrate, but not in a particle, is illustrated in Figure 4.1b which has only one minima at the composition $\phi_1 = 1, \phi_2 = 0$; hence, fluid 1 will coat these boundaries.

The trajectories of the suspended particles are evolved in space and time using standard particle dynamics algorithms. A random distribution of particle positions in the thin film is generated as the initial configuration. Consistent with Brownian motion, particle velocities are calculated by [37]:

$$v_i = \eta_i \mathbf{F}_i^T$$

(4.8)

where $v_i$, $\eta_i$, and $\mathbf{F}_i^T$ are the velocity, mobility, and total force acting on particle $i$. The force on each particle has three different contributions, $\mathbf{F}_i^T = \mathbf{F}_{i}^{pp} + \mathbf{F}_{i}^{stoc} + \mathbf{F}_{i}^{cap}$, corresponding to a steric particle-particle repulsion force, a stochastic Brownian force, and a capillary force exerted locally by the fluid-fluid interfaces, respectively. The particle-
particle interaction forces are calculated using the following equation:

\[ F_{pp}^i = A (r_{ij} - 2(r_p + r_h))^n, \]  \hspace{1cm} (4.9)

where \( r_{ij} \) is the distance between the positions of particles \( i \) and \( j \), \( r_p \) is the defined radius of the particle, and \( r_h \) is an additional halo distance around the particles that is used to improve the numerical computations of the fluid-fluid-particle interactions (see [37] for a discussion). The pre-factor \( A \) and the exponent \( n \) determine the magnitude of the force, which we define as a very short-range repulsion.

Figure 4.2 displays the relationship between the particle volume fraction \( \psi \) and the radius parameters \( r_p \) and \( r_h \). The halo parameter defines a diffuse interfacial width of the particle surfaces, which improves the numerical implementation of the model by preventing particle overlap and ensuring a smooth transition of the fluid parameters \( \phi_1 \) and \( \phi_2 \) from their values in the bulk to those within the particles.

The stochastic Brownian forces on particles are calculated by:

\[ F_{i,\text{stoc}} = B (R_1 F_{i,x}^{\text{stoc}} + R_2 F_{i,y}^{\text{stoc}} + R_3 F_{i,z}^{\text{stoc}}), \]  \hspace{1cm} (4.10)

where \( R_1, R_2, \) and \( R_3 \) are randomly generated numbers between -0.5 and 0.5 and \( B \) is a force constant similar to \( A \) in Eq. (4.9) used to scale the force magnitude.

In the usual formulation of the Cahn-Hilliard model a single order parameter is typ-
Table 4.1: CH/BD simulation parameters used in this study.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\delta$</td>
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</tr>
<tr>
<td>$\Delta t$</td>
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</tr>
<tr>
<td>$M_i$</td>
<td>1.0</td>
</tr>
<tr>
<td>$\kappa$</td>
<td>1.0</td>
</tr>
<tr>
<td>$w$</td>
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</tr>
<tr>
<td>$\eta_i$</td>
<td>0.4</td>
</tr>
<tr>
<td>$A$</td>
<td>50.0</td>
</tr>
<tr>
<td>$B$</td>
<td>20.0</td>
</tr>
<tr>
<td>$D$</td>
<td>2.0</td>
</tr>
<tr>
<td>$n$</td>
<td>-7.0</td>
</tr>
<tr>
<td>$r_p$</td>
<td>4.0</td>
</tr>
<tr>
<td>$r_h$</td>
<td>2.5</td>
</tr>
<tr>
<td>$\beta_{max}$</td>
<td>5.0</td>
</tr>
</tbody>
</table>

ically used to represent the different components of the binary system. In this hybrid CH/BD model we represent each component with a separate order parameter that represents its concentration, which considerably simplifies the identification of particle-fluid-fluid triple junctions and hence the calculation of capillary forces applied to particles at fluid-fluid interfaces.

The capillary forces are calculated by:

$$F_{i}^{cap} = D \int \psi_i \phi_1 \phi_2 (\langle r_{ijk} - r_{i}^{cm} \rangle) dV,$$

(4.11)

where $\psi_i$ is the $\psi$ field of particle $i$, $r_{ijk}$ is the position of the $ijk$ grid point, $r_{i}^{cm}$ is the vector position of the center of mass of particle $i$, and $D$ is a force constant. This method for calculating the capillary force assumes a $90^\circ$ contact angle (neutral wetting of the particle by both fluids). For a discussion of the validity of this method see [37]. Particle positions are updated in time according to their velocities using an Euler algorithm, and corresponding changes are made to the $\psi_i$ fields stored on the grid. For every forward step in time for the particles the fluids are relaxed for 20 CH time steps in order to allow the fluids to equilibrate around the particles.

Table 4.1 displays all of the model parameters used in this study. Most values are consistent with our previous work [37]; however, a large range of $\beta_{max}$ values was inves-
tigated to ensure absolute substrate wetting by fluid 1, as observed in experiments and other simulations [33, 35, 36]. We did not observe any qualitative change in the wetting behavior when varying the $\beta_{\text{max}}$ parameter between values of 0.1 and 10.

In all simulations, periodic boundary conditions where used in the lateral x- and y-directions. The top and bottom surfaces in the z-direction are considered complete-wetting surfaces, which are enforced using two boundary conditions: a no-flux condition enforced within Equation 4.1, and a surface wetting condition (as described by the $\beta(z)$ function in Equation 4.7). These boundary conditions are similar to those used in earlier works [20, 38]. All simulations had lateral x- and y-dimensions of $390\delta \times 390\delta$, while the film thickness, $h = n_z\delta$, was varied. The global particle volume fraction is given by:

$$\phi_P = \frac{4}{3} \pi R^3 \frac{n_x n_y n_z \delta^3}{N},$$

(4.12)

where $N$ is the number of particles, $R$ is an effective particle radius, and $n_x n_y n_z \delta^3$ is the volume of the overall film. Note that $\phi_P$ is a global particle volume fraction (distinguishable from $\psi_i$ which is a local particle volume fraction used to indicate the position of particle $i$). For all simulations, the particle radius, $r_p$, was kept constant (see Table 4.1) and the number of particles, $N$, was varied in order to give different values of $\phi_P$. Because the particles have a diffuse interface, an effective particle radius of $R = 5.0$, which is slightly larger than the value of $r_p$ given in Table 4.1, was used to calculate $\phi_P$. All simulations consisted of 50/50 symmetric fluid compositions starting from a uniformly mixed state with fluctuations in $\phi_1$ and $\phi_2$ in the range of $\pm 0.05$ about the average value. Initiation of the simulations corresponds to an instant quench into the two-phase spinodal region and the start of phase separation. Due to the large number of degrees of freedom in these simulations, all were executed with a parallel processing scheme, whereby the grid was decomposed into sub-grids each assigned to one of many processing cores.

4.4 Simulation Results and Discussion

For immiscible binary fluids in thin films without particles, the phase-separation dynamics are correlated to the thickness of the film, as has been demonstrated by several previous studies [29, 31, 33, 39]. In the numerical study by Hore and Laradji [33], it was
Figure 4.3: Cahn-Hilliard simulation of thin film viscous binary mixtures undergoing surfaced-directed spinodal decomposition with no particles present. Wetting component is yellow and both components have been made semi-transparent in the side views allowing visibility into the core of the film. The simulation cell is $L_x = L_y = 390\delta$ and $h = 60\delta$, showing (top) side views of the thin film, and (bottom) center cross-sections. The time evolution of the thin film is shown from left to right, the simulation times being $1\tau \times 5.0 \times 10^4 \tau$, and $7.5 \times 10^5 \tau$.

demonstrated that such thin films undergo three distinct stages during their evolution. In order to validate our computational model, we first simulate SDSD morphology in thin films without particles, and compare our results to those of Hore and Laradji [33].

Figure (4.3) depicts the different morphological stages that occur within the film during phase separation without particles. The first morphological stage is marked by the formation of wetting layers at the top and bottom surfaces, as well as the initial formation of bicontinuous domains within the inner regions of the film (left-most images in Figure 4.3). Transition to the second stage occurs when the bicontinuous nature of the inner domains is replaced with discrete columnar domains of the wetting phase that bridge the top and bottom wetting layers (middle images in Figure 4.3). During this stage, the wetting component is depleted from the core of the film. Also during this stage, those columnar domains that have a sufficiently large radius grow while those with a smaller radius shrink and disappear. In the third stage, the stable columnar domains grow in diameter via thinning of the top and bottom wetting layers (right-most images in Figure 4.3).

The number of stable columnar domains that form is correlated to the thickness of the film as first noted in Laradji’s study [33]. To illustrate this correlation, the area density
Figure 4.4: The evolution of areal channel density for four different film thicknesses undergoing surface-directed spinodal decomposition. Circles, squares, diamonds, and triangles correspond to film thicknesses of 40δ, 50δ, 60δ, and 70δ. Data for each thickness was averaged over three separate simulations. The maximum channel density decreases as film thickness increases as shown by the inset plot. The curve is a decaying exponential model fit to the data points (circles).

of columnar domains (in units of δ⁻²) throughout time was calculated for a variety of film thicknesses between h = 40δ and h = 70δ, as shown in Figure 4.4. For each thickness, the data was averaged over three separate simulations. As the film thickness increases, the maximum amplitude of the channel density peak decreases until it is non-existent for films that are too thick to support the formation of stable columns (data for larger thicknesses not shown). The thickness at which no stable channels are formed indicates departure from the SDSD regime and the assumption of bulk spinodal decomposition characteristics. The CH simulations here are in excellent agreement with Laradji’s work [33], in which the same morphological stages were observed in addition to the decrease in maximum column density with increasing film thickness.

We now turn our attention to thin-film bijel structures, in which suspended particles are included in the simulations. Here, we systematically varied the particle volume fractions and the film thickness so as to be able to compare our results with the experiments of Composto et al. [36]. Initially, the particles are randomly (and uniformly) dispersed throughout the film interior. In addition, as before, the two fluids are initially homogeneously mixed. Very early in the separation process, when the fluid domains are small, essentially all particles are in contact with the fluid-fluid interfaces, due simply to the large interfacial area that has first developed (left-most images in Figure 4.5). As
Figure 4.5: CH/BD simulation of thin film bijel evolution with $\phi_p = 0.055$, $L_x = L_y = 390\delta$, and $h = 60\delta$. Again, side views (top) and corresponding center cross-section views (bottom) for simulation times $1\tau$, $5.0 \times 10^3\tau$, $1.25 \times 10^5\tau$, and $5.0 \times 10^5\tau$ are shown. The emerging thin film morphology is discrete with columns that bridge between the two wetting layers.

The fluid domains coarsen, the interfacial area decreases, and the particles (which mostly remain attached to the interfaces) are forced into closer proximity with one another until they form a densely-packed jamming monolayer. This interfacial particle jamming slows, and eventually halts, further coarsening of the fluid domains, resulting in a metastable bijel morphology.

Depending on the film thickness and particle loading, a stabilized morphology that is either discrete or bicontinuous emerges as the steady-state configuration. Figure (4.5) illustrates the time-dependent formation of a discrete morphology bijel film in which $h = 60\delta$, while Figure (4.6) illustrates the same for a bicontinuous morphology bijel film with a larger film thickness of $h = 180\delta$. The discrete morphology corresponds to isolated columns bridging the top and bottom wetting layers. The bicontinuous morphology consists of interpenetrating domains stabilized between the wetting layers.

By fixing the particle volume fraction, $\phi_p$, and only varying the thickness of the film, we are able to observe the transition from discrete to bicontinuous domain structures as illustrated in Figure (4.7). The trend observed is that for a given $\phi_p = 0.055$, there is a film thickness sufficiently small that the morphology is discrete, and that as the thickness is increased the bicontinuous morphology prevails. The primary impact of the suspended particles is their ability to jam the domains and prevent any further coarsening that would progress indefinitely otherwise. This is true for both a discrete and bicontinuous
Figure 4.6: CH/BD simulation of thin film bijel evolution with $\phi_P = 0.055$, $L_x = L_y = 390\delta$, and $h = 180\delta$. The simulation times shown are the same as those shown in Figure 5. The emerging thin film morphology is bicontinuous.

Figure 4.7: Stabilized thin film bijel morphologies for film thicknesses (from right to left) of $h = 90\delta$, $h = 120\delta$, $h = 150\delta$, $h = 180\delta$ and $\phi_P = 0.055$, illustrating the transition from discrete to bicontinuous morphology brought on by increasing film thickness. For these simulations $L_x = L_y = 390\delta$.

A comparison of the average channel diameter in two equivalent films, one with particles and one without particles, is shown in Fig (4.8). As might be expected, in the system with particles, the average channel diameter converged to a steady-state value due to the jammed interfaces. On the other hand, in the system without particles, the average column diameter continues to increase indefinitely.

As was proposed by Composto et al [35, 36], the relationship between discrete and bicontinuous bijel morphologies in thin films, and the corresponding transition between the two states, can be explained by a simple geometric model. If we assume a planar
packing factor, or the ratio of the cross-sectional area of interfacially-attached particles to total interfacial area, is \( D = \frac{A_{\text{part cov}}}{A_{\text{interface}}} \), we can use the number of particles present in the system to estimate the total interfacial area in a stabilized bijel as \( A_{\text{interface}} \approx \frac{A_{\text{part cov}}}{D} = \frac{N \pi R^2}{D} \), where \( N \) is the total number of particles and \( R \) is the particle radius. This assumes that all particles are arranged in a monolayer along the interfaces. Assuming a value of \( D = \frac{\pi}{2 \sqrt{3}} \approx 0.91 \) corresponding to a hexagonally close-packed 2D particle arrangement, Compasto et al. [35, 36] proposed the following geometric model:

\[
\frac{n}{A_{\text{film}}} = \frac{3 \phi_P}{4DR} = \frac{3\sqrt{3}h \phi_{NP}}{2\pi R} \tag{4.13}
\]

where \( n \) is the interfacial area normalized by the cross-sectional area of the film, and \( h \) is the film thickness. Solving Eq. (4.13) for \( h \) as a function of \( \phi_P \), and assuming \( n = 2 \) corresponds to a trilayer morphology which represents a division between discrete columns and bicontinuous domains, they predicted a theoretical transition curve for the bicontinuous-to-discrete morphologies in the \((h, \phi_P)\) function space. They verified this geometrically-based morphology map by experimentally creating thin film polymeric bi-jels with varying film thickness and nanoparticle volume fraction with a fixed nanoparticle radius [36]. In our corresponding simulations, we see an identical trend in the morphology map as shown in Figure (4.9). The dotted line in Figure (4.9) corresponds to Compasto’s geometric model while the solid black line corresponds to the same geometric model with a value of \( D = 0.60 \) that matches the discrete-to-bicontinuous transition we observe in our simulation data.

The fact that we observe a planar packing factor, \( D \), below the theoretical close-packed value may be associated with several factors. First, the particles in our simulation cannot come into direct contact with one another due to the small halo region that surrounds each particle (which is included to improve the fluid-fluid-particle contact region). Hence, a smaller areal particle density is to be expected. Second, the interfacial model of Compasto assumes a flat interface, whereas the interfaces that exist in our simulations have distinct curvature, which further reduces the particle coverage in these systems. Finally, the geometric model assumes that all of the particles in the bijel are located along the fluid-
Figure 4.8: Comparison of average channel diameter versus simulation time with, and without, particles, for a film thickness of $h = 60\delta$ and $L_x = L_y = 390\delta$. In the biel simulation, $\phi_P = 0.055$. The biel reaches a jammed state and the fluid domains have stopped coarsening.

fluid interfaces, which is not entirely true in our simulations. Although we observe that the vast majority of particles are absorbed on interfaces, a small fraction of particles are expelled from the interfaces, particularly at regions where the interfacial curvature is high, or where an interface may have recently pinched off from a nearby interface. Due to these three observations, observing a transition that corresponds to a geometric model with $D = 0.60$ instead of $D = 0.91$ is reasonable. Nevertheless, the overall trend of the geometric model agrees well with our simulation data.

Another possible reason for the discrepancy between our data and Composto’s is that the thicker films that we identify as having bicontinuous morphology may not have fully reached their metastable states. From qualitative observation of the simulation animations (see Supplemental Material [40]), it appears that the systems have reached a steady state. In the animations we observe that the particles have fully saturated the interfaces in a dense monolayer by intermediate times. At this point only a few large scale fluctuations in the fluid domains are observed corresponding to areas of high interfacial curvature. At late times, no large scale fluctuations throughout the film are observed and qualitatively appear to have reached full stabilization. Although, it is possible that a slow coarsening, not qualitatively noticeable in the animations, could continue until at extremely late times a discrete morphology emerges. However, this seems unlikely.

One interesting observation that we made from our simulation data was that the pres-
Figure 4.9: Morphology map made from CH/BD simulations showing the relationship between discrete and bicontinuous morphologies with varying film thickness and particle volume fraction. Blue dots correspond to discrete morphology, red dots correspond to bicontinuous morphology, and purple dots correspond to mixed morphology. The dashed line corresponds to Composto’s model with $D = 0.91$ while the black line corresponds to the same model using $D = 0.60$.

ence of the particles seems to extend the stability of the discrete morphology in thin films to thicknesses above those associated with the SDSD. In our simulations without particles, we found that the channel density as a function of thickness decays exponentially with increasing film thickness as illustrated by the inset plot in Figure 4.4. Indeed, at thicknesses of $h = 120\delta$ and larger we saw no stable columnar channels form. However, due to the presence and jamming effect of the particles in our thin film bijels, the simulations showed that stable columns could form for thicknesses up to $h = 150\delta$ with $\phi_P = 0.045$. Additionally, our morphology map indicates that for particle volume fractions less than $\phi_P = 0.045$, stable columns should form for thicknesses greater than $h = 150\delta$. The mechanism for this behavior seems to be the stabilizing effect of the particle jamming which can prevent shrinking columns from ultimately dissolving. This further illustrates how the presence of particles can further be used to tune the morphology of these thin film systems.

4.5 Conclusion

In this work we have presented novel simulation results obtained using a CH/BD hybrid model for thin-film bijels. The simulation results were compared directly with the previous simulations of Hore and Laradji [33] and experiments by Composto and cowork-
ers [36] and were found to have qualitative agreement in both cases. These comparisons provide strong validation of the model's predictive capabilities. We also observed that the introduction of particles in the thin films extended the range of thicknesses at which stable columnar channels form. Our simulations indicated that the particle jamming at the interfaces necessary for bijel formation is the mechanism behind this phenomenon.

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Bibliography


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[40] In supplemental movie s1, we show bicontinuous bijel formation in a thin film; in supplemental movie s2, we show discrete bijel formation in a thin film.
Chapter 5

Paper 2: Diverse morphologies in thin-film bijels by varying film thickness and composition

5.1 Abstract

Thin-film bijels have many potential energy and environmental applications. In this work, the metastable bijel morphology space in thin-film confinement is explored with a Cahn-Hilliard/Brownian-Dynamics computational model. The key parameters varied are the bijel liquid phase blend ratio and the bijel film thickness. Simulations reveal a broad spectrum of structurally unique morphologies that have yet to be observed in experiments and which could have interesting applications in membrane science and other domains. Extensive analyses of surface-to-volume ratios, interfacial particle attachment statistics, and topological interfacial curvatures within the bijels are presented for a complete characterization of the morphological structure.

5.2 Introduction

Since its discovery a little over a decade ago [1], the bijel (short for “bicontinuous jammed emulsion gel”) has peaked the interest of many researchers due to its interesting properties [2–8] and potential applications [9–16] as a versatile soft material. In particular, thin-film bijels that use nanoparticles as their stabilizers hold promise for creating advanced membranes that derive enhanced functionality from both their structural morphology as well as their stabilizing nanoparticles [17]. Indeed, the rapidly-accelerating field of nanoparticle design is still in need of a complementary field focused on efficient methods for incorporating nanoparticles, and their reactive and catalytic properties, into useful material structures and systems. Thin-film bijels are one potential solution for this effort.

The basic constituents of a bijel system include (i) an immiscible (or partially miscible) binary liquid mixture and (ii) colloidal particles. The colloidal particles, with proper surface treatment, serve as the emulsifying or jamming agent by segregating to the interfaces driven by the thermodynamic reward of reducing interfacial area. Imparatively, the
particles must exhibit similar wetting affinity for each liquid phase to facilitate the interfacial segregation [18]. In order for the morphology to be bicontinuous, the composition of the binary mixture needs to be in the spinodal region of the phase diagram, otherwise a discontinuous Pickering emulsion will emerge by droplet-based nucleation and growth mechanisms [19]. The phase separation process inherent to bijel formation is commonly induced by temperature quenching, or a rest period following vigorous fluid mixing, or even through the introduction of an anti-solvent agent [20, 21]. As the multi-phase system develops, the suspended particles become attached to the fluid interfaces and are held there by capillary forces. The system will continue to coarsen with increasing domain size and decreasing interfacial area, to the point whereby the particle packing assumes a dense two-dimensional configuration that jams the interfaces and locks the morphology in a thermodynamically metastable state.

To date, most experimental and theoretical bijel studies have focused on bulk behavior and properties [2, 22]. Only a select few investigations have explored thin-film bijel systems [11, 23–26]. In thin films, where confining surfaces are present, phase separation is complicated by surface interactions, most notably the relative wetting properties of the two liquids with one or more surfaces. In many cases, one phase will preferentially wet a confining surface, leading to surface-directed spinodal decomposition (SDSD). SDSD has been investigated in detail for simple multi-phase fluids without particle suspensions (the following papers constitute good reviews [27, 28]). When particle suspensions are added, the combined effects of particle jamming and surface interactions enable unique morphologies with non-equilibrium metastable structures, as evidenced by the experiments of Composto et al. [25] and the simulations of our group [11, 23].

In this study, we provide a broad analysis of thin-film bijel morphologies with a particular emphasis on the fluid composition - a parameter that has not been varied significantly to date - and film thickness. We employ massively parallel computer simulations of thin-film bijels using a hybrid Cahn-Hilliard/Brownian Dynamics (CH/BD) model. This model captures the coupled liquid phase separation and colloidal particle dynamics, as well as surface wetting effects, within a confined film with top and bottom surfaces. We
uncover a variety of non-equilibrium morphologies with metastable configurations that are both unique and potentially useful for membrane applications.

5.3 Methods

5.3.1 Computational Model

The hybrid Cahn-Hilliard/Brownian Dynamics (CH/BD) computational model used in this work has been described in detail in a previous publication by our group, but for the sake of completeness, a summary of the model will be given here. For a more complete treatment see [23].

The hybrid CH/BD model numerically describes the co-evolution of binary liquid phase separation and the Brownian motion of colloidal particles dispersed within the binary liquid matrix. The binary liquid mixture is evolved by numerically solving the Cahn-Hilliard equation while the colloidal particles are evolved using standard Brownian particle dynamics. There is direct coupling between the liquid phase separation and the Brownian motion of the colloidal particles via interfacial capillary forces and the binary mixture’s free energy of mixing. In addition, the model also captures adjustable surface wetting effects associated with SDSD by altering the free energy of mixing.

5.3.2 Cahn-Hilliard Component

The binary liquid phase separation is described by a set of Cahn-Hilliard (CH) equations:

\[
\frac{\partial \phi_i}{\partial t} = M_i \nabla^2 \delta F \frac{\delta F}{\delta \phi_i} + \zeta
\]

(5.1)

where \( \phi_i \) is a field variable that is continuous in space and time and represents the volume fraction of liquid \( i \). When solving the CH equation numerically, \( \phi_i \) are only sampled discretely on a uniform cartesian grid in three-dimensions. The parameter \( M_i \) and \( \zeta \) in Eq. (5.1) are the mobility of liquid \( i \) and a Gaussian thermal noise term. The symbol, \( F \), in Eq. (5.1), is the free energy density functional of the binary mixture. It represents the local free energy of the mixture and is therefore a function of \( \phi_i \) which is itself a function of space and time. The partial derivative, \( \frac{\delta F}{\delta \phi_i} \), is then the chemical potential of liquid \( i \).

In our CH/BD model, we use a polynomial functional form for \( F(\phi_i) \) that approxi-
Figure 5.1: Schematic (top) showing binary mixture (yellow and blue) with particle (green) at the liquid-liquid interface. Plot (bottom) shows numerical values of the three order parameters, $\phi_1$, $\phi_2$, and $\psi$ along the thick black dashed line that intersects the particle at the interface. Note that the order parameters transition smoothly as opposed to sharply at the interfaces.

mates the Flory-Huggins model for polymer solutions,

$$F = \int [ f(\phi_1, \phi_2, \psi) + \kappa (\nabla \phi_1)^2 + \kappa (\nabla \phi_2)^2 ] dV. \quad (5.2)$$

where $f(\phi_1, \phi_2, \psi)$ is the bulk free energy density and the gradient terms accounts for the liquid-liquid interfacial energy. The $\kappa$ parameter is a coefficient that scales the interfacial energy. The parameter $\psi$ is a field variable that denotes the presence of the colloidal particles. Figure 5.1 illustrates the relationship of the variables, $\phi_1$, $\phi_2$, and $\psi$ to one another in a three-phase system (liquid-liquid-particle). The field variables assume values of one only in regions of space they occupy and smoothly transition to values of zero in regions they do not occupy. All three order parameters are conserved throughout time.

The functional form of the bulk free energy density used in this model can be expressed as,

$$f = w(f_{ll} + f_{lp} + f_{ls}), \quad (5.3)$$

where $f_{ll}$ accounts for liquid-liquid interactions, $f_{lp}$ for liquid-particle interactions, $f_{ls}$ for liquid-surface interactions, and $w$ is a scaling coefficient. These components are defined
by:

\[ f_{ll} = (3\phi_1^4 - 4\phi_1^3) + (3\phi_2^4 - 4\phi_2^3) + 6\phi_1^2\phi_2^2 \] (5.4)

\[ f_{lp} = 6\psi(\phi_1^2 + \phi_2^2) \] (5.5)

\[ f_{ls} = \beta(z)[(\phi_1 - 1)^2 + \phi_2^2] \] (5.6)

\( f_{ll} \) is a double-well function with minima at \((\phi_1, \phi_2) = (1, 0), (0, 1)\) and a miscibility gap between the two minima. This term drives the phase separation of the two liquid phases.

\( f_{lp} \) is only activated when inside a particle and alters the bulk free energy density to have the form of a single well with a minimum at \((\phi_1, \phi_2) = (0, 0)\) which serves to drive values of \(\phi_1\) and \(\phi_2\) to zero inside regions occupied by colloidal particles. \( f_{ls} \) is only activated in near proximity to surfaces and transforms the energy functional to exhibit a single minimum located at \((\phi_1, \phi_2) = (1, 0)\) thereby inducing the preferential surface wetting by the \(\phi_1\) phase. The \(\beta(z)\) function in \( f_{ls} \) has the following functional form:

\[
\beta(z) = \begin{cases} 
\beta_{\text{max}} \frac{(5\delta - z)}{4\delta} & 1\delta \leq z \leq 5\delta \\
0 & 5\delta < z < \delta(n_z - 5) \\
\beta_{\text{max}} \frac{(z - (n_z - 4)\delta)}{4\delta} & \delta(n_z - 5) \leq z \leq n_z\delta 
\end{cases}
\] (5.7)

where \(\delta\) is the cartesian grid spacing used in all spatial directions.

The above form of the CH equation using two order parameters, \(\phi_1\) and \(\phi_2\), is uncommon with respect to other implementations of the CH equation. It is more common to utilize a single order parameter \(\phi = \phi_1 - \phi_2\). However, using two order parameters as we do here simplifies the calculation of capillary forces on particles at liquid-liquid interfaces, as described below.

### 5.3.3 Brownian Dynamics Component

The trajectories of the colloidal particles are evolved in space and time using standard particle dynamics algorithms. The net force on each particle is calculated and used to
determine the particle velocity according to the Langevan dynamics:

$$v_i = \eta_i F^T_i,$$

(5.8)

where $v_i$, $\eta_i$, and $F^T_i$ are the velocity, mobility, and total force of particle $i$. Velocities are then used to update particle positions. Once positions have been updated, the $\psi$ order parameter is updated to reflect these changes. $F^T_i$ itself has three different contributions, $F^T_i = F_{pp}^i + F_{stoc}^i + F_{cap}^i$, corresponding to a steric particle-particle repulsion force, a stochastic Brownian force, and a capillary force exerted locally by the liquid-liquid interfaces.

The particle-particle interactions are calculated using the following relation:

$$F_{pp}^i = A(r_{ij} - (r_{pi} + r_{pj} + 2r_h))^n,$$

(5.9)

where $r_{ij}$ is the center-to-center particle distance, $r_{pi}$ and $r_{pj}$ are the radii of particles $i$ and $j$. $r_h$ is an additional halo region around the particles used for calculating the capillary force $F_{cap}^i$. The result of equation 5.9 is a static repulsion as a function of the surface-to-surface separation distance between particles scaled by the pre-factor $A$ and the exponent $n$. In this and previous work [11] values of $A = 50$, $n = -7.0$, and $r_h = 2.5$ were used. This causes the particles to have an effective radius larger than the specified radius $r_{pi}$. This is necessary to ensure that halo regions never overlap which would complicate the capillary force calculation. A discussion of the consequences of this effect is given in the ESI. For the details of how the stochastic Brownian force and capillary force terms are calculated see [11].

A Gaussian distribution of particle radii with mean $\mu$ and standard deviation $\sigma$ were used to approximate the polydispersity of particle size distributions in experimental conditions. A uniform random distribution of particle positions was also used to select the particles’ initial positions. Particles also have a soft-repulsive interaction with the top and bottom walls identical to particle-particle interactions.
5.3.4 Simulation Setup and Numerical Solution Scheme

The computational domains were discretized with cartesian grids of size $390 \times 390 \times 60$ and $390 \times 390 \times 180$ with a uniform grid spacing of $\delta = 1.0$. These grids were used to solve the CH equations with standard finite difference schemes, namely central finite differencing for the laplacian operations and forward finite differencing for the time derivatives. Particle positions were not restricted to nodes on the grid. Periodic boundary conditions were enforced in the x- and y-directions, and no-flux boundaries were imposed in the z-direction for both the CH variables and the particles. The wetting phenomenon is not induced by the no-flux condition, rather it is driven by the free energy density functional described in the previous section.

Eight different fluid mixture ratios were simulated: $\phi_1/\phi_2 = 10/90, 20/80, 30/70, 40/60, 60/40, 70/30, 80/20, \text{ and } 90/10$. The total volume fraction of particles was constant in all simulations with a value of 0.055 (or 5.5%). A monodisperse distribution of particle sizes was used with an average particle radius of $5.0\delta$ and standard deviation of $1.5\delta$. The variables $\phi_1$ and $\phi_2$ were initialized uniformly throughout the domain (with a small degree of random fluctuation) corresponding to an initially mixed state (within particles, $\phi_1$ and $\phi_2$ were set to zero). The start of each simulation corresponds to an instant quench from the single-phase state on the phase diagram to the two-phase state. Due to the large number of degrees of freedom and long run times in these thin-film bijel simulations, the computational domain was divided into subdomains and a parallel processing scheme was used to distribute the computational work across many processing cores (typically 100 cores for several days per simulation). For each condition, three independent runs were performed to obtain averaged data analysis concerning morphology evolution as described below. See the ESI for model parameter values used in this work.

5.3.5 Interface tracking and Curvature Analysis

Visualization and tracking of the fluid-fluid interfaces was accomplished with the ParaView software suite [29]. In particular, isosurfaces were rendered for the variable $\phi = \phi_1 - \phi_2$ at a value of $\phi = 0$. Interfacial curvature was also analyzed with the assistance of Paraview. In particular, the recent curvature analysis performed on experimental bijels
Figure 5.2: 3D thin-film bijel renderings for thickness $6d$ ($d$ = particle diameter, or 60 points in the z-direction) with different blend ratios. A top view with corresponding side view is shown for each blend ratio. The wetting phase volume is rendered yellow, the non-wetting phase volume is rendered blue, the interface between the two phases is rendered gray, and colloidal particles are represented by the green spheres. Both yellow and blue volumes are semi-transparent to allow perception into the bijel interior. Starting from the top left and going left to right are blend ratios (wetting-phase/non-wetting-phase) of 10/90, 20/80, 30/70, 40/60. The bottom row blend ratios are 60/40, 70/30, 80/20, 90/10.

by Thijssen et al. [30] was used as a guide for developing our curvature analysis. At any interfacial location, two principle curvatures can be calculated $\kappa_1 = \frac{1}{R_1}$ and $\kappa_2 = \frac{1}{R_2}$ where $R_1$ and $R_2$ are the principle radii of curvature at that point. From the principle curvatures, we can calculate the area-averaged Gaussian curvature by:

$$\langle K \rangle = \frac{1}{A} \int_A (\kappa_1 \cdot \kappa_2) \, dA$$

and the area-averaged Mean curvature by:

$$\langle H \rangle = \frac{1}{A} \int_A \frac{1}{2} (\kappa_1 + \kappa_2) \, dA$$
where $A$ is the surface area of the liquid-liquid interface. In order to reduce small-scale noise in the $\phi$-isosurface due to thermal fluctuations added to the CH equation, a certain down-sampling of data resolution was performed as described in the Supplementary Material. Eliminating such small-scale noise allowed more accurate calculations of the actual interface curvature.

![Figure 5.3: Thin film bijel structure of thickness $18d$ with different blend ratios.](image)

Starting from the top left and going left to right are blend ratio (wetting-phase/non-wetting-phase) of 10/90, 20/80, 30/70, 40/60. The bottom row blend ratios are 60/40, 70/30, 80/20, 90/10.

5.4 Simulation Results

As described above, the parameters varied in this work include the fluid volume fraction and the film thickness. The particle loading was held constant. Two different thicknesses were chosen: one above and one below the transition thickness for SDSD for a 50/50 fluid ratio. In our previous work [23], it was found that bijels with a thickness below the transition thickness ($h_{\text{transition}} \approx 140\delta \pm 15\delta$ for particles with radius $r_p = 5.0$)
Figure 5.4: Unique thin film bijel morphologies that emerge when varying film thickness and blend ratio. Top row consists of systems of thickness $18d$ and blend ratios, from left to right, of $20/80$, $40/60$, $60/40$, and $80/20$. The systems depicted in the bottom row have thickness $6d$ and are for the same blend ratios as the top row.

Evolved via SDSD to a jammed state with a discrete two-dimensional morphology characterized by channels of the wetting phase spanning the thickness of the film. On the other hand, bijels with thickness above the transition thickness evolved to three-dimensional bicontinuous morphologies characterized by a network of interpenetrating domains sandwiched between the top and bottom wetting layers.

Figure 5.2 shows three-dimensional renderings of the particle-jammed systems in the thinner films ($z = 60\delta$). The different phases are indicated by the semi-transparent yellow and blue colors and the colloidal particles are rendered as green spheres. Four unique morphologies emerged: tri-layer, discrete, 2D-bicontinuous, and compressed-droplets. For blends of $10/90$, $20/80$, and $30/70$ the morphology is tri-layer. The tri-layer morphology is characterized by the non-wetting phase ($\phi_2$ rendered blue, does not wet the bounding surfaces) being concentrated in the center of the film and sandwiched between the two
wetting layers of the wetting phase ($\phi_1$ rendered yellow, preferentially wets the bounding surfaces). The 40/60 blend system is a discrete morphology characterized by the non-wetting phase occupying the center of the film sandwiched between the wetting layers with the addition of discrete columns of the wetting phase spanning between the top and bottom wetting layers. This morphology was also observed in our previous study of 50/50 blends [23].

Increasing the blend ratio to 60/40 and also 70/30 results in a very interesting morphology that we label 2D-bicontinuous. Here, the wetting and non-wetting phases exhibit bicontinuity in the xy-plane but not in the z-direction. This morphology contains tortuous internal channels that fully percolate in the lateral directions of the film, yet reside fully within the film. Lastly, systems with blends of 80/20 and 90/10 formed compressed-droplet morphologies. These morphologies are much like Pickering emulsions where the droplets have been flattened due to the confining boundaries.

Figure 5.3 shows the jammed states for systems with identical blend ratios as those shown in Figure 5.2 but with a thickness above the transition thickness described earlier ($z = 180\delta$). These systems also evolved from the mixed state to one of four unique morphologies: tri-layer, inverted 2D-bicontinuous, 3D-bicontinuous, and droplet (Pickering emulsion). The systems with blends of 10/90, 20/80, and 30/70 have tri-layer morphologies just as those with the smaller thickness. The system with blend ratio of 40/60 has an inverted 2D-bicontinuous structure in which the wetting fluid forms two wetting layers and also a continuous, tunnel-like internal domain. This internal domain is similar to that observed in the thinner bijel film, but here the wetting fluid is inverted with the non-wetting fluid, hence the name inverted 2D-bicontinuous. The systems with blends of 60/40 and 70/30 are 3D-bicontinuous and are characterized by a bulk bijel morphology sandwiched between two wetting layers. Finally, systems with blends of 80/20 and 90/10 evolved to droplet morphologies, or Pickering emulsions sandwiched between two wetting layers.
5.5 Analysis and Discussion

Figure 5.4 shows renderings of the particle jammed systems collected from Figures 5.2 and 5.3 that summarize all the unique morphologies. Comparing the top and bottom rows of morphologies in Figure 5.4 allows us to clearly see the collective effects of the liquid blend ratio and surface-directed spinodal decomposition on the bijel film morphology. For the 20/80 and 80/20 blends, the thinner film morphologies are simply squashed versions of the thicker film morphologies. This result is intuitive. However, when comparing the thicker and thinner morphologies for the 40/60 and 60/40 blends we get a less intuitive result. In particular, the emergence of the 2D-bicontinuous morphology was not expected, yet its unique two-dimension percolating structure may have applications for membrane or quasi-two-dimensional applications. The variety of distinct morphologies demonstrates the high degree of morphology tunability in thin-film bijels.

5.5.1 Interface Surface-to-Volume Ratio

In analyzing these simulation results, one question of interest is whether the systems have fully reached steady state. Another way of expressing this is to ask if the systems are still coarsening. To address this question, the liquid-liquid interface surface-to-volume ratio ($S/V$) was calculated at evenly spaced time intervals, with results shown in Fig. 5.5.
In this figure, the red curves represent systems with small thickness \((z = 60\delta)\) and the blue curves represent systems with large thickness \((z = 180\delta)\). We ran multiple simulations for each set of parameters so the curves in Figure 5.5 are the averaged values and the semitransparent bands represent the standard deviations.

The \(S/V\) for each system asymptotically approaches a value corresponding to the final jammed state. As can be seen in Figure 5.5, systems with the smaller thickness have reached, or are very close to reaching, this asymptotic \(S/V\) value. However for systems with larger thickness only blend ratios of 20/80 and 80/20 seem to have fully reached steady state. The other two blends appear to be close to reaching steady state, but not completely there. Despite this, we do not believe the steady state morphology would be significantly different than what is shown at the end of our simulation runs. We have confidence that any further coarsening will be on a small scale and would not qualitatively modify the general morphology classification given. We provide simulation animations in the supplementary material which demonstrate how little the morphologies are changing in the later stages of the simulation. These animations are also useful for understanding other trend features in the surface-to-volume ratio curves shown in Figure 5.5. For example, in the 20/80 blend ratio films the thinner film’s \(S/V\) is nearly constant while the thicker film’s \(S/V\) monotonically decreases to the tri-layer value. This difference is explained by the animations which depict the early formation of droplets in the film core for the thicker film, which then shrink and eventually disappear.

Another interesting feature of the curves in Figure 5.5, is that thinner films always have higher \(S/V\) values than thicker films. Indeed in Figure 5.5 we see that all the thinner films, except the 80/20 blend, have much higher surface-to-volume ratios. We believe that SDSD is one of the primary causes of this difference. SDSD causes interfaces to have a preferred geometry parallel to the top and bottom surfaces. Consequently, when the thickness of the film is increased and the core of the film is not influenced by the wetting surfaces, the liquid domains can take on shapes with more curvature, as opposed to being more flat. The curved surfaces minimize their total surface area per unit volume more efficiently leading to a smaller overall surface-to-volume ratio for thicker films.
5.5.2 Particle Interface Attachment

Figure 5.6: Fraction of particles attached to the interface as a function of simulation time for thicker films. Legend indicates blend ratios.

Figure 5.7: Fraction of particles attached to the interface as a function of simulation time for thinner films. Legend indicates blend ratios.

In studying the visual renderings of the simulated bijels in Figures 5.2-5.4 one notices the different degrees of particle attachment on the interfaces. For some films, almost all of the particles are attached and stay attached to the liquid-liquid interface throughout the evolution of the film morphology (i.e. the 60/40 blend ratio systems depicted in Figure 5.4). On the other hand, for other films there are lots of particles detached from the interface by the end of the simulation. We tracked the total number of particles on the interface and this information is represented in Figures 5.6 and 5.7. Again, the solid lines represent the average of the simulation runs and the semitransparent banded regions
represent the standard deviations about the average.

In general, the thinner films retain more particles on their interfaces than the thicker films. We identified two main reasons for this. The first being that there is just less interfacial surface area per unit volume in the thicker films than in the thinner films. The second reason is related to how SDSD suppresses particle detachment. By carefully observing the simulation animations we identified the primary mechanisms leading to particle attachment or lack thereof. At the start of any simulation the liquids are finely mixed and all particles are in contact with an interface. As the liquids phase separate and the interfacial area decreases, some particles are left detached from interfaces. These detachments are primarily associated with droplets shrinking and disappearing as well as long tubular peninsula domains that retract into larger domains. The peninsula-like domains are usually formed when a bicontinuous network undergoes a pinch-off event. Figure 5.8 shows a time-series of snapshots corresponding to a particle detachment event.

![Figure 5.8](image)

**Figure 5.8: Time series snapshots of the formation of a peninsula domain created by a pinch off event in one of the thicker 60/40 blend bijels. The earliest time starts with image (a) and proceeds forward in time to image (c). A single particle which gets detached from the bijel interface is marked with a star in each image.**

The particle that detaches is marked with a star in each image. In each image the bijel interface is represented by an isosurface fit to locations where $\phi = \phi_1 - \phi_2 = 0$. The isosurface is colored by Gaussian curvature with scale denoted by the color bar next to the images. Starting in image (a) we see a tubular neck covered by particles. A short
time later, shown in image (b), the tubular domain has necked down significantly. In image (c) the neck has pinched off resulting in a peninsula-like domain with high positive Gaussian curvature at the location of the starred particle. In the final frame depicted in image (d), we see the detached particle and the absence of the peninsula-like domain due to its retraction.

In the thinner films, the formation of these types of domains (droplets and peninsulas) that lead to particle detachment are suppressed. This leads to more particles staying on the interfaces in the thinner films compared to thicker films. Comparing Figures 5.6 and 5.7 demonstrates this point. Furthermore, the more asymmetric the fluid composition (e.g. 20/80 or 80/20), the more susceptible the system is to particle detachment.

**Figure 5.9:** Time evolution of area-averaged curvatures for systems of varying blend ratio and thickness. The top row of figures correspond to the $z = 180\delta$ thickness films and the bottom row corresponds to $z = 60\delta$ thickness films. Legends indicate blend ratio and curvature type (Gaussian or Mean). The plotted points represent the average over three separate simulation runs while the blue and red shading indicates the standard deviation from the average of the three runs (mean curvature standard deviations are so small that they are not visible in the plots).

### 5.5.3 Interfacial Curvatures

In addition to particle interface attachment, we also used topological curvature analysis to study the simulated bijel structures. The area-averaged Gaussian curvatures (AGC)
and the area-averaged mean curvature (AMC) where calculated as functions of simulation time for each of the systems and are shown in Figure 5.9. Each plot in Figure 5.9 is for a particular blend ratio with the top row corresponding to thicker films and the bottom row corresponding to thinner films. The layout of Figure 5.9 matches the layout of Figure 5.4 with a direct correspondence. The plot for each system shows the time evolution of both the AGC (blue curve) and the AMC (red curve). Note that the AGC values in the plots are multiplied by a factor of 100. This is done to place both data sets in the same value range (note that Gaussian curvatures are obtained by the product of the two principle curvatures, as opposed to the sum of the two principle curvatures associated with the mean curvature, hence Gaussian curvature is typically much smaller in magnitude than mean curvature).

When AGC is positive, the principle curvatures at that point have the same sign (i.e. both positive or both negative) that indicates a concave surface shape. In our curvature calculations, we define negative curvature as being curved toward the non-wetting (blue) phase. Negative AGC at a point on the interface is caused by the principle curvatures being of opposite sign and denotes a saddle-shaped surface. AGC is a measure of the average shape of the interfacial surface, whether concave or saddle-like. Thus, we would expect morphologies with more droplet-like shapes to have a positive AGC and those with a gyroid-like bicontinuous morphology to have negative AGC. When AGC = 0, the interface only has curvature in one dimension. This corresponds to cylindrically-shaped or flat surfaces. On the other hand, AMC is simply a measure of the average of the distribution of curvatures. A negative AMC value indicates that the average interface shape is curved more towards the non-wetting phase and visa versa.

For the thick and thin 20/80 blend ratio systems (tri-layer morphologies) their asymptotic AGC behavior is the same, staying at a very small negative AGC value. If the top and bottom wetting layers in these systems were perfectly flat then the AGC values would be exactly zero; but they have undulations in them, more so for the thicker films. The small negative AGC values indicate that the average interface shape is more saddle-like than concave. This makes sense in that to stay approximately flat, curvature towards one
phase would have to be negated by curvature towards the other resulting in more saddle shapes than concave ones. The initial positive AGC for the thicker tri-layer system and its subsequent decay comes from droplets that form early in the core of the film and later shrink and disappear.

The AGC curves for thick and thin films with blend ratios of 40/60 and 60/40 all have the same general trend shape. They all start negative and become less negative through time, approaching some asymptotic value. The thin 40/60 blend ratio (discrete morphology) is almost identical to the tri-layer morphology with the exception of channels that form of the wetting phase that span between the top and bottom wetting layers. In fact, the asymptotic AGC values for these two systems are essentially the same. The difference in the early transient behavior is due to the fact that the bicontinuous network that forms and then breaks up is sustained longer in the 40/60 blend system than the 20/80 blend system. This can be seen in the simulation animations.

The thick 40/60 blend system (inverted 2D-bicontinuous morphology) has a more negative initial and asymptotic AGC value than its thinner counterpart. This is to be expected considering that it has a 2D-bicontinuous structure sandwiched between its two wetting layers. Notice also that the thick 40/60 blend system has an asymptotic AGC value that is not much higher than the thick trilayer system. This means that the 2D-bicontinuous structure embedded between the two wetting layers adds only a small negative contribution to the overall AGC of the system. This is also intuitive because the 2-D bicontinuous structure has mostly cylindrically-shaped interfaces which have very small negative AGC contributions. This is verified by observing the asymptotic AGC values for the thin 60/40 blend system (2D-bicontinuous morphology). This system has essentially the same morphology as the thick 40/60 blend except it has no wetting layers.

The thick and thin 80/20 blend systems are the only ones with positive asymptotic AGC values. This is because their morphologies are droplet-like which have little to no saddle-shaped interfaces. These systems also have a noticeable negative asymptotic AMC value relative to all the other systems whose asymptotic AMC values are very close to zero. For these two systems, the absolute values of the AMC is inversely proportional
to the average droplet size. Mathematically, this is stated $L \approx AMC^{-1}$ where $L$ is the average domain size of the droplets (or flattened droplets for the thinner system).

Lastly, we wish to comment on the dynamical behavior of AMC values for the non-droplet morphology systems which are all approximately zero. For systems with negative AGC values we expect the AMC values to be very close to zero because saddle-shaped interfaces have opposite signed principle curvatures which tend to cancel each other out in the mean curvature calculation. The very early transient behavior of the AMC curves for all the systems is informative. Systems other than the thin tri-layer system have non-zero positive or negative initial AMC values. This initial value is related to the blend ratio. There is always a preferred curvature towards the minority phase. This is evidenced by the fact that the initial AMC values transition from being positive to negative when going from the 40/60 blend systems to the 60/40 blend systems.

In summary, the curvature data presented here does a nice job of capturing most of the differences in morphology and morphological evolution in these systems. The combined AGC and AMC trends for a given system also present a unique thumbprint for each morphology’s evolution.

5.6 Summary

Here, we have presented numerical simulations that provide insight into thin-film bijels that reveal a large variety of morphologies. We primarily investigated the inter-relationships between fluid composition and SDSD influenced by film thickness, and how these parameters combined can promote the emergence of non-intuitive morphologies. Extensive analysis of each of the observed structures was presented in the form of interfacial surface-to-volume ratios, interfacial particle attachment statistics, and the topological curvatures of the fluid-fluid interfaces.

Some of the less intuitive morphologies, such as the 2D-bicontinuous example shown in Figure 5.4, may have interesting new technological applications. For example, this structure could be solidified followed by the (chemical) removal of the non-wetting phase, resulting in a thin membrane with an internal, fully-percolated network of pore structures with or without the presence of the particles. Such a structure could be used to facilitate
the in-plane transport of a variety of stimuli-responsive fluids, or the exchange of electrical charge or thermal energy.

5.7 Supplementary Material

5.7.1 Curvature Calculation

To calculate curvatures on a simulated bijel, the data, stored in the Legacy VTK file format, is loaded into paraview. An isosurface filter is then applied for values of $\phi = 0$ which represents the interface between the two binary phases as mentioned previously. Due to the high density of particles that attach to the bijel interfaces and the random fluctuations in $\phi_i$ from the thermal noise term in the Cahn-Hilliard equation, the interface has roughness which introduces significant noise into the calculated isosurface. In order to smooth out the isosurface to more accurately represent the bijel interface, the VTK data was downsampled by a factor of six nodes using Paraview’s extract subset filter before applying the isosurface filter. Several different downsampling rates were tested and a six node rate was identified as the rate that produced the most accurate match to the real interface. After downsampling, Paraview’s curvature filter was applied to the isosurface to calculate both $K$ and $H$ at each point on the isosurface. Next, Paraview’s threshold filter was applied to filter out any extreme curvature values resulting from remaining artifacts in the isosurface. Any curvatures corresponding to a radius of curvature smaller than the particle’s average radius were filtered out in this step. Lastly, the area-averaged curvatures were extracted using the integrate variables filter in Paraview. This entire procedure was scripted in the Python programming language and executed via Paraview’s Python interface. Benchmarking in a similar fashion to the work of the Thijssen group [30] was carried out to ensure results were as expected.

The curvature analysis process using Paraview outlined above was benchmarked using periodic gyroid (with $L =$ unit cell size for the gyroid) and spherical structures to probe the accuracy of the method. The area-averaged Gaussian and Mean curvatures vary with the average domain size of the bijel; Consequently, it is necessary to normalize the curvatures in some way to allow for comparison of morphologies with differing average domain sizes. This is done by normalizing the curvatures with the interface area to
Figure 5.10: Test cases for curvature analysis with the Paraview software suite. Gyroid structure with dimensions $400 \times 400 \times 60 \delta^3$ and spheres with a diameter of $20\delta$. The gyroid structure has $L = 60\delta$. Area-averaged curvatures normalized by surface-to-volume ratio and corresponding error for the gyroid structure are $\langle K \rangle \Sigma^{-2} = -1.8946$, $\epsilon_r = 12.4\%$ and $\langle H \rangle \Sigma^{-1} = -0.0103$, $\epsilon_a = 1.0\%$. Area-averaged curvatures normalized by surface-to-volume ratio and corresponding error for the spheres are $\langle K \rangle \Sigma^{-2} = -2.1673$, $\epsilon_r = 1.55\%$ and $\langle H \rangle \Sigma^{-1} = 4.6880$, $\epsilon_r = 0.87\%$.

The normalized curvatures are then given by $K \Sigma^{-2}$ and $H \Sigma^{-1}$. The data presented in the paper is not normalized in this fashion because we found the non-normalized data to be more intuitive and thus easier to interpret.

Spheres and gyroid structures were generated in thin-film geometries as shown in Figure 5.10. Area-averaged and normalized curvatures were calculated for these topologies and the results compared against their analytical values. Results, including relative and absolute errors, are shown in the caption for Figure 5.10. Additionally, a test of the curvatures dependence on the domain size for the gyroid structures was conducted and results are shown in Figure 5.11. It was found that significant errors were produced when the domain size of the gyroid is reduced below $15\delta$. This is due to the discreteness of the gyroid data which does not provide enough resolution to accurately capture the gyroid surface. To account for this situation, during the early stages of binary phase separation in our bijel simulations, when domain sizes are very small, curvature calculations were not performed (for the first 10,000 time steps).
Figure 5.11: The top plot shows the area-averaged curvatures for the gyroid structure as a function of $L$. The bottom plot shows the fraction of curvature data ($FCD$) for a given $L$ used to generate each data point in the top plot. The reason for the fraction being so low for small values of $L$ is that most of the curvatures calculated are very extreme and are consequently filtered out by the Paraview threshold filter.

5.7.2 Interfacial Particle Coverage

In addition to the fraction of particles attached to the interface, we also tracked the percentage of interfacial area covered by the particles. This was calculated by assuming that the portion of interface covered by a particle was flat and that the particles covered an area equal to their largest cross-sectional area $A_c = \pi r_p^2$, where $r_p$ is the particle radius. This calculation is therefore not exact and tends to undershoot the true value, more so for thick films because they have a higher ratio of curved to flat interface than the thinner films. Nonetheless, it should still give a good approximation of the actual particle coverage. The percent of the interface covered by particles calculated in this fashion is given in Figures 5.12 and 5.13 for thick and thin films, respectively.

Notice in Figures 5.12 and 5.13 that despite the spread in magnitude for the different blend ratios, the asymptotic behavior of all the films, both thick and thin, are all in the
same general range of about 40-80% coverage. For a flat interface populated by particles with uniform size, the maximum percentage of interfacial area the particles can cover is equal to approximately 90.7% (i.e., close-packed structure). This happens when particles are packed as tightly as possible. The interfacial coverage percentage in our simulated bijel films is somewhat lower than this theoretical packing density for a number of reasons. First, the particles' Brownian motion and soft repulsive interactions never allows the particles to come into direct contact with one another. Second, the interface between the two liquid phases is never completely flat in the locality of an attached particle. Third, the particles themselves have variance in their size which frustrates close packing. Lastly,
in many of the films, there is still interfacial area available that could accommodate more particles (especially in the tri-layer case).

5.7.3 Simulation Parameters

Table 5.1 lists all the simulation parameters and their numerical values. Although the mean particle radius $\mu$ has a value of 4.0, the diffuse interfaces of the particles cause the effective particle radius to be larger than this (in our case by an increase of about 1 grid spacing $\delta$). This effective particle radius is what is used to calculate the total volume fraction of particles in the system.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Description</th>
<th>Value</th>
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<td>$\delta$</td>
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<tr>
<td>$\Delta t$</td>
<td>time step</td>
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</tr>
<tr>
<td>$M_i$</td>
<td>liquid phase mobilities</td>
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<td>$\kappa$</td>
<td>interfacial energy par.</td>
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<td>$w$</td>
<td>double well energy barrier par.</td>
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</tr>
<tr>
<td>$\eta_i$</td>
<td>particle mobility</td>
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</tr>
<tr>
<td>$\mu$</td>
<td>mean particle radius</td>
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</tr>
<tr>
<td>$\sigma$</td>
<td>particle radius std.</td>
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</tr>
<tr>
<td>$\beta_{\text{max}}$</td>
<td>wetting strength par.</td>
<td>5.0</td>
</tr>
<tr>
<td>$n_z$</td>
<td>number of nodes in the z-dir.</td>
<td>60 or 180</td>
</tr>
</tbody>
</table>

Bibliography


[18] Stefan Frijters, Florian GÄijnther, and Jens Harting. Domain and droplet sizes in


Chapter 6
Paper 3: Tuning Thin-film Bijels with Applied External Electric Fields

6.1 Abstract

The tunability of thin-film bijels using applied external electric fields is explored using a Cahn-Hilliard Langevin Dynamics computational model. Dielectric contrast between liquid domains governs liquid domain alignment and was varied in the simulations. Dielectric contrast between colloidal particles and liquid matrix induces dipolar particle interactions and was also varied in the simulations. The study reveals unique internal morphologies including those with through-thickness liquid domains. Significant results include identification of electric field effects on phase evolution and final morphology as well as relevant mechanisms. It was also found that particle chains act as nucleation sites for phase separation. The resultant morphologies were analyzed in terms of particle attachment, interfacial area-to-volume ratio, and average channel diameter. Electric field effects and mechanisms on morphology are identified and compared with other morphology-tuning parameters such as particle loading and liquid-liquid composition.

6.2 Introduction

Bijels are a class of soft materials discovered fairly recently in 2005 [1, 2]. The term bijel stands for “Bicontinuous Interfacially Jammed Emulsion Gel”. Although their formation process is a topic of current research [3–5], it generally involves a system of two phase separating liquids, usually close to the critical composition, with the addition of colloidal particles. Processing routes typically involve quenching the system into the spinodal region thereby inducing phase separation via spinodal decomposition. This phase separation is eventually arrested by particle jamming at the interfaces between the two liquids. The colloidal particles must have fairly equal affinity for both liquids which results in a solid/liquid/liquid contact angle of approximately 90°. As phase separation proceeds, the particles form a dense monolayer on the interface and halt the separation process. The jammed liquid domains form a bicontinuous network where the average domain size, or separation distance between interfaces, is approximately constant.
property is similar to that of the geometric gyroid structure [6], however without long-range order. This jammed bicontinuous state is what is typically referred to as a bijel. In this work we will show how such morphologies in thin-film geometries can be drastically modified by the application of external electric fields to create aligned morphologies that retain colloidal particles attached to the liquid-liquid interfaces.

Bijels have many promising applications in the soft materials industry due to their unique properties and morphology tunability. Bijels have been used as template scaffolds [7] for creating many novel materials such as monolithic porous metals [8–10], battery electrodes [11], and cell delivery materials [12]. Most bijel studies, theoretical and experimental, have been performed in bulk conditions. Bijels confined to thin-films are a new area of research in this field with only a few studies having been completed [13–15]. The study of thin-film bijels is motivated by factors such as the potential for roll-to-roll processing, morphology diversity and tunability [15], and the creation of membranes with enhanced properties due to the interfacial nanoparticles.

The application of an electric field is known to align the domains of immiscible homopolymer blends [16, 17] and block copolymers [18–20]. Furthermore, electric fields can assemble colloidal particles suspended in a solvent into 1D chains or 2D walls [21, 22], depending on the particle volume fraction, with the classic example being an electrorheological fluid. The basic principle for either case is the difference between the dielectric properties of the two matrix phases, or between the particles and the matrix.

This work is focused on simulating the effects of applied external electric fields to thin-film bijels composed of viscous liquids, such as polymer solutions, and their morphology evolution from initial quench to a final jammed state. Although one might speculate that domain and particle alignment should occur, the true effect of the electric field on the structure of the bijel domains, or the structure of the particle-coated interfaces, is not known. For example, is it possible that an electric field of sufficient strength may detach particles from the interface? Previous studies have shown that interfacially-attached particles in oil-in-water droplets remain attached in electric fields, which can elongate the droplets [23] or re-organize the particle arrangements [24]. Here, we have extended a
Cahn-Hilliard Langevin Dynamics computational model developed in our previous work [13, 15] to simulate applied electric fields to thin-film bilayers.

6.3 Methods

6.3.1 Computational Model

The Cahn-Hilliard Langevin Dynamics computational model is composed of two sub-models which are then directly coupled. The first sub-model is a Cahn-Hilliard model which evolves a set of order parameters through space and time. For this work, there are three order parameters that are evolved on a Cartesian grid. Two of these order parameters, $\phi_1(x, y, z, t)$ and $\phi_2(x, y, z, t)$, represent the volume fraction for each constitutive liquid phase. The assumption of high viscosity is due to the fact that the Cahn-Hilliard equation models diffusion-based transport only and does not account for convective transport. The third order parameter, $\psi(x, y, z, t)$, represents the local presence of a solid particle. It is not evolved by the Cahn-Hilliard equation but is used in the coupling of the two sub-models which will be explained shortly. Additionally, the Cahn-Hilliard model is modified from its normal form by including a term to account for the effects of an applied external electric field.

The other sub-model is a Langevin particle dynamics model which evolves a suspension of solid colloids through space and time and is very similar to a classical molecular dynamics model. The Langevin dynamics model is also modified to simulate the Brownian motion of the particles in the presence of an electric-field.

6.3.2 Cahn-Hilliard model

The modified Cahn-Hilliard (CH) equation is given by:

$$\frac{\partial \phi_i}{\partial t} = M_i \nabla^2 \frac{\delta F}{\delta \phi_i} + k_z \frac{\partial^2 \phi_i}{\partial z^2} + \zeta$$  (6.1)

where $i = 1, 2$ yielding a set of CH equations for evolving each liquid volume fraction, $\phi_1(x, y, z, t)$ and $\phi_2(x, y, z, t)$, through space and time. In Eq. (6.1), $M_i$ is a mobility term for liquid $i$ and $\zeta$ is a small random fluctuation term that models thermal noise in the liquid order-parameter fields. The $k_z \frac{\partial^2 \phi_i}{\partial z^2}$ term is a modification that models the liquid domain alignment in the electric field direction (here, the $z$-direction) [25]. It models an
electrostatic pressure on the interfaces by adding an energetic penalty for z-gradients in the $\phi_i$ parameters. $k_z$ is proportional to the square of the electric field strength, $E_0$, and the square of the dielectric discrepancy between phases $(\epsilon_1 - \epsilon_2)$:

$$k_z = \frac{\epsilon_0 v_0}{k_B T} \frac{2E_0^2 (\epsilon_1 - \epsilon_2)^2}{(\epsilon_1 + \epsilon_2)} \quad (6.2)$$

where $\epsilon_0$ is the permittivity of free space, $v_0$ is the volume of one monomer, $E_0$ is the strength of the electric field which is oriented in the z-direction or perpendicular to the film, and $\epsilon_1$ and $\epsilon_2$ are the dielectric constants of the two liquid phases. In typical experimental conditions for a polymer blend, for example PS/PMMA, a value of $k_z = 0.1$ corresponds to an electric field strength of $8V/\mu m$ [26].
The free energy density $F$ in Eq. (6.1) is given by:

$$F = \int \left[ f(\phi_1, \phi_2, \psi) + \kappa(\nabla \phi_1)^2 + \kappa(\nabla \phi_2)^2 \right] dV. \tag{6.3}$$

where $f(\phi_1, \phi_2, \psi)$ is the bulk free energy density and the gradient terms account for the liquid-liquid interfacial energy. The $\kappa$ parameter is a coefficient that scales the interfacial energy. The relationship between the three order parameters $\phi_1$, $\phi_2$, and $\psi$ are schematically represented in Fig. 6.1. The $\psi$ order parameter is a mapping of the function in Eq. 6.4 to the local region of the grid occupied by each particle.

$$\psi_j(\mathbf{r}) = \begin{cases} 
1 - \left( \frac{|\mathbf{r} - \mathbf{r}_{cm}^j|}{\text{rad}_j} \right)^2 & 0 \leq |\mathbf{r} - \mathbf{r}_{cm}^j| \leq \text{rad}_j \\
0 & \text{rad}_j < |\mathbf{r} - \mathbf{r}_{cm}^j| 
\end{cases} \tag{6.4}$$

In Eq. 6.4, the vector $\mathbf{r}$ represents a location in the simulation domain, $\text{rad}_j$ and $\mathbf{r}_{cm}^j$ are the radius and center-of-mass position vector of the $j^{th}$ particle, and $\psi_j(\mathbf{r})$ is mapped for every single particle in the system.

The functional form of the bulk free energy density, $f(\phi_1, \phi_2, \psi)$ in Eq. (6.3) is a polynomial function of $\phi_1$, $\phi_2$, and $\psi$ of the form:

$$f = w(f_{ll} + f_{lp}), \tag{6.5}$$

where:

$$f_{ll} = (3\phi_1^4 - 4\phi_1^3) + (3\phi_2^4 - 4\phi_2^3) + 6\phi_1^2\phi_2^2 \tag{6.6}$$

$$f_{lp} = 6\psi(\phi_1^2 + \phi_2^2) \tag{6.7}$$

$f_{ll}$ accounts for liquid-liquid interactions, $f_{lp}$ for liquid-particle interactions, and $w$ is a scaling coefficient. $f_{ll}$ is a double-well function with minima at $(\phi_1, \phi_2) = (1, 0), (0, 1)$ and a miscibility gap between the two minima which approximates the Flory-Huggins free energy density model for polymer solutions [27, 28]. $f_{lp}$ is only ever activated in regions of the simulation domain occupied by particles (i.e. where $\psi$ is nonzero). This
changes the free energy density model inside particles to have a single energy minima at $(\phi_1, \phi_2) = (0, 0)$ which serves to drive both liquid species out of domains occupied by particles. An in-depth discussion of the model given in Eq. (6.3) is available in previous publications [14, 15].

6.3.3 Langevin Dynamics model

The Langevin dynamics sub-model evolves a system of colloidal particles in space and time according to their equations of motion. The equation of motion for particle $j$ is given by:

$$m_j a_j = F_{pp}^j - F_{d}^j + F_{s}^j + F_{c}^j$$

(6.8)

where $m_j$ and $a_j$ are the mass and acceleration of particle $j$, and $F_{pp}^j$, $F_{d}^j$, $F_{s}^j$, and $F_{c}^j$ are the particle-particle interaction force, drag force, stochastic Brownian force, and capillary force exerted on particle $j$, respectively.

Particle-particle interaction forces have two main components. First there is a soft steric repulsion force calculated on particle $j$ from particle $i$ as:

$$F_{rep}^{ij} = \sigma \left( \frac{2r_{avg}}{r_{ij}} \right)^n,$$

(6.9)

where $r_{ij}$ is the center-to-center particle distance, $r_{avg}$ is the average radius of particle $i$ and $j$, $\sigma$ is a constant used to scale the repulsive force strength, and $n$ is an integer exponent ($n = 7$ for this work). The second component of the particle-particle interaction force is an electric-field induced dipole-dipole force. Using the point dipole approximation [29] it is calculated as:

$$F_{dip}^{ij} = R_{dd} \left[ (3\cos^2\theta - 1) \hat{r} + (\sin 2\theta) \hat{\theta} \right]$$

(6.10)

$$R_{dd} = \frac{r_{avg}^6 C^2 E_0^2}{r_{ij}^4}$$

(6.11)

where $C = (\epsilon_p - \epsilon_m)/(\epsilon_p + 2\epsilon_m)$ is the particle polarizability or Clausius-Mossotti relation and $\theta$ is the angle between the particle separation vector $r_{ij}$ and the direction of the electric field (here, the $z$-direction). In the Clausius-Mossotti relation, $\epsilon_p$ is the dielectric
constant of the particle and $\epsilon_m$ is the dielectric constant of the liquid-liquid matrix in which the particle resides. $\hat{r}$ is the unit vector pointing in the direction of the separation vector of the two particles $r_{ij}$, and $\hat{\theta}$ is the corresponding orthogonal unit vector pointing in the theta rotation direction.

The particle-particle interaction force on particle $j$ in Eq. (6.8) is given as the sum of the steric repulsion forces and dipole-dipole interaction forces:

$$F_{pp}^j = \sum_{i=1}^{nbrs} (F_{rep}^{ij} + F_{dip}^{ij})$$  \hspace{1cm} (6.12)

where the sum is over all the neighbor particles to particle $j$ within a cutoff radius distance, $r_{\text{cut}}$.

The drag force on the $j^{th}$ particle is calculated by:

$$F_{d}^j = -\gamma v_j$$  \hspace{1cm} (6.13)

where $\gamma$ is the drag coefficient, which is related to the viscosity of the liquid matrix in which the colloids are dispersed, and $v_j$ is the velocity of particle $j$.

The stochastic or Brownian force is calculated using the following relation:

$$F_{s}^j = \sqrt{2 \cdot \gamma \cdot \nu \cdot R}$$  \hspace{1cm} (6.14)

where $\nu$ is a parameter used to scale the Brownian motion strength and is related to temperature. $R$ is a vector with each $xyz$ component drawn from a uniform random distribution over the interval $[-1, 1]$.

The capillary force on the $j^{th}$ particle is calculated using order parameter information from the Cartesian grid:

$$F_{c}^j = D \sum_k \sum_l \sum_m \psi_{j}^{klm} \phi_1^{klm} \phi_2^{klm} (r_{klm} - r_{j}^{cm})$$  \hspace{1cm} (6.15)

$D$ is a force constant used to scale the capillary force and the triple summation is over the local section of the grid occupied by particle $j$. $r_j^{cm}$ is the center-of-mass position vector.
of particle $j$, $r_{klm}$ is the position vector of the local grid node, and $\psi_j^{klm}$, $\phi_1^{klm}$, and $\phi_2^{klm}$ are the values of the order parameters at the local node. This form of the capillary force calculation ensures that capillary forces are only non-zero when located at liquid-liquid interfaces and has been validated to produce correct capillary forces for spherical particles [13].

### 6.3.4 Coupling of Cahn-Hilliard and Langevin Dynamics Submodels

In both the sub-models described above, surface tension or interfacial energy is the key parameter linking the two models. In the Cahn-Hilliard sub-model, the interfacial energy between liquids $\phi_1$ and $\phi_2$ is non-linearly proportional to the product of $w$ in Eq. (6.5) and $\kappa$ in Eq. (6.3):

$$\sigma_{12} \sim \sqrt{w \cdot \kappa}$$

(6.16)

Thus, for example, by increasing the surface tension in the model by increasing $w$ or $\kappa$, the energy barrier for nucleation of a minority phase in a highly off-critical composition would increase.

In the Langevin Dynamics sub-model, the capillary forces on particles are directly proportional to the surface tension between the two liquids. Thus, the scaling factor $D$ in Eq. (6.15) represents the influence of surface tension on particles. Thus, by increasing the value of $D$ in our model, the particles experience stronger capillary forces due to increased surface tension. The way that particles induce jamming of liquid-liquid phase separation in the Cahn-Hilliard sub-model is by literally covering up or removing liquid-liquid interface. This is facilitated when liquids are expelled from regions occupied by particles which is induced by the $f_{lp}$ term of Eq. (6.5).

### 6.3.5 Length and Time Scales

There are two primary time scales for the computational model: one associated with the Brownian motion of the colloids which we denote $\tau_{part}$ and the other associated with the diffusion based transport of polymers species which we denote as $\tau_{pol}$. By assuming a size for colloidal particles, the Brownian motion time scale can be estimated using the Stokes-Einstein relation $\tau_{part} = \frac{6\pi \eta_m r_p^3}{k_b T}$, where $\eta_m$ is the viscosity of the suspension matrix, $r_p$ is the radius of the colloids, $k_b$ is Boltzmann’s constant, and $T$ is
the absolute temperature. An estimate for the time scale for phase separation kinetics can be calculated using $\tau_{pol} \approx (2r_p)^2/D_{pol}$, where $D_{pol}$ is the mutual diffusion coefficient of the liquids. For a system of PS/PMMA in a semidilute solution and dispersion of Silica nanoparticles, typical parameters such as absolute temperature $T \approx 300 \, K$, average polymer molecular weight $M_w \sim 10^2 \, kg \cdot mol^{-1}$, matrix viscosity $\eta_m \sim 10^{-2} \, Pa \cdot s$ [30–32], average polymer diffusion coefficient $D_{pol} \sim 10^{-7} \, cm^2 \cdot s^{-1}$ [31–33], and nanoparticle diameters of 200 $nm$, results in $\tau_{pol} \sim 10^{-3} \, s$ and $\tau_{part} \sim 10^{-2} \, s$. Using a time step $\Delta t = 0.1\tau_{pol}$ for a simulation consisting of $1.5 \times 10^6$ steps correlates to a simulation time on the order of 2 $min$ for the sample parameters given. Parameters for a polymer melt system can be substituted in the above equations to estimate simulation times for polymer melt experiments; however, it should be noted that for polymer melts the Stokes-Einstein relation can significantly overestimate the Brownian motion time scale [31, 32]. The length scales of the simulation are set by the assumed nanoparticle sizes. In our simulations, particle diameters are typically $6\delta - 10\delta$ grid nodes in length. The simulation domain is discretized into a cartesion grid with uniform node spacing denoted as $\delta$ and has a value of $\delta = 1.0$ for all the simulations. For an assumed particle diameter of 200 $nm$ used in the above example, $\delta$ corresponds to a length of about 20 – 30 $nm$. This results in simulation domain sizes of roughly $5 \, \mu m \times 5 \, \mu m \times 2 \, \mu m$ for the $x \times y \times z$ dimensions.

6.3.6 Simulation Setup and Numerical Solution Scheme

Each simulation evolves a system of immiscible liquids with a suspension of colloidal particles from an initial homogeneous state with some liquid/liquid composition ($\phi_1, \phi_2$) and particle loading ($\phi_p$). The start of each simulation corresponds to an instantaneous thermal quench below the binodal curve, and the system is then evolved for a specified number of simulation steps.

The coupled Cahn-Hilliard Langevin Dynamics model is implemented in the Meso simulation code [34] developed in our group. The code is parallelized to run on modern supercomputer clusters to allow large simulations to be run in practical amounts of time. The Cahn-Hilliard sub-model is numerically integrated using a semi-implicit spectral
method [35] that utilizes the FFTw implementation of the Fourier transform [36]. The Langevin Dynamics sub-model uses a standard velocity-Verlet algorithm to numerically integrate the equations of motion. Boundary conditions for both the Cahn-Hilliard and Langevin Dynamics sub-models are periodic in the thin-film’s lateral dimensions (x- and y-directions). At the z-boundaries (top and bottom of the film), a no-flux boundary is implemented by imposing single layers of solid material with $\psi = 1.0$.

Figure 6.2: Top down and side-view snapshots showing time evolution of the multi-phase morphology. From left to right, corresponding time stamps in terms of number of simulation steps taken are: 0 (initial condition), 380,000, 750,000, and 1,500,000 steps. Liquid domains are rendered as red (majority phase) and blue (minority phase) semitransparent volumes and interfaces rendered white. Colloidal particles are rendered as white spheres. The simulated thin film has a 65/35 fluid composition, a mesh size of $256 \times 256 \times 96$ in the xyz-dimensions, $C = k_z = 0.8$, particle volume fraction of 5.0% and particle diameter of $d_p = 8.0\delta$ where $\delta$ is the grid spacing.

For all simulations, particle positions are initialized randomly throughout the domain or, in cases with larger particle loading, on a cubic lattice with random displacements. This is followed by an equilibration run where the only active forces are the soft steric repulsions between particles and stochastic Brownian forces. This allows particles to settle into an initial state which is physically realistic. Following particle equilibration, the liquid domains are initialized about a chosen composition with small amounts of random noise. From this initial state, the simulation is launched. Since $\tau_{part}/\tau_{pol} \sim 10^1$, particle positions are updated after every 5 Cahn-Hilliard updates. Also, the applied external electric field is a constant, uniform DC field in the z-direction throughout the simulation domain for the duration of the entire simulation.
For each unique set of simulation parameters, three separate simulation runs were made to allow for the collection of statistics. For a list of all simulation parameters, see the supplementary information †. Several analysis tools were implemented to characterize the structures. Particle attachment at liquid-liquid interfaces was determined by looping over regions of the grid that particles occupy and searching for the existence of triple junctions between the liquids and particle (i.e. where $\phi_1, \phi_2 > 0.5$ and $\psi > 0.1$). The Hoshen-Kopelman algorithm [37] is used to calculate the number of liquid domains and their average size.

6.4 Simulation Results

We performed several parametric studies by independently varying the particle polarizability parameter $C$ (see Eq. 6.10), the liquid-liquid dielectric contrast parameter $k_z$ (see Eqs. 6.1), the particle loading, and the liquid-liquid composition. Note that $k_z$ and the dipole force $F_d^j$ have the same dependence on the electric-field strength $E_0$, which means that varying the electric-field strength changes $k_z$ and $F_d^j$ in the same way. Consequently, by varying $k_z$ and $C$ in the model, we are effectively varying the dielectric contrast between liquid phases, $(\epsilon_1 - \epsilon_2)/((\epsilon_1 + \epsilon_2))$, and the dielectric contrast between particles and liquid matrix, $(\epsilon_p - \epsilon_m)/((\epsilon_p + 2\epsilon_m))^2$.

![Image](image_url)

**Figure 6.3:** Stabilized morphologies with through-thickness channels and varying degrees of particle loading. From left to right, the systems have $\phi_p$ values of 2.1%, 6.5%, 9.7%, and 15.0%. Each system has a 65/35 composition, a mesh size of $256 \times 256 \times 96$ in the xyz-dimensions, $C = k_z = 0.8$, and particle diameter $d_p = 8.0\delta$ where $\delta$ is the grid spacing.

Simulations with values for $k_z$ and $C$ in the ranges $k_z = [0, 1]$ and $C = [0, 1]$ with
Figure 6.4: Stabilized morphologies with through-thickness channels and varying composition. From left to right, the systems have 50/50, 60/40, 70/30, and 80/20 compositions, particle loading of $\phi_p = 5.0\%$, and a mesh size of $256 \times 256 \times 96$ in the xyz-dimensions, $C = k_z = 0.8$, and particle diameter $d_p = 8.0\delta$ where $\delta$ is the grid spacing.

Varying film dimensions and particle sizes were run. Figure 6.2 shows a sequence of renderings of the time evolution of a thin film with $C = k_z = 0.8$. The binary liquid mixture has a composition of 65/35 ($\phi_1/\phi_2$) and particle loading of $\phi_p = 5.0\%$. At the start of the simulation the system is very homogeneous and there are no interfaces. Also, particles are randomly and homogeneously distributed throughout the film. As time progresses, phase separation initiates and alignment of the phase domains in the electric-field direction occurs. The effect of the electric field transforms the three-dimensional bicontinuous morphology to that of a two-dimensional discrete morphology with through-thickness channels.

Particles also form chain-like structures due to their induced dipole-dipole interactions. Most of these chains become attached to the channel (phase) interfaces early on in the simulation. Throughout time, the channels coarsen due to Ostwald ripening. This corresponds to the shrinkage and disappearance of small channels, which feed the growth of larger channels. During this process, particle chains that exist on the interfaces can be swept along with the motion of the interface. Furthermore, the presence of particle chains on the channel interfaces can stabilize small channels and prevent them from dissolving. However, it seems that a certain number of particle chains is required to prevent the dissolution of a shrinking channel. Based on observation, this critical number of chains seems to be four, as evidenced by the disappearance of many channels with only three
full chains attached and the continual existence of channels with four or more attached chains (see supplemental movie 1†).

The number of chains required to stabilize a channel is a function of particle size. We saw evidence of this in simulations with smaller particle diameters \(d_p = 6\delta\) which required five particle chains to stabilize channels. In simulations with larger particles \(d_p = 10\delta\), we did not observe stabilized channels with three particle chains but suspect that this is due to the fact that \(d_p = 8\delta - 10\delta\) is not quite large enough to stabilize channels with only three particle chains. We predict that increasing the particle size further would eventually result in channels stabilized by only three particle chains. The mechanism for this particle size dependence is the capillary force’s variance with particle size. The size dependence of the capillary force defined in Eq. (6.15) comes from the fact that the magnitude of the vector difference \(r_{klm} - r_{cmj}\) increases with increasing particle diameter. We also expect channels stabilized by only three particle chains to be the lower limit of this effect; in other words, we believe it to be impossible to stabilize channels with only two particle chains.

Figure 6.3 shows views of several film morphologies with different degrees of particle loading. Each simulation was run for the same number of simulation steps (1.5 million steps). Particle loading ranges from 2.1%-15.0% particle volume fractions. The necessary time to reach a fully jammed state is a function of particle loading. Note that the system with the smallest particle loading \(\phi_p = 2.1\%\) has larger channels which are not fully loaded with particle chains. This system has not reached a fully jammed state. With increasing \(\phi_p\), a greater number of particle chains are attached to channel interfaces. The systems with the two highest particle loadings have fully jammed channel interfaces. Another interesting observation is the nature of the distribution of channel sizes. Morphologies that have not yet reached steady state have more unimodal distributions of channel sizes. Those that have reached a fully jammed state have more of a bimodal distribution of channel sizes. This seems to be due to the prevention of small-channel disappearance by the existence of four or more particle chains. Hence, the system exhibits a large number of small channels, and a few larger channels, with a distribution differing
from that occurring during traditional Ostwald ripening.

Figure 6.4 shows renderings of several morphologies with different liquid/liquid compositions. As was the case for varying particle loading, each simulation was run for the same number of simulation steps (1.5 million steps). Going left-to-right in Figure 6.4, systems have compositions of 50/50, 60/40, 70/30, and 80/20. For the 50/50 composition, the morphology is two-dimensional but remains largely bicontinuous in the lateral dimensions. For compositions of 60/40 and up, the morphology is discrete with through-thickness channels and particle chains on the channel interfaces.

In addition, we ran simulations with a composition of 90/10, which generally will not exhibit phase separation due to a large nucleation barrier. However, we found that particle chaining can actually induce heterogeneous nucleation of the minority phase, as shown in Figure 6.5. Two simulations are shown, both with 90/10 composition, with one in which particle chaining occurs (due to dipole-dipole interactions), and one where particle chaining does not occur. Phase nucleation is observed when vertical particle chains begin forming, as shown in Figure 6.5c, d (also, see supplemental movie 2 †). The aligned particle chains cause perturbations in the liquid concentration fields that favor nucleation events.

The above results illustrate the effect of varying levels of particle loading and fluid/fluid composition in electric-field aligned bijel films. These results all kept constant the influence of the electric field (constant values of $C = k_z = 0.8$). Varying the parameters associated with the electric field can significantly alter the film morphology. Figure 6.6 shows the four main morphologies that emerge when varying $k_z$ and $C$. These morphologies represent the extreme points in the two-dimensional parameter space. Figure 6.6a is the stabilized morphology that evolves for weak particle polarizability and weak dielectric contrast between liquids (i.e. $k_z = C = 0.001$). It has large bicontinuous domains with densely coated particle interfaces, and the particles do not form chains. Figure 6.6b is the case for weak particle polarizability and strong dielectric contrast between liquid phases (i.e. $k_z = 1.0, C = 0.001$). The morphology is discrete with through-thickness channels that are also densely covered with particles. Figure 6.6c is the case of strong particle po-
Figure 6.5: a)-b) Top-down views of two simulations, each with a 90/10 composition and \( \phi_p = 5.0\% \). a) shows a film with strong particle polarizability \( C = 0.5 \) with particle chains and nucleated channels. b) show a film with weak particle polarizability \( C = 0.05 \) with no particle chaining and no nucleation process. c) and d) are side views of the system shown in a) at early simulation times (50,000 steps and 60,000 steps) which illustrate three nucleation events occurring at particle chain sites.

polarizability and weak dielectric contrast between liquids (i.e. \( k_z = 0.001, C = 1.0 \)). The morphology is similar to that in Figure 6.6a with the exception that all particles form chains, several of which have influenced the formation of channel-like structures. Despite this, discrete through-thickness channels have not formed as in the morphology in Figure 6.6b. Finally, in Figure 6.6d we have the case of strong particle polarizability and strong dielectric contrast between liquids (i.e. \( k_z = C = 1.0 \)). The morphology is very similar to that in Figure 6.6b except that particles have formed chains, and consequently their arrangement on the interface is different. Notice there are more stabilized channels in this morphology compared to the one in Figure 6.6b.

6.5 Analysis and Discussion

From the morphologies shown in Figure 6.6, it seems that in order for channels to form, the dielectric contrast between liquid phases must be higher than some threshold value. This is true no matter the strength of particle polarizability (at least in the ranges we studied). This being the case, we studied varying strengths of particle polarizability
Figure 6.6: Four basic morphologies found at the $C$ and $k_z$ parameter space extremes. 

a) corresponds to $C = 0.001$, $k_z = 0.001$, b) to $C = 0.001$, $k_z = 1.0$, c) to $C = 1.0$, $k_z = 0.001$, and d) to $C = 1.0$, $k_z = 0.001$. The composition is 65/35 for all morphologies.

The minority phase is rendered as a semitransparent red volume and particles as solid white spheres. For clarity, only particles attached to the interfaces are rendered. Each system has a mesh size of $256 \times 256 \times 64$ in the $xyz$-dimensions, as well as a $\phi_p = 12.7\%$ with particle diameter $d_p = 6.0\delta$ where $\delta$ is the grid spacing.

and its effect on channel formation and channel size for films with fixed particle loading $\phi_p = 12.7\%$ and liquid composition 65/35. We considered values of polarizability $C = 0.1, 0.3, 0.6, 0.9$ for two values of dielectric contrast between liquids, $k_z = 0.1, 0.9$. $k_z = 0.1$ corresponds to a slow rate of liquid domain alignment (which is still above the threshold), and $k_z = 0.9$ corresponds to a fast rate of liquid domain alignment. For $k_z = 0.9$, all domains align with the electric field within the first 5,000 simulation steps $\tau$ (simulation steps = simulation time$/dt$ where $dt$ is the time step). For $k_z = 0.1$, all domains reach full alignment by about 100,000 simulation steps. Before full alignment occurs, the morphology is a mixture of both through-thickness domains and unaligned domains. Eventually, however, with these parameters the morphologies all evolve into discrete through-thickness channels due to the electric field. We now investigate how the average channel diameter depends on the various material parameters specified in the model. Other membrane parameters, membrane renderings, and simulation animations for these systems are included in the supplementary information.

Figure 6.7 shows the time evolution of the average channel diameter (ACD) for varying
values of $k_z$ and $C$. This data was calculated using the Hoshen-Kopelman algorithm [37].

For slow liquid domain alignment ($k_z = 0.1$), varying the strength of particle polarizability does not have a statistically significant effect on the ACD (left plot in Figure 6.7). In contrast, for fast liquid domain alignment, it does (right plot in Figure 6.7). This is because fast liquid domain alignment creates many smaller-sized channels early on which can then be stabilized by particles. However, the very small channels will only stabilize if there are also strong dipolar particle interactions, causing the formation of dense particle chains, which enhance the stabilization of small channels.

Figure 6.7: Average channel diameter as a function of simulation steps $\tau$. Each curve corresponds to the average value of three simulations with identical parameters, but different random initializations. The shaded regions about each curve show the standard deviation of the runs. Each simulation had a 65/35 composition, particle loading of $\phi_p = 12.7\%$, and a mesh size of $128 \times 128 \times 64$ in the xyz-dimensions, and particle diameter of $d_p = 6.0\delta$.

Figure 6.8 shows the fraction of particles attached to liquid/liquid interfaces through time for the same conditions as Figure 6.7. These plots clearly indicate the dependence of particle attachment on the strength of particle polarizability $C$. As the particle polarizability strength increases so does the fraction of particles attached to interfaces for both slow and fast liquid domain alignment; however, the effect is more pronounced for fast liquid domain alignment. This is due to the coupled effect of small diameter channels forming early on and becoming stabilized by tightly packed particle chains. Stronger dipolar interactions between particles also make it harder for particles to be detached.
from channels shrinking due to Ostwald ripening because particles now experience a significant attractive force to one another. Particle chains also have a weak attraction to other chains that can allow them to form walls [21, 22]; however, in our simulations the capillary forces and Brownian forces overshadow this effect.

Figure 6.8: Fraction of particles attached to liquid-liquid interfaces as a function of simulation steps $\tau$. Each simulation had a 65/35 composition, particle loading of $\phi_p = 12.7\%$, and a mesh size of $128 \times 128 \times 64$ in the xyz-dimensions, and particle diameter of $d_p = 6.0\delta$.

We also investigated how the ACD varied with liquid/liquid composition. Figure 6.9 shows the time evolution of ACD for five films with varying compositions (left plot) and their final ACD values at the end of the simulations (right plot). Here, the electric-field parameters have values of $k_z = 0.8, C = 0.8$. The range of stabilized ACD values in Figure 6.9 has a size of about $10\delta$. This is about the same variation for the range of ACD values as that in Figure 6.7.

Varying the particle loading has a much stronger effect on the ACD than the liquid-liquid composition or electric properties of the system. Figure 6.10 (left plot) shows the time evolution of ACD for a variety of films with varying degrees of particle loading (including the structures shown in Fig. (6.3)). The final stabilized ACD values are shown in the right plot. The range of ACD values produced by varying the particle loading is much larger than that produced by varying either the liquid-liquid composition or the electric properties of the system, with a variation of about $30\delta$. Each of these three main parameters (particle loading, composition, and electric properties of the system), can be
considered as tuning knobs that have different strengths in their effect on channel sizes in these thin-film, particle-stabilized emulsions.

6.6 Experimental Application

Most bijels have been experimentally fabricated using low molecular weight polar and non-polar mixtures (oil and water based) [38]. A few studies have used higher molecular
weight liquids such as polymer melts or two non-polar oligomers [39–41]. Due to our simulations only capturing diffusion based liquid and particle transport, they best describe systems with higher viscosity liquid mixtures such as semidilute polymer solutions or polymer melts. In terms of electric fields, experiments have been done in which nanoparticles have been aligned in polymer solutions and melts [42–46]; however, to the best of the Authors’ knowledge, no experiments of polymer bijels in the presence of electric fields have been published. We hope these simulation results will inspire experimental investigation into bijel systems fabricated from partially to fully immiscible polymer solutions or melts with nanoparticle suspensions in the presence of AC electric fields. Model experimental systems would need to have two different polymer species having low and high dielectric contrast correlating to the low and high $k_z$ values of the simulations. Likewise, at least two different kinds of colloidal nanoparticles would need to be used, one with a dielectric constant similar to the average polymer species dielectric constant and one much higher. These would correlate to the low and high particle polarizabilities modeled in our simulations. Binary polymer systems and colloidal nanoparticles that fit these descriptions include PS/PMMA ($\epsilon_{PMMA} - \epsilon_{PS} \approx 1$), PS/Polybutadiene ($\epsilon_{PB} - \epsilon_{PS} \approx 0$), and Silica ($\epsilon_{Si} \approx 3.8$) [47] and Barium Titinate ($\epsilon_{BT} \approx 2000$) [46, 48] nanoparticles. These two polymer systems and two nanoparticle types could be combined to create four unique thin-film polymer bijel systems. We hypothesize that the four resulting morphologies would qualitatively match those of our simulations presented in Fig. 6.6. Additionally, the main reason we suggest using AC versus DC electric fields in experiments is that use of DC electric fields is known to result in drifting of particles to one-side of the film due to an electrophoretic force caused by inhomogeneity in the DC field [42, 46]. This unwanted field gradient effect can be negated in experiments by using high frequency AC fields which approximate the same effect as the idealized DC fields assumed in our simulations. Other experiments also reported faster and more uniform particle alignment using AC vs DC electric fields [43, 45]. Furthermore, the nanoparticles would need to be surface treated to ensure they segregate to the polymer-polymer interfaces as has been done in previous experiments [39, 40, 49].
To ensure polymer domain alignment in experiments, the Clausius-Mossotti relation suggests the use of an AC field with high $E_{RMS}$ but still below strengths that result in dielectric breakdown of the polymers. Previous experiments on electric field alignment of polymers can be used as guides for making initial estimates on what field strengths fit this criteria such as these experimental works [16–18, 46, 50–53]. Lastly, we would also expect the simulations to correlate to films with thicknesses on the order of 20-100 particle diameters. For nanoparticles with diameters in the range of 10-500 nm which have been used in previous thin-film polymer nanocomposite experiments [39, 40, 46], estimates of film thicknesses would be in the range of 1-50 µm. Also worth noting is that simulations presented here do not account for surface wetting as was included in our previous simulations [14, 15]. This was done in order to isolate the effects of electric fields on the thin-film bijel morphology; consequently, we would expect experiments to see some effect from surface wetting on the thin-film morphology. In future research we expect to explore the combined effects of surface wetting and AC and DC electric fields using our computational bijel model.

6.7 Summary

To summarize, we have presented a simulation study of the effects of applied external electric fields on bijel morphology in thin films. The model captures the coupled effects of electric field alignment of liquid domains and dipole-dipole interactions of suspended particles that lead to chain formation. The rate of liquid domain alignment is controlled by the strength of the dielectric contrast between the two liquid phases. For slow rates of alignment, the morphology starts out bicontinuous and is transformed into a discrete morphology with through-thickness channels during the early stages of phase separation. During these early stages, phase separation is mediated by coalescence. It then changes to Ostwald ripening once the morphology is completely composed of discrete channels. For fast rates of alignment, the morphology is discrete with many small-diameter channels forming very early in the simulations. At these very early times, while channels are very small, phase separation proceeds via a mixture of channel coalescence and Ostwald ripening.
Despite the alignment of particles into chains by the electric field, it was found that unless a sufficient dielectric discrepancy between the liquid phases exists, through-thickness channels will not form. When channels do form, the strength of particle dipolar interactions has a strong effect on the organization of particles on the channel interfaces. With weak dipolar interaction, particles do not form chains and organize into two-dimensional close-packed monolayers on the interfaces. With strong dipolar particle interactions, particles form dense chains that promote channel jamming at smaller channel diameters due to the attractive dipolar forces between particles. Once a threshold value of particle chains are attached to a channel’s interface, the channel will persist indefinitely. Furthermore, it was also found that particle chains act as nucleation sites for phase-separation.

Varying the dielectric contrast between liquids and the particle polarizability influences the average channel diameter to a similar degree as varying the liquid-liquid composition. The impact of varying particle loading on average channel diameter, however, is much stronger. This illustrates the coarse-to-fine tuning of channel sizes that can be accomplished using these parameters. The potential to tune these thin-film systems, their bottom-up assembly process, and their amenability to large-scale processing techniques (such as roll-to-roll processing) make them attractive candidates for creating new functional membranes.

6.8 Acknowledgments

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6.9 Supplementary Material

6.9.1 Simulation Parameters

There were four different parametric studies corresponding to the simulation results reported on. The first parametric study corresponds to the extreme values in the $C$ and $k_z$ parameter space resulting in four unique membrane morphologies. The second, cor-
Table 6.1: Cahn-Hilliard Langevin Dynamics simulation studies and corresponding simulation parameters.

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<td>$\nu$</td>
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<td>$D$</td>
<td>capillary force strength</td>
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<td>0.6, 1.8</td>
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<tr>
<td>$\sigma$</td>
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<tr>
<td>$n$</td>
<td>repulsive force exponent</td>
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<tr>
<td>$E_0$</td>
<td>electric field strength</td>
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<td>$k_z$</td>
<td>liquid E-field alignment rate</td>
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<td>0.8</td>
<td>0.1-0.9</td>
</tr>
<tr>
<td>$C$</td>
<td>particle polarizability</td>
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<td>0.8</td>
<td>0.1-0.9</td>
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<td>$n_{x,y}$</td>
<td>grid nodes in xy-directions</td>
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<td>$n_z$</td>
<td>grid nodes in z-direction</td>
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<td>thermal noise strength</td>
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<td>$\phi_1/\phi_2$</td>
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<td>0.5-0.9</td>
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<tr>
<td>$\phi_p$</td>
<td>particle volume percent (%)</td>
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<td>2.1-15.0</td>
<td>5.0</td>
<td>12.7</td>
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responds to varying the particle loading. The third varied the liquid-liquid composition. Finally, the fourth, was a more thorough study of the $C, k_z$ parameter space sampling an array of values with $C, k_z = 0.1, 0.3, 0.6, 0.9$. Table 6.1 lists all the simulation parameters and their numerical values for each of the parametric studies. The studies listed above are referred to in the table as studies 1-4 with the study number corresponding to the order in which they are described above.

Figure 6.11 shows the final simulation step of sample morphologies from the more thorough parameter study of the $k_z$, $C$ parameter space. The parameters used for these simulations are given in table 6.1 in the study 4 column. The renderings only show a top-down view of the films and are for the smaller particle size. From left-to-right the particle polarizability, $C$, increases from a value of 0.1 to 0.9. From top-to-bottom the dielectric contrast between liquids, $k_z$, increases from a value of 0.1 to 0.9. For these systems with smaller particles, the threshold number of particle chains to fully stabilize a channel is five chains. For membranes with weak particle polarizability that do not form
Figure 6.11: Top-down views of stabilized morphologies with through membrane channels and varying particle polarizability, $C$, and dielectric contrast between liquids, $k_z$. Each column corresponds to $C$ values of 0.1, 0.3, 0.6, and 0.9. Each row corresponds to $k_z$ values of 0.1, 0.3, 0.6, and 0.9. All systems have particle loading of $\phi_p = 12.7\%$, and a mesh size of $128 \times 128 \times 64$ in the $xyz$-dimensions, and particle diameter $d_p = 6.0\delta$ where $\delta$ is the grid spacing.

Particle chains, the particles are significantly more spread out on the channel interfaces and consequently only much larger channels get stabilized.

6.9.2 Simulation Movies

We have included two animation movies taken from the pool of simulations performed. These animations are referred to in the body of the article. Supplemental movie 1 is taken
from study 2 with a particle volume fraction of 15% (it corresponds to the rightmost image shown in Fig. 2 of the main body of the article).

Supplemental movie 2 has parameter values of $C = 0.5$, $k_z = 0.5$, particle loading $\phi_p = 5.0\%$, and liquid composition 90/10. This animation shows the nucleation of minority phase domains at the onset of the formation of vertical particle chains.

Bibliography


[11] JA Witt, DR Mumm, and A Mohraz. Microstructural tunability of co-continuous bijel-derived electrodes to provide high energy and power densities. *Journal of Ma-


[52] Ganesh Venugopal and Sonja Krause. Development of phase morphologies of

Chapter 7
Conclusion

7.1 Conclusions

This dissertation contains three published articles which explore the thin-film Bijel morphologies and their kinetic pathways. Bijels are a versatile soft material that have great promise to deliver hierarchically porous membranes functionalized by nanoparticles which self-assemble in partially miscible binary polymer mixtures. The significance of the research in these articles is grounded in the belief that computational modeling of materials can be used to discover new material structures never before realized in the laboratory in the same spirit of the discovery of the Bijel itself. Its importance is also supported by the need for a better understanding of bottom-up self-assembly process that are scalable and have potential to functionalize bulk materials with the unique properties of nanostructures. The articles included are:


The research presented in this dissertation validates a unique computational model suitable for modeling Bijels in confined thin-film geometries. It utilizes this model to develop an understanding of the effects of surface-directed spinodal decomposition, binary mixture composition, film thickness, particle loading, and the effects of electric fields on the resulting Bijel morphologies and dynamics. Its conclusions are listed below:

1. The Cahn-Hilliard model for polymer phase separation confined to thin-films can accurately capture surface-directed spinodal decomposition effects. Further, when this Cahn-Hilliard model is coupled with a Brownian dynamics model, it is capable
of qualitatively reproducing the experimental creation of thin-film polymer Bijels and their morphology dependence on film thickness and particle loading.

2. For polymer phase separation in thin-films without particles, the surface directed spinodal decomposition effects only dominate the internal thin-film morphology up to a certain threshold thickness. Simulations of thin-film polymer Bijels demonstrate that this threshold thickness is increased when the phase separation kinetics is modified by the addition of colloidal particles. The mechanism for this increased threshold is the jamming effect of particles.

3. The thin-film Bijel morphology space supports a diverse spectrum of both 2D and 3D morphologies, several of which are highly non-intuitive. These morphologies are accessed by varying the liquid-liquid composition, particle loading, and film thickness. Additionally, the kinetic pathways that lead to these morphologies are well understood through analysis of particle attachment and interfacial curvature analysis.

4. A two-dimensional bicontinuous thin-film morphology was discovered which may have interesting new technological applications. The morphology supports an internal, fully-percolated network of pore structures, which could be functionalized by the jamming nanoparticles. It could be used to facilitate high throughput, inter-membrane transport for a variety of stimuli-responsive fluids. It could also potentially be used as a MEMs scale heat exchanger or heat dissipation membrane.

5. A coupled Cahn-Hilliard and Langevin particle dynamics model is capable of simultaneously capturing the coupled effects of electric field alignment of liquid domains and the formation of particle chains caused by electric field induced dipol-dipole interactions. These coupled effects are determined by the electric properties of the liquids and particles, namely their dielectric constants $\epsilon_{\text{liq}1}$, $\epsilon_{\text{liq}2}$, and $\epsilon_{\text{part}}$.

6. Applied electric fields above a certain threshold value have the ability to transform the Bijel thin-film morphology to promote the formation of cylindrical through film
channels decorated by nanoparticles. Furthermore, the dominant liquid coarsening mechanism changes from coalescence to Ostwald ripening when this morphology transformation takes place and is dependent on the rate of liquid domain alignment which is controlled by the dielectric contrast between liquids and electric field strength.

7. For the case when electric fields transform the morphology to support through membrane channels, the strength of particle dipole-dipole interactions has a strong influence on the arrangement of particles on the interface by forming particle chains. These parameters as well as liquid composition and particle loading allow precise tuning of the channel number density, average channel size, and channel size distribution.

7.2 Future Work

The mesoscale computational modeling of thin-film Bijels done in this dissertation has laid a foundation for many new and exciting research studies into soft-materials. Due to the flexibility of the coupled Phase-field particle dynamics model, many new ideas can be easily explored by extending the model to include any new relevant physics for variations in thin-film Bijel like systems. Additionally, the simulation code that the Author has been assisting to develop is open source (see the bibliography for Chapter 6 for links to the code repositories) and is becoming more user-friendly through successive software development cycles. The Author hopes that it will eventually become a tool that assists many researchers study and explore soft-material systems. Some ideas from the Author for future research are listed below:

1. There are still large amounts of parameter space to be explored in thin-film Bijels. One idea that the Author has always been interested in but not had the time to develop is considering the case of two types of colloidal particles and varying their wetting properties as well as their electric properties. This is a fantastically large parameter space with lots of potential for creating metastable thin-film morphologies never discovered in the lab. It is known that the wetting of particles characterized
by their liquid-liquid-particle contact angle can induce preferred curvatures in the bijel interface. Also, if one particle has weak electric polarizability and the other has strong electric polarizability, many new kinds of interactions and directed self-assembly routes are available when an electric field is employed. Also the electric field can be turned on and off at any point during the formation process as well as change directions. This opens up many opportunities to further direct and change the kinds of interactions happening. A mastery of this large parameter space has the potential to provide almost unlimited control and engineering design freedom for soft material based thin-films modified by colloidal particle suspensions.

2. There are specific scientific questions related to my dissertation research that have yet to be answered. With regards to electric field alignment, the surface wetting that was modeled in Chapter’s 4 and 5 was not included in the model for Chapter 6. How will the electric field alignment of liquid domains be altered by the presence of this wetting? Can the wetting layers induced by the surface wetting significantly alter the electric field modified morphologies? If so, how will it effect the kinetic pathways to these modified morphologies? Also, what happens to liquid phase separation via spinodal decomposition in the presence of pre-aligned particles? The results from Chapter 6 demonstrated that liquid domain alignment was a prerequisite for through channel membrane formation; however, could pre-aligned particle chains that are present from the start of the phase separation induce channel formation or other aligned morphology features? These are just a few of the unanswered questions that could be readily addressed using our already developed model.