Theory of Binary Mixtures of Diblock Copolymers: A New Route to the Bicontinuous Double-Diamond & Plumber's Nightmare Phases

THEORY OF BINARY MIXTURES OF DIBLOCK COPOLYMERS: A NEW ROUTE TO THE BICONTINUOUS DOUBLE-DIAMOND & PLUMBER'S NIGHTMARE PHASES

BY

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A THESIS

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Abstract

We study the formation of novel bicontinuous phases in binary mixtures of AB diblock copolymers (DBCP) using the polymeric self-consistent field theory. We predict that the bicontinuous double-diamond (DD) and plumber's nightmare (P) phases, which are metastable phases of neat diblock copolymers, could be stablized in gyroid-forming A-minority DBCPs via the blending of specifically designed A-majority DBCPs. The mechanisms of stabilizing different bicontinuous phases are revealed by analyzing the spatial distribution of the different DBCPs. It is found that the A-majority DBCPs residing mainly in the nodes of the structure, thus alleviating the packing frustration of the A-blocks. Furthermore, a local segregation of the two DBCPs occurs at the AB interface, thus regulating the local curvature of the interfaces. A synergetic interplay of these two mechanisms results in a larger stable region of the DD and P phases via the addition of tailored A-majority DBCPs. The theoretical study provides an efficient route to obtain novel bicontinuous phases.

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Notation and abbreviations

We present below the definitions of all notation and abbreviations used in the main body of the thesis.

DBCP	diblock copolymer
DIS	disordered
L	lamellar
Н	hexagonally-packed cylindrical
S	body-centered-packed spherical
G	double gyroid
DD	double diamond
Р	plumber's nightmare
CMC	constant mean curvature
SCFT	self-consistent field theory
HL	homopolymer-like
$N^{(i)}$	number of statistical segments constituting polymer
	species i
b_{eta}	Kuhn length of monomer type β
$ ho_{0,eta}$	inverse statistical segment volume of monomer type β
$\phi_eta(oldsymbol{r})$	microscopic segment density of monomer type β
$\delta(\cdot)$	Dirac delta function
n_i	number of polymer chains belonging to species i
$N_{ m A}^{(i)}$	number of A-statistical segment constituting polymer
	species i
S	segment number
z_i	polymer activity of polymer species i
$\mathcal{Z}(V)$	partition function in the grand canonical ensemble
V	volume

$Z(n_1, n_2)$	quantity that is proportional to the partition function
	in the canonical ensemble
$oldsymbol{r}^{(i)}(s)$	space curve describing the configuration of a polymer
	chain of species i
$\chi_{ m AB}$	Flory-Huggins parameter
k_b	Boltzmann constant
T	temperature
$P[oldsymbol{r}^i(s)]$	statistical weight of a polymer chain of species β with a
	configuration described by $\boldsymbol{r}^{(i)}(s)$
$\Xi(oldsymbol{r})$	pressure field
$\omega_eta(oldsymbol{r})$	chemical conjugate field associated with monomer type β
g	Gibbs free energy density
Q_i	single-chain partition function
$q_i(oldsymbol{r}, N^{(i)})$	forward chain propagator of polymer species i
$q_i^{\dagger}(oldsymbol{r}, N^{(i)})$	backward chain propagator of polymer species i
$ar{\phi}$	average volume fraction
$\lambda_{ m SM}$	parameter controlling descent speed for simple mixing
M	number of numerically calculated free energy densities
d_{\max}	deviation of free energy density
L	unit cell edge or period
λ_L	parameter controlling the relative accuracy of the
	determined optimal period
α	polymer chain length ratio, $N^{(2)}/N^{(1)}$
$f_{ m A}$	fraction of A-statistical segments, $N_{\rm A}/N$
$ar{d}$	normalized distance, z/L_z
H	mean curvature
R_g	radius of gyration
$\langle H \rangle$	area-averaged mean curvature
σ	area-averaged deviation from constant mean curvature

Below, the notation and abbreviations used in the appendices of the thesis is defined.

Φ assumed $f_{\rm A}$	
q wave vector, $2\pi/L$	
$oldsymbol{r}$ (x,y,z)	
g_{110}, g_{111} symmetry functions	
Δx interval spacing for numerical integration	
$d_{eta}(m{r})$ deviation function associated with monomer type	β
Λ paramter governing the relative contribution of in	put fields
A coefficients vector for Anderson mixing	
\mathbb{U} deviation matrix	
D deviation vector	

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Chapter 1

Introduction

Polymers are chain-like macromolecules composed of many repeating units called monomers connected together via covalent bonds. When only one type of monomer is used, the resulting polymer is termed a homopolymer. A block copolymer is obtained by joining two or more chemically distinct homopolymers together via covalent bonds. The most distinguishing feature of block copolymers is their ability to selfassemble into a plethora of nanoscopically ordered structures due to the competition between molecular connectivity and inter-monomer interactions. The repulsive interaction drives differents blocks to separate, but the connectivity at the molecular level prevents macroscopic phase separation, leading to the formation of polymeric domains [1, 2]. These nanoscopic domains further arrange to form ordered phases. The simplest type of block copolymer is the linear AB-diblock copolymers (DBCP), which is formed from two chemically distinct homopolymers, A and B, connected at their ends. The self-assembly of DBCPs has received a significant amount of academic [3, 4] and industrial interest [5, 6, 7, 8, 9] because the structure can be systemically varied by tuning the relative lengths of the two chemically different blocks [10].

The types of ordered equilibrium structures accessible to block copolymers is plentiful. For monodisperse DBCP melts, where the length of every polymer chain is identical, a large number of ordered phases have been identified. The group of morphologies include some simple structures which are termed the classical phases. The three classical phases are the striped lamellar (L), the hexagonally packed cylindrical (H), and the body-centered packed spherical (S) phase (c.f. Fig. 1.1). Another class of ordered structures of DBCPs that have attracted great theoretical [11, 12, 13, 14, 15, 14, 16, and experimental [17, 18] attention is the cubic bicontinuous phases, which includes the double-gyroid (G), the double-diamond (DD), and the so-called "plumber's nightmare" (P) (c.f. Fig. 1.2). These bicontinuous phases could be described as two intertwining networks composed of the minority monomers interwoven in a matrix of the majority block. The bicontinuous structures has been attracting tremendous attention not only due to their fascinating morphologies, but also because of their potential industrial applications. Potential applications of the ordered bicontinuous phases of block copolymers include the production of high-conductivity mediums [19], nano-porous materials [20], materials with low refractive index [21],



Figure 1.1: Schematics of the (a) lamellar (L) phase, (b) hexagonally-packed cylinderical (H) phase, and (c) body-centered packed spherical (S) phase.



Figure 1.2: Schematics of the (a) double-gyroid (G) phase, (b) double-diamond (DD) phase, and (c) plumber's nightmare (P) phase.

ceramic membranes [22, 23], hybrid solar cells [24, 25], and 3D photonic crystals [26].

Generically, the bicontinuous phases could be regarded as structures composed of two components: struts (tubes) and nodes (junctions) that are connected to form two continuous networks [27]. The tendency to form a structure with constant mean curvature (CMC) in order to minimize the interfacial surface energy will lead to structures dominated by the struts [27]. At the same time, the nodes will be bulkier than the struts. In other words, there will be points located in the nodes, such as at the centers, that are farther away from the interface than any points within the struts. Thus, in order to fill the volume occupied by the nodes, chains will have to stretch excessively from the AB interface [11, 12], leading to an increase of the chain free energy due to packing frustration. Moreover, the degree of packing frustration will grow with the disparity in bulkiness between the nodes and the struts. This difference will also increase with the number of tubes per junction. It has been proposed that the correlation between the packing frustration and the strut-to-node ratio provides an understanding on why there is only one stable cubic bicontinuous phase in monodisperse melts, namely the G morphology [27]. The G phase experiences the lowest amount of packing frustration, because it has only 3 connectors per node, whereas the DD, and P phases have 4 and 6, respectively.

The packing frustration of the bicontinuous phases could be relaxed by introducing additives into the melt. For example, it has been shown that the addition of minority-selective solvent particles to the DBCP melt could lead to a larger stability region of the G phase [17, 11]. Furthermore, it has been demonstrated that the addition of homopolymers to the DBCP melt could stabilize bicontinuous morphologies other than the G phase. In particular, Matsen and Bates predicted the formation of the DD phase in blends of G-forming DBCPs and shorter A-homopolymers [27]. Subsequently, Martínez-Veracoechea et al. extensively examined the formation of various bicontinuous phases in homopolymer-DBCP mixtures [11, 12, 13, 14, 15, 14, 16]. In Ref. [12], direct evidence of packing frustration was detected in G-forming systems through dissipative particle dynamics and Monte Carlo simulations. Martínez-Veracoechea, and coworkers furthermore predicted the stabilization of the DD and P phases via the addition of homopolymers using Monte Carlo simulations [13], molecular dynamics simulations [14], and self-consistent field theory (SCFT) [14, 15]. More recently, the spatial arrangement of individual polymer chains within the bicontinuous phases was examined using thermal integration techniques [16], yielding information on the relative size of the struts and nodes. They found that as the nodes become larger from $G \rightarrow DD \rightarrow P$, the struts shrink in both length and width. Despite the considerable progress made by Martínez-Veracoechea and coworkers, their efforts focused on the effects of homopolymer additives. It is an open question whether the stabilization of the DD, and P phases could be achieved in binary blends of DBCPs in which the additive is another DBCP.

A significant number of studies, both experimentally [28, 29, 30, 31, 32]. In Ref. [30] and theoretically [33, 34, 35, 36, 37], have been carried out on the phase behavior of binary mixtures of DBCPs. Binary systems often exhibit much richer behavior than their single-component counterparts. Shi and Noolandi [33], as well as Matsen and Bates [34], investigated the effects of blending and chemical composition on the phase behaviour of binary blends composed of two AB DBCPs with equal lengths. They concluded that when the chemical compositions are similar, the self-assembled morphology closely matches with the equilibrium structure found in DBCP melts having the same average A-monomer concentration. However, this one-component approximation breaks down when the dissimilarity between the two DBCPs is too large. For example, asymmetric H-forming DBCPs mixed with symmetric L-forming DBCPs could form a spherical morphology [35]. These theoretical works are complimented by extensive experiments conducted by Hashimoto and coworkers, examining the effects of molecular weight ratio, temperature, chemical, and volume composition in bidisperse melts of polystryene-block-polyisoprene [28, 29, 30, 31, 32]. In Ref. [30], a stable cylindrical phase was observed in a mixture of two nearly symmetric, L-forming, DBCPs. By blending an asymmetric species with a longer symmetric one, Hashimoto

and colleagues also discovered a stable L phase [28] at average A-monomer concentrations where other ordered structures would instead exist in monodisperse melts. These experiments, together with corresponding theoretical predictions [35, 36], suggested that the equilibrium morphology in blends can be strikingly different from the underlying phases formed individually by its two constituents. This conclusion from previous studies could be exploited to design binary mixtures with the purpose of realizing structures which are inaccessible in single-component melts. Taking advantage of the inter- and intra-domain segregation between the two DBCPs, Liu et al. showed the blending of two AB DBCPs with different chain length and composition could lead to the formation of the Frank-Kasper phases [37]. Often encountered in metallurgy, the Frank-Kasper phases are complex spherical-like structures possessing multiple types of micelles of different sizes in a single unit cell. It follows from these previous works that the vast parameter space of binary DBCP mixtures presents opportunities to procure exotic morphologies unavailable in monodisperse systems. One unexplored possibility is tailoring binary blends of DBCPs with the goal of stabilizing novel bicontinuous structures.

In this thesis, we investigate the formation of novel bicontinuous phases in binary mixtures of DBCPs. Specifically, we examine the effects of relative chain lengths, segregation strength, chemical, and blending composition on the phase behavior of AB/AB DBCP blends using SCFT. In particular, the stabilization of the DD and P phases is achieved in mixtures consisting of G-forming A-minority DBCPs and tailored A-majority DBCPs. We find that the relative stability of the bicontinuous morphologies is improved compared to the case of a homopolymer additive. We subsequently examine mechanisms leading to the occurrence and enhanced stability of these novel phases.

The thesis is organized as follows. Section 2 introduces the theoretical framework of SCFT in the context of binary blends of DBCPs. Section 3 details the numerical procedures used in the current work. The results of the study is presented in Section 4. Section 5 discusses the predicted phase behavior, and concluding remarks are presented in Section 6.

Chapter 2

Theory

Various theoretical approaches have been developed to study the phase behavior of block copolymers. These theoreties could be broadly divided into two, particlebased and field-based, approaches. Within the particle-based approach, the degrees of freedom of the system are the positions and momenta of the individual particles or molecules. The equilibrium behavior of the system is obtained by integrating over the positions and momenta, or trajectories, of the particles. Due to the intermolecular interactions, the required calculations over the particle trajectories cannot be carried out analytically in general. Instead, numerical methods are commonly employed for this task, including molecular dynamics and Monte Carlo simulations. An alternative is the field-based approach, in which the degrees of freedom of the system are the various fluctuating fields such as the densities of the different molecules. For the case of polymeric systems, a successful field-based approach is the self-consistent field theory (SCFT). SCFT replaces the description of the polymer melt using the entire ensemble of particles with a small number of scalar fields. Since its conception by Edwards [38], the SCFT has been further developed by many authors [39, 40, 41, 42, 43]. It has successfully been used to study the equilibrium behavior for a wide range of polymeric systems [10, 44, 45, 46]. In principle the field-based approach is equivalent to the particle-based approach. When fluctuations of the fields are included, the SCFT is an exact theory. However, carrying out the integration over the fields is a formidable task. Instead a mean-field approximation to the exact SCFT is often made. Within the mean-field theory, density fluctuations are ignored, which could become important near the order-disorder transition [1, 47]. On the other hand, it has been shown by numerous authors that the mean-field SCFT provides accurate descriptions of the phase behaviour of polymeric systems. In the current work, we will apply the SCFT to binary mixtures of DBCPs to examine the relative stability of various bicontinuous phases. We present below a derivation of the SCFT in the specific context of binary DBCP blends.

The essential idea of SCFT is to describe a melt of polymer chains as a collection of connected statistic segments interacting with a set of conjugate fields. In turn, the conjugate fields represent the monomer-monomer interactions. Usually the melt is assumed to be incompressible. Each statistical segment of length b, often referred to as the Kuhn length, corresponds to a number of monomers. This number is chosen such that on the the scale of a Kuhn length, the chain could be described as a Gaussian chain obeying random-walk statistics. The number of statistical segments for polymer species, i, is denoted $N^{(i)}$. Following the coarse-graining of the monomers, the intermolecular interactions, which are assumed to be short-range on the scale of b, is decoupled by introducing auxiliary fields. At the end of the particle-to-field transformation, SCFT effectively reduces the many-body problem to a problem of a single chain interacting with the mean fields. In the canonical ensemble, phase coexistences are determined via the commontangent construction [48]. However, obtaining tangents requires the relevant Helmholtz free energies to be calculated to a relatively high degree of numerical accuracy. Therefore, we will instead work in the grand canonical ensemble, where identifying coexistence regions can be accomplished through a simple comparison of the Gibbs free energies. To describe a binary DBCP mixture within the framework of SCFT, we first define the microscopic segment density,

$$\hat{\phi}_{\mathrm{A}}(\boldsymbol{r}) = \rho_{0}^{-1} \sum_{i=1}^{2} \sum_{j=1}^{n_{i}} \int_{0}^{N_{\mathrm{A}}^{(i)}} \mathrm{d}s \,\delta(\boldsymbol{r}_{j}^{(i)}(s) - \boldsymbol{r}), \quad \hat{\phi}_{\mathrm{B}}(\boldsymbol{r}) = \rho_{0}^{-1} \sum_{i=1}^{2} \sum_{j=1}^{n_{i}} \int_{N_{\mathrm{A}}^{(i)}}^{N^{(i)}} \mathrm{d}s \,\delta(\boldsymbol{r}_{j}^{(i)}(s) - \boldsymbol{r})$$

$$(2.1)$$

Here, $\delta(\cdot)$ is the Dirac delta function, n_i and $N_A^{(i)}$ is the number of polymers, and of statistics segments, respectively, for the A-block of species *i* for i = 1, 2. The spatial position of segment *s* belonging to the *j*th chain of species *i* is denoted $\mathbf{r}_j^{(i)}(s)$. For simplicity, we assume that the Kuhn length and the inverse volume of the statistic segments, ρ_0 , for the two types of blocks are the same, i.e. $b_A = b_B = b$, and $\rho_{0,A} = \rho_{0,B} = \rho_0$. It is also important to note that the total concentration of either polymer species is not a parameter controlled directly in the grand canonical ensemble, but adjusted through their associated polymer activity, z_i [1]. Furthermore, the two activities are not independent due to the incompressibility condition. We are free to set z_1 to a reference value, and vary solely z_2 to tune the blending composition [34]. The partition function of DBCP blends in the grand canonical ensemble can be written as [1]

$$\mathcal{Z}(V) = \sum_{n_1, n_2=0}^{\infty} \frac{z_1^{n_1} z_2^{n_2}}{n_1! n_2!} Z(n_1, n_2, V)$$
(2.2)

where V is the volume of the system and $Z(n_1, n_2, V)$ is proportional to the canonical

ensemble for a melt of n_i chains of species i,

$$Z(n_{1}, n_{2}, V) = \prod_{j_{1}=1}^{n_{1}} \int \mathcal{D}\boldsymbol{r}_{j_{1}}^{(1)}(s) P[\boldsymbol{r}_{j_{1}}^{(1)}(s)] \prod_{j_{2}=1}^{n_{2}} \int \mathcal{D}\boldsymbol{r}_{j_{2}}^{(2)}(s) P[\boldsymbol{r}_{j_{2}}^{(2)}(s)] \times \exp\left[-\rho_{0} \int_{V} \mathrm{d}\boldsymbol{r} \,\chi_{\mathrm{AB}} \hat{\phi}_{\mathrm{A}}(\boldsymbol{r}) \hat{\phi}_{\mathrm{B}}(\boldsymbol{r})\right] \times \delta(1 - \hat{\phi}_{\mathrm{A}}(\boldsymbol{r}) - \hat{\phi}_{\mathrm{B}}(\boldsymbol{r})).$$
(2.3)

Here, \mathcal{D} denotes functional integration, χ_{AB} is the Flory-Huggins parameter expressed in units of thermal energy, k_bT , k_b is the Boltzmann constant, and T is the temperature. The Flory-Huggins parameter quantifies the strength of the repulsive ($\chi_{AB} > 0$) monomer-monomer interaction. Empirically, it is common to express the χ_{AB} parameter as

$$\chi_{\rm AB} = \frac{C}{T} + D, \qquad (2.4)$$

where C and D are fitting coefficients [49, 50]. In Eq. (2.4), the temperaturedependent term is often called the 'enthalpic part' of χ_{AB} , while D is referred to as the 'entropic part' [50]. The statistical weight of a polymer chain of species i with a configuration described by $\mathbf{r}^{(i)}(s)$ is denoted $P[\mathbf{r}^{(i)}(s)]$. Its analytic form will depend on how the molecular details of the polymer chains is described. In the present work, we assume the polymers are completely flexible, and therefore $P[\mathbf{r}^{(i)}(s)]$ is given by a Gaussian distribution [1],

$$P[\mathbf{r}^{(i)}(s)] = \exp\left[-\frac{3}{2b^2} \int_0^{N^{(i)}} \mathrm{d}s \, \left|\frac{\mathrm{d}\mathbf{r}^{(i)}(s)}{\mathrm{d}s}\right|^2\right].$$
 (2.5)

Under this assumption, a polymer chain is represented by a continuum bead-spring model. The chains are penalized for deviating from ideal random-walk statistics, where the entropic cost of stretching a statistical segment of length Δs by Δr is $(3/2b^2) |\Delta r/\Delta s|^2$ (in units of $k_b T$) according to Eq. (2.5). Finally, the functional Dirac delta function, $\delta(1 - \hat{\phi}_{\rm A}(\boldsymbol{r}) - \hat{\phi}_{\rm B}(\boldsymbol{r}))$, ensures that only configurations that everywhere obey the incompressibility condition, $1 = \hat{\phi}_{\rm A}(\boldsymbol{r}) + \hat{\phi}_{\rm B}(\boldsymbol{r})$, is included in the partition function.

The next step is to make use of the following alternative integral of the functional Dirac delta function in order to introduce the conjugate and pressure fields,

$$\delta(1 - \hat{\phi}_{\mathrm{A}}(\boldsymbol{r}) - \hat{\phi}_{\mathrm{B}}(\boldsymbol{r})) = \int \mathcal{D}\Xi(\boldsymbol{r}) \exp\left\{-\rho_0 \int_V \mathrm{d}\boldsymbol{r} \,\Xi(\boldsymbol{r})[1 - \hat{\phi}_{\mathrm{A}}(\boldsymbol{r}) - \hat{\phi}_{\mathrm{B}}(\boldsymbol{r})]\right\}, \quad (2.6)$$

$$\delta(\hat{\phi}_{\beta}(\boldsymbol{r}) - \phi_{\beta}(\boldsymbol{r})) = \int \mathcal{D}\omega_{\beta}(\boldsymbol{r}) \exp\left\{-\rho_{0} \int_{V} \mathrm{d}\boldsymbol{r} \,\omega_{\beta}(\boldsymbol{r}) [\hat{\phi}_{\beta}(\boldsymbol{r}) - \phi_{\beta}(\boldsymbol{r})]\right\}, \quad (2.7)$$

where $\Xi(\mathbf{r})$ is the pressure field, $\omega_{\beta}(\mathbf{r})$ is the conjugate field associated with monomer type β , and the bounds of the functional integration extend from $-i\infty$ to $+i\infty$. Using Eqs. (2.6)–(2.7), the partition function [c.f. Eq. (2.2)] after rescaling lengths by $b/\sqrt{6}$ can be rewritten as

$$\mathcal{Z}(V) = \int \mathcal{D}\Xi(\mathbf{r}) \prod_{\beta=A,B} \int \mathcal{D}\phi_{\beta}(\mathbf{r}) \int \mathcal{D}\omega_{\beta}(\mathbf{r}) \exp\left(-\rho_{0}Vg\right), \qquad (2.8)$$

where $g = g[V, \omega_{\rm A}(\boldsymbol{r}), \omega_{\rm B}(\boldsymbol{r}), \phi_{\rm A}(\boldsymbol{r}), \overline{\phi}_{\rm B}(\boldsymbol{r}), \Xi(\boldsymbol{r})]$ denotes the Gibbs free energy density in units of $k_b T$,

$$g = \frac{1}{V} \left\{ \int_{V} d\boldsymbol{r} \, \chi_{AB} \phi_{A}(\boldsymbol{r}) \phi_{B}(\boldsymbol{r}) - \omega_{A}(\boldsymbol{r}) \phi_{A}(\boldsymbol{r}) - \omega_{B}(\boldsymbol{r}) \omega_{B}(\boldsymbol{r}) - \Xi(\boldsymbol{r}) [1 - \phi_{A}(\boldsymbol{r}) - \phi_{B}(\boldsymbol{r})] \right\} - \sum_{i=1}^{2} z_{i} Q_{i} [V, \omega_{A}(\boldsymbol{r}), \omega_{B}(\boldsymbol{r})],$$

$$(2.9)$$

where a constant factor of $1/\rho_0$ has been absorbed into the polymer activities, z_i .

Furthermore, $Q_i[V, \omega_{\rm A}(\boldsymbol{r}), \omega_{\rm B}(\boldsymbol{r})]$ is the partition function of a single chain interacting with the conjugate fields,

$$Q_{i}[V, \omega_{\mathrm{A}}(\boldsymbol{r}), \omega_{\mathrm{B}}(\boldsymbol{r})] = \frac{1}{V} \int \mathcal{D}\boldsymbol{r}(s) \exp\left[-\frac{3}{2b^{2}} \int_{0}^{N^{(i)}} \mathrm{d}s \left|\frac{\mathrm{d}\boldsymbol{r}(s)}{\mathrm{d}s}\right|^{2} - \int_{0}^{N^{(i)}_{\mathrm{A}}} \mathrm{d}s \,\omega_{\mathrm{A}}(\boldsymbol{r}(s)) - \int_{N^{(i)}_{\mathrm{A}}}^{N^{(i)}} \mathrm{d}s \,\omega_{\mathrm{B}}(\boldsymbol{r}(s))\right] \qquad (2.10)$$
$$= \frac{1}{V} \int_{V} \mathrm{d}\boldsymbol{r} \, q_{i}(\boldsymbol{r}, N^{(i)}),$$

and $q_i(\mathbf{r}, N^{(i)})$ denotes the forward chain propagator, which satisfies a modified diffusion equation [1],

$$\frac{\partial q_i(\boldsymbol{r},s)}{\partial s} = \nabla^2 q_i(\boldsymbol{r},s) - \omega_i(\boldsymbol{r},s)q_i(\boldsymbol{r},s), \quad q_i(\boldsymbol{r},0) = 1,$$

$$\omega_i(\boldsymbol{r},s) = \begin{cases} \omega_A(\boldsymbol{r}) & 0 \le s \le N_A^{(i)} \\ \omega_B(\boldsymbol{r}) & N_A^{(i)} \le s \le N^{(i)}. \end{cases}$$
(2.11)

The quantity $q_i(\mathbf{r}, s)$ corresponds to the conditional probability that a chain, interacting with the conjugate fields, has its s^{th} segment at position \mathbf{r} , given that its first segment could be found anywhere in the volume of the system.

At this point, the transformation from a particle-based model to a field-based theory is complete. It is important to note that no mathematical approximations have been made so far, and evaluation of $\mathcal{Z}(V)$ from either Eq. (2.2) or Eq. (2.8) remains analytically intractable. In order to proceed, we will exploit the saddle-point or meanfield approximation [1], which in essence, assumes that the only contributions to the functional integrals in Eq. (2.8) comes from $\Xi(\mathbf{r})$, $\phi_{\beta}(\mathbf{r})$, and $\omega_{\beta}(\mathbf{r})$ that extremize the argument of the exponent, g, in the integrand. Extremizing the free energy density given by Eq. (2.9) with respect to $\phi_{\beta}(\mathbf{r})$, $\omega_{\beta}(\mathbf{r})$, and $\Xi(\mathbf{r})$ leads to the following set of self-consistent equations:

$$\omega_{\rm A}(\boldsymbol{r}) = \chi_{\rm AB}\phi_{\rm B}(\boldsymbol{r}) + \Xi(\boldsymbol{r}), \quad \omega_{\rm B}(\boldsymbol{r}) = \chi_{\rm AB}\phi_{\rm A}(\boldsymbol{r}) + \Xi(\boldsymbol{r}), \quad (2.12)$$

$$\phi_{A}(\boldsymbol{r}) = \sum_{i=1}^{2} z_{i} \int_{0}^{N_{A}^{(i)}} ds \, q_{i}(\boldsymbol{r}, s) q_{i}^{\dagger}(\boldsymbol{r}, N^{(i)} - s),$$

$$\phi_{B}(\boldsymbol{r}) = \sum_{i=1}^{2} z_{i} \int_{N_{A}^{(i)}}^{N^{(i)}} ds \, q_{i}(\boldsymbol{r}, s) q_{i}^{\dagger}(\boldsymbol{r}, N^{(i)} - s),$$

$$\phi_{A}(\boldsymbol{r}) + \phi_{B}(\boldsymbol{r}) = 1,$$
(2.14)

where $q_i^{\dagger}(\boldsymbol{r}, s)$ is the backward chain propagator, satisfying a modified diffusion equation similar to Eq. (2.11),

$$\frac{\partial q_i^{\dagger}(\boldsymbol{r},s)}{\partial s} = \nabla^2 q_i^{\dagger}(\boldsymbol{r},s) - \omega_i^{\dagger}(\boldsymbol{r},s) q_i^{\dagger}(\boldsymbol{r},s), \quad q_i^{\dagger}(\boldsymbol{r},0) = 1,$$

$$\omega_i^{\dagger}(\boldsymbol{r},s) = \begin{cases} \omega_{\rm B}(\boldsymbol{r}) & 0 \le s \le N^{(i)} - N_{\rm A}^{(i)} \\ \omega_{\rm A}(\boldsymbol{r}) & N^{(i)} - N_{\rm A}^{(i)} \le s \le N^{(i)}.
\end{cases}$$
(2.15)

Intuitively, we can think of $q_i^{\dagger}(\mathbf{r}, s)$ as the conditional probability for finding a polymer chain of species *i* with its s^{th} segment, counting backwards starting from $s = N^{(i)}$, at spatial position \mathbf{r} . The condition is that the $s = N^{(i)}$ segment could be found anywhere in the volume of the system.

For a given set of parameters, there are many solutions satisfying Eqs. (2.12)-(2.14), corresponding to the multitude of possible metastable phases. Furthermore, since obtaining these solutions is still analytically intractable, we must rely on numerical methods, which are presented in the subsequent section. We therefore need

to restrict our attention to a certain number of morphologies that are relevant to the problem at hand due to the constraint of time and computational resources. The candidate structures we will examine include the classic phases seen in Fig. 1.1, alongside the bicontinuous phases of the G, DD, and P morphologies illustrated in Fig. 1.2. Once all the solutions of the candidates are obtained, the equilibrium phase or phase coexistence is determined through a comparison of their associated Gibbs free energy density [c.f. Eq. (2.9)]. We may then relate the polymer activity, z_2 , to the average volume fraction of either DBCP species, $\bar{\phi}^{(i)}$, via

$$\bar{\phi}^{(2)} = z_2 N_2 Q_2 = 1 - \bar{\phi}^{(1)} = 1 - N_1 Q_1,$$
(2.16)

where the last inequality follows from setting $z_1 = 1$ as reference and the incompressiblity condition, Eq. (2.14).

Chapter 3

Methodology

3.1 Numerical SCFT

Obtaining analytic solutions that satisfy the set of self-consistent equations defined by Eqs. (2.12)-(2.14) is impossible in general. Instead, numerical techniques are often used to obtain numerical solutions of the SCFT equations. The first attempt to numerically compute the SCFT solutions for DBCP melts was made by Helfand and coworkers for the lamellar phase under the narrow interface approximation [51]. Shull subsequently carried out a similar numerical calculation without the restriction of a narrow interface [52]. Soon after, Vavasour and Whitmor numerically constructed the phase diagram for DBCPs within the unit cell approximation [53]. The first general numerical procedure to solve the SCFT equations free of additional approximations was developed by Matsen and Schick [54, 55]. Since then, a plethora of computational algorithms designed to solve the SCFT equations have been developed. The exact numerical recipes used by different authors will thus vary from work to work, but they could be categorized into three types: real-space, spectral, and pseudo-spectral. In the real-space and spectral method, the modified diffusion equations, defined by Eqs. (2.11) and (2.15), are solved in the real and reciprocal space, respectively. For our purposes, we employ the pseudo-spectral method [56, 57, 58], described in Appendix B, in order to solve the modified diffusions equations. Readers are referred to Refs. [59, 60, 61, 62, 63] for details on real-space algorithms and Refs. [54, 64] for the spectral method.

Our implementation to numerically solve the SCFT equations begins with initial monomer densities, $\phi_{\beta}^{(0)}(\boldsymbol{r})$, which is constructed based upon the symmetry of the phase being considered. For completeness, the analytic form of $\phi_{\beta}^{(0)}(\boldsymbol{r})$ for each candidate morphology studied in this work is given in Appendix. A. We then insert $\phi_{\beta}^{(0)}(\boldsymbol{r})$ into Eq. (2.12) to obtain the corresponding conjugate fields, $\omega_{\beta}^{(0,in)}(\boldsymbol{r})$. Once $\omega_{\beta}^{(0,in)}(\boldsymbol{r})$ is constructed, we proceed with the following steps to iteratively obtain a solution:

- 1. Starting with the conjugate fields determined from the n^{th} iteration, $\omega_{\beta}^{(n,\text{in})}(\boldsymbol{r})$, the forward, and backward chain propagators, $q_i^{(n)}(\boldsymbol{r},s)$, and $q_i^{\dagger(n)}(\boldsymbol{r},s)$ are determined via Eqs. (2.11) and (2.15), where we set $\omega_{\beta}(\boldsymbol{r}) = \omega_{\beta}^{(n,\text{in})}(\boldsymbol{r})$. As mentioned above, solving the required partial differential equations can be done using a real-space, spectral, or pseudo-spectral approach. For the present work, a pseudo-spectral method is used (c.f. Appendix B). We denote the first iteration as n = 0.
- 2. From $q_i^{(n)}(\boldsymbol{r}, s)$, and $q_i^{\dagger(n)}(\boldsymbol{r}, s)$, we calculate $\phi_{\beta}^{(n)}(\boldsymbol{r})$ from Eq. (2.13), setting $q(\boldsymbol{r}, s) = q_i^{(n)}(\boldsymbol{r}, s)$, and $q_i^{\dagger}(\boldsymbol{r}, s) = q_i^{\dagger(n)}(\boldsymbol{r}, s)$. We have adopted the Simpsons Rule [c.f. Appendix C] to carry out numerical integrations.

3. We now update the pressure field,

$$\Xi^{(n+1)}(\boldsymbol{r}) = \frac{\omega_{\rm A}^{(n,\rm in)}(\boldsymbol{r}) + \omega_{\rm B}^{(n,\rm in)}(\boldsymbol{r}) - \chi_{\rm AB}}{2}, \qquad (3.1)$$

which follows from the incompressibility condition, and Eq. (2.12).

4. The output chemical potential fields are then calculated from

$$\omega_{\mathrm{A,B}}^{(n,\mathrm{out})}(\boldsymbol{r}) = \chi_{\mathrm{AB}}\phi_{\mathrm{B,A}}^{(n)}(\boldsymbol{r}) + \Xi^{(n+1)}(\boldsymbol{r}).$$
(3.2)

5. In order to proceed with the next iteration, we require a procedure to generate a new set of input fields, ω_β^(n+1,in)(**r**), based upon the input and output fields from past trials. The two most common schemes are "simple" mixing and Anderson mixing [65]. Below, we present the details of simple mixing, and refer readers to Appendix D for the technical aspects of Anderson mixing.

Simple mixing is motivated by (functional) gradient descent [66], since the solutions we seek are local extremums in the infinite-dimensional free energy landscape. In essence, the current set of inputs fields are simply "mixed" with the output fields. Thus the new input conjugate chemical fields are given by

$$\begin{split} \omega_{\mathrm{A,B}}^{(n+1,\mathrm{in})}(\boldsymbol{r}) &= \omega_{\mathrm{A,B}}^{(n,\mathrm{in})}(\boldsymbol{r}) - \lambda_{\mathrm{SM}} \frac{\delta g}{\delta \omega_{\mathrm{A,B}}^{(n,\mathrm{in})}} \\ &= \omega_{\mathrm{A,B}}^{(n,\mathrm{in})}(\boldsymbol{r}) - \lambda_{\mathrm{SM}} \left[\omega_{\mathrm{A,B}}^{(n,\mathrm{in})}(\boldsymbol{r}) - \chi_{\mathrm{AB}} \phi_{\mathrm{B,A}}^{(n)}(\boldsymbol{r}) - \Xi^{(n+1)}(\boldsymbol{r}) \right] \quad (3.3) \\ &= (1 - \lambda_{\mathrm{SM}}) \, \omega_{\mathrm{A,B}}^{(n,\mathrm{in})}(\boldsymbol{r}) + \lambda_{\mathrm{SM}} \, \omega_{\mathrm{A,B}}^{(n,\mathrm{out})}(\boldsymbol{r}), \end{split}$$

where $\lambda_{\rm SM}$ is a dimensionless parameter controlling how rapid the descent is, and the last equality follows from Eq. (3.2). For numerical stability, we typically choose $\lambda_{\rm SM} < 1$.

6. With the new set of input fields in hand, we calculate the free energy density, $g^{(n)}$, as well as the associated deviation from the free energies of the past M_g iterations,

$$d_{\max}^{(n)} = \max_{1 \le m \le M_g} \left| 2 \frac{g^{(n)} - g^{(n-m)}}{g^{(n)} + g^{(n-m)}} \right|.$$
(3.4)

Steps 1. to 6. are repeated until the desired tolerance for $d_{\max}^{(n)}$ is reached, at which point the solution is considered to be self-consistent. For reference, we calculate all solutions to a numerical accuracy of at least 10^{-6} with $M_g = 3$ in the present work. It is also worthwhile to note that the order of steps within a single iteration may differ from one implementation to another. However, this will not affect the converged solution, as it is largely dictated by the initial conjugate fields.

Finding one solution for a particular phase is insufficient for any given set of parameters. We seek the solution that minimizes the free energy density with respect to the period or the size of the unit cell, which is obtained via the optimization method detailed in the following section.

3.2 Optimization of the Period

In this section, we discuss the procedure to determine the optimal period of a particular morphology. For all the candidate phases being considered in the current work, the unit cell size in the x- and y-direction are proportional to the one in the z-direction, with the proportional constant given by the symmetry of the morphology. In the case of the three dimensional cubic phases (i.e. S, G, D, and P), the unit cell sizes are simply related by $L_x = L_y = L_z = L$, while for the hexagonally packed cylinders, we have $L_y = \sqrt{3}L_z$. Therefore, the presented approach is a one-variable optimization algorithm, inspired by the gradient descent [66].

Starting with an initial period, $L^{(2)}$, we calculate $g(L^{(1)})$, $g(L^{(2)})$, and $g(L^{(3)})$, where g(L) is the free energy density for given unit cell length, L, and $L^{(1\pm 1)} = (1 \pm \lambda_L)L^{(1)}$. The dimensionless parameter, λ_L , controls the relative accuracy of the determined optimal period. Once this is done, there will be two possibilities¹:

Case 1: (a)
$$g(L^{(1)}) \le g(L^{(2)}) \le g(L^{(3)})$$
 or (b) $g(L^{(3)}) \le g(L^{(2)}) \le g(L^{(1)})$, or
Case 2: $g(L^{(2)}) \le \min[g(L^{(1)}), g(L^{(3)})]$.

We first discuss case 1 (a), for which the next step is to increase the unit cell edge to $L^{(4)} = (1 + \lambda_L)L^{(3)} = (1 + \lambda_L)^2 L^{(2)}$, and compute $g(L^{(4)})$. For the case 1 (b), the length is decreased. This step is repeated, where we denote the period of the n^{th} iteration as $L^{(n+3)} = (1 + \lambda_L)^n L^{(2)}$, until a higher free energy density is obtained upon incrementation. Let the total number of calculated free energies up to this point be M_L . The desired minima, L^* , is determined by fitting the three-point set, $\{g(L^{(M_L-2)}), g(L^{(M_L-1)}), g(L^{(M_L)})\}$ to the quadratic form,

$$g_{\rm fit}(L) = pL^2 + qL + r,$$
 (3.5)

where p, q, and r are fitting parameters (c.f. Appendix E), and proceeding to use the

¹ Technically, the case where $g(L^{(2)}) \ge \max[g(L^{(1)}), g(L^{(3)})]$ is a rare possibility, which is commonly due to two separate causes. One is when the initial guess is centered between nL^* , and $(n+1)L^*$, where $n \ge 1$ is an integer. Increasing or decreasing $L^{(2)}$ will correct this oddity. In the second case, the free energy density as function of the period could be quite flat. As a result, the energy differences between $L^{(2)}$ and its two adjacent points could be smaller than the allowed tolerance for $d_{\max}^{(n)}$, which may lead to a false maximum. Decreasing the tolerated $d_{\max}^{(n)}$ (i.e. increasing the precision) should remedy the situation.



Figure 3.1: (a) Typical search for the optimal periodicity with the starting unit cell length, $L^{(2)}$, shown in blue. (b) Quadratic fit of the three-point set, $\{g(L^{(M_L-2)}), g(L^{(M_L-1)}), g(L^{(M_L)})\}$, from (a) with $(L^*, g_{\text{fit}}(L^*))$ shown in red.

following analytic expression,

$$L^* = \frac{-q}{2p}.\tag{3.6}$$

We note that in the case where $g(L^{(2)}) \leq \min \left[g(L^{(1)}), g(L^{(3)})\right]$, we take $M_L = 3$, and follow the procedure outlined above.

The last step is to calculate $f(L^*)$, which is then taken as the free energy density of the considered phase. A typical example of the presented algorithm is shown in Fig. 3.1 where $\lambda_L = 0.01$.

3.3 Construction of the Phase Diagram

Upon obtaining the free energy densities, g, for each of the candidate phases using the numerical methods detailed in Sections 3.1 and 3.2, the phase behavior can be readily detemined. The equilibrium behavior of polymeric systems is typically depicted in



Figure 3.2: A plot of the (a) Gibbs free energy density, g, and (b) the average concentration of the second polymer species, $\bar{\phi}^{(2)}$, as a function of z_2 for $N^{(2)}/N^{(1)} = 2.32$, $f_A^{(1)} = 0.34$, $f_A^{(2)} = 0.95$, and $\chi_{AB}N^{(1)} = 22.5$. Each region of phase coexistence is labelled with **i**, **ii**, and **iii**, corresponding to G+DD, DD+P, and P+G. The values of $\bar{\phi}^{(2)}$ spanned by the arrows indicate the range of each phase coexistence.

the form of a phase diagram. We outline below the procedure to construct a phase diagram using the SCFT solutions. For concreteness, we will work with a sample binary DBCP blend specified by $N^{(2)}/N^{(1)} = 2.32$, $f_A^{(1)} = 0.34$, $f_A^{(2)} = 0.95$, and $\chi_{AB}N^{(1)} = 22.5$. We plot in Fig. 3.2(a) the numerically obtained g from SCFT of several candidate phases as a function of the polymer activity of the second polymer species, z_2 . The equilibrium structure at any given z_2 corresponds to the morphology having the lowest g out of all the candidates. Since the phase behavior is often studied in its relation to the average concentration of either polymer species, we map z_2 to $\bar{\phi}^{(2)}$ via Eq. (2.16). The conversion is done for the system under consideration in Fig. 3.2(b). If we now take for instance, the initial point of $z_2 \approx 0.0089$, the G phase is predicted to be the ground state for $\bar{\phi}^{(2)} \approx 0.06$.

As z_2 , or equivalently, $\bar{\phi}^{(2)}$ is increased in our example, the free energy of the
DD structure will eventually become lower than that of the G phase, signifying a transition from the G to the DD. We find that the change in morphology is naturally accompanied by an intersection of the free energy curves of the G and DD phase. This marks the appearance of a phase coexistence between two phases. The boundary of the coexistence region is determined from the two values of $\bar{\phi}^{(2)}$ associated with the point where the crossing in g occurs. In our example, there are three windows of phase coexistence predicted, which we have labelled **i**, **ii**, and **iii**, corresponding to G+DD (discussed presently), DD+P, and P+G, respectively in Fig. 3.2(b). The range of $\bar{\phi}^{(2)}$ spanned by the coexistence regions is furthermore indicated by the arrows.

At last, we present the predicted equilibrium behavior in a more transparent fashion through a phase diagram, which for our example is shown in Fig. 3.3. Here, the segregation strength, $\chi_{AB}N^{(1)}$, is chosen as the second parameter to be varied. Several other data points, representing the phase boundaries, have been included for illustration purposes. We again include arrows, and labels at $\chi_{AB}N^{(1)} = 22.5$, which indicate the same series of stable morphologies, and phase coexistences shown in Fig. 3.2(b) as $\bar{\phi}^{(2)}$ is increased.



Figure 3.3: A sample phase diagram as a function of the segregration strength, $\chi_{AB}N^{(1)}$, and the average concentration of the second polymer species, $\bar{\phi}^{(2)}$, for $N^{(2)}/N^{(1)} = 2.32$, $f_A^{(1)} = 0.34$, and $f_A^{(2)} = 0.95$. The arrows alongside their associated labels indicate the same series of transitions depicted in Fig. 3.2(b).

Chapter 4

Results

The number of parameters governing the equilibrium structure for binary DBCP mixtures is too big for a brute-force numerical approach. In other words, we cannot simply consider every combination of $\alpha = N^{(2)}/N^{(1)}$, $f_A^{(1)}$, $f_A^{(2)}$, and $\chi_{AB}N^{(i)}$ with the available computational resources. Instead, we start with the homopolymer/DBCP blends where the formation of the DD and P phases has been examined [13, 14, 15]. These binary systems are modified by replacing the homopolymers with DBCPs which are homopolymer-like (HL) in that their B-blocks are short, for example, with $f_A^{(2)} = f_A^{HL} = 0.95$. The resultant phase behavior is subsequently studied using SCFT.

We first examine a binary mixture of G-forming DBCPs with $f_A^{(1)} = f_A^{\text{DBC}} =$ 0.33, and the HL DBCPs in the relatively strong segregation regime, $\chi_{AB}N^{(1)} =$ $\chi_{AB}N^{\text{DBC}} = 25$, to study the effects of the relative chain lengths on the equilibrium phase. In Fig. 4.1, we plot the phase diagram as a function of $\alpha = N^{\text{HL}}/N^{\text{DBC}}$ and the average volume fraction of the HL DBCPs, $\bar{\phi}^{\text{HL}}$. The single-phase regions are denoted accordingly, while the two-phase coexistences are left unlabelled unless necessary hereinafter. Furthermore, the additive-rich disordered phase is denoted as



Figure 4.1: Phase diagram of a binary DBCP mixture as a function of $\alpha = N^{\rm HL}/N^{\rm DBC}$, and $\bar{\phi}^{\rm HL}$ with $f_{\rm A}^{\rm DBC} = 0.33$, $f_{\rm A}^{\rm HL} = 0.95$, and $\chi_{\rm AB}N^{\rm DBC} = 25$. The circular points represent the numerically computed data, while the lines serve as guide for the eyes. Unlabeled areas on the phase diagram denote regions of phase coexistence between the two bordering phases. The stabilization of DD phase occurs between $\alpha \approx 1.4$ to $\alpha \approx 1.67$.

DIS. We find that by adjusting the blending composition from ~ 16% to ~ 20%, the DD phase can be stabilized for $\alpha \gtrsim 1.4$. Whereas Martínez-Veracoechea et al. predicted the occurrence of the DD morphology when the additive species is shorter than the DBCPs [13, 14, 15], the opposite trend is found in the current blends. We also observe that the further increase of $\bar{\phi}^{\text{HL}}$ leads to the DD phase reverting to a G morphology for all values of α examined in Fig. 4.1. This is again different from the case of a homopolymer additive, where adding homopolymers to a stable DD structure will induce one of two following transitions. The first possibility is that the system macro-phase separates to a homopolymer-rich DIS phase and a DD phase. The second alternative is the equilibrium morphology briefly evolves to a P phase, which is then closely followed by a similar macro-phase separated state, P+DIS [14, 15]. Based on this difference in phase behavior, it could be concluded that the change of



Figure 4.2: Phase diagram of a binary blend composed of an A-homopolymer and a G-forming DBCP as a function of $\alpha = N^{\text{homo}}/N^{\text{DBC}}$ and average homopolymer concentration, $\bar{\phi}^{\text{homo}}$. The parameters used were $f_A^{\text{DBC}} = 0.33$ and $\chi_{AB}N^{\text{DBC}} =$ 25. With the addition of ~ 15% homopolymers in volume, the system macro-phase separates into the homopolymer-rich DIS phase, and either the G or H morphology.

A-homopolymers additives to HL DBCPs delays the onset of macro-phase separation.

To test our hypothesis, we repeat the SCFT calculation with the HL DBCPs replaced by A-homopolymers. The segregation strength remains unchanged for consistency, and a larger range of α is explored. The resulting phase diagram is depicted in Fig. 4.2. We find that the DD phase is not only absent, but the blend macro-phase separates at a relatively low concentration of homopolymers, $\bar{\phi}^{\text{homo}} \approx 0.15$. The predicted behavior supports our postulate that macro-phase separation is circumvented by introducing B monomers to the additive. Consequently, since our binary system permits a higher volume fraction of additives, the predicted stable G phase before the G+DIS coexistence possesses an average A-monomer concentration ranging from 45% to 60%. This result is quite remarkable, considering the fact that the G phase



Figure 4.3: Phase diagram of a binary DBCP mixture as a function of α and $\bar{\phi}^{\rm HL}$ with $f_{\rm A}^{\rm DBC} = 0.34$, $f_{\rm A}^{\rm HL} = 0.95$, and $\chi_{\rm AB}N^{\rm DBC} = 25$. The stability region of the DD phase has widen considerably both in α and $\bar{\phi}^{\rm HL}$ from the case of $f_{\rm A}^{\rm DBC} = 0.33$. The region for $\bar{\phi}^{\rm HL} \geq 0.45$ is not included due to dimensions of the unit cells for the bicontinuous phases growing too large for our present computational capabilities.

in monodisperse melts is stable only for a narrow range of volume compositions, $\bar{\phi}_{A} \approx 0.31$ to 0.35, and $\bar{\phi}_{A} \approx 0.65$ to 0.69 [10]. Before proceeding, we note that the series of stable bicontinuous phases from relatively smaller to larger nodes (i.e. G \rightarrow DD) found upon the initial blending of additives is similar to what is predicted in Refs. [13, 14, 15].

As an effort to obtain the optimal conditions for stabilizing the DD or P morphology, we examine the phase behavior of a binary DBCP system that is nearly identical to the one considered previously but with $f_A^{\text{DBC}} = 0.34$. We choose to increase the chemical composition of the G-forming DBCPs since the formation of the P phase is predicted for this particular value of f_A^{DBC} in the case of homopolymer additives [15]. In Fig. 4.3, we present the calculated phase diagram, again as a function of α and $\bar{\phi}^{\text{HL}}$. It is clear that large differences in the phase behavior are induced by



Figure 4.4: Phase diagram of a binary DBCP mixture as a function of α and $\bar{\phi}^{\text{HL}}$ with $f_{\text{A}}^{\text{DBC}} = 0.35$, $f_{\text{A}}^{\text{HL}} = 0.95$, and $\chi_{\text{AB}}N^{\text{DBC}} = 25$. The DD phase is no longer stable here, but has been replaced by a lamellar phase.

the small adjustment to the molecular architecture. The most prominent change is that the DD phase now occupies a larger region of the phase diagram; not only is it stable for an extended range of α , but its stability region now spans ~ 10% in $\bar{\phi}^{\text{HL}}$ at $\alpha = 2.32$. In contrast, the predicted windows of stability for the DD morphology in homopolymer-DBCP blends so far spans up to a maximum of ~ 6% in the additive concentration [14, 15]. We also find the formation of the DD phase occurs at larger values of α when $f_A^{\text{DBC}} = 0.34$ compared to $f_A^{\text{DBC}} = 0.33$. Furthermore, while the stability region of the DD structure narrows with increasing α for $f_A^{\text{DBC}} = 0.33$, it instead expands here for $f_A^{\text{DBC}} = 0.34$. We note that prior to encountering the expected macro-phase separated state, G+DIS, the dimensions of the unit cells for the bicontinuous phases grows large enough where numerical accuracy is a concern. Therefore, given our current computational capabilities, we have only presented the phase behavior for $\bar{\phi}^{\text{HL}} \leq 0.45$ in Fig. 4.3.

Noting the success that came when $f_{\rm A}^{\rm DBC}$ was increased to 0.34, the calculation



Figure 4.5: Phase diagram of a binary DBCP blend as a function of the segregation strength, $\chi_{AB}N^{DBC}$ and $\bar{\phi}^{HL}$ with $f_A^{DBC} = 0.34$, $f_A^{HL} = 0.95$, and $\alpha = 2.32$. Alongside the stable DD phase, the P phase can be also stabilized for lower segregation strengths, $\chi_{AB}N^{DBC} \leq 23$.

is repeated once more for the case of $f_{\rm A}^{\rm DBC} = 0.35$. We depict the computed phase diagram as a function of α and $\bar{\phi}^{\rm HL}$ in Fig. 4.4. The changes to the phase behavior accompanying this increase of $f_{\rm A}^{\rm DBC}$ is as drastic as its first adjustment from 0.33 to 0.34. We find that the DD morphology is no longer stable for a similar range of α studied in Fig. 4.3, being replaced by the lamellar phase. From the extremely sensitive transformations seen in the stability region of the DD phase as one tunes $f_{\rm A}^{\rm DBC}$ from $0.33 \rightarrow 0.34 \rightarrow 0.35$, we conclude that its formation is sensitive to the molecular architecture of the G-forming DBCPs. This is similar to the findings of Ref. [15]. It is also worth pointing out that the P phase has always been found to be metastable in all three blends considered so far.

Up to this point, we have probed how the blending composition, $\bar{\phi}^{\text{HL}}$, the chemical composition, $f_{\text{A}}^{\text{DBC}}$, and the relative chain length, α , changes the relative stability of the bicontinuous phases. The effect of the segregation strength remains unexplored.

In our attempt to understand the role played by the segregation strength in realizing the novel bicontinuous phases, we choose to focus on a blend of G-forming DBCPs, $f_A^{\text{DBC}} = 0.34$, and the HL DBCPs with fixed $\alpha = 2.32$. The selected chain length asymmetry is based upon the stability of the DD phase being the greatest when $\alpha =$ 2.32 (c.f. Fig. 4.3). We plot in Fig. 4.5 the phase diagram as a function of $\chi_{\text{AB}}N^{\text{DBC}}$, and $\bar{\phi}^{\text{HL}}$. There are a number of observations to be made here. Alongside the expected DD morphology, the phase diagram now features the P phase for segregation strengths up to $\chi_{\text{AB}}N^{\text{DBC}} \approx 23$. In the vicinity of $\chi_{\text{AB}}N^{\text{DBC}} \approx 23$, an elaborate sequence of bicontinuous phases is observed, $G \to \text{DD} \to P \to \text{DD} \to G$, as $\bar{\phi}^{\text{HL}}$ increases. We can lastly further enhance the relative stability of the DD morphology by slightly decreasing the segregation strength from $\chi_{\text{AB}}N^{\text{DBC}} = 25$. By the same token, the stability region of the DD structure progressively narrows as the segregation strength increases. Having now predicted the stabilization of both the novel DD and P phases, we will now examine some of the mechanisms leading to their occurrence and improved stability in the subsequent section.

Chapter 5

Discussions

The spatial segregation of the two polymer species in homopolymer-DBCP blends can be considered as a primary factor to stabilizing the DD, and P phase. The homopolymers are confined predominately in the junctions, resulting in a reduction of the packing frustration of the DBCPs. Following an approach by Martínez-Veracoechea et al., we examine the spatial distribution of the HL DBCPs in the vicinity of a node, thus probing the segregation behavior of the DBCPs. In Fig. 5.1, we plot the $\phi^{\text{HL}}(\mathbf{r})$ as function of the distance, \bar{d} , rescaled by the unit cell edge from a nodal center of a P phase in the [111] direction. One finds that $\phi^{\text{HL}}(\mathbf{r})$ remains near unity for $\bar{d} \ll 0.25$ (i.e. close to the center of a node), and rapidly decreases as the AB interface is approached. As customary, we define the AB interface to be where $\phi_{\text{A}}(\mathbf{r}) = 0.5$. The observed behavior is consistent with the idea that the HL chains are segregated to the junctions, thus alleviating packing frustration. While the current and following analyses are conducted only using the P morphology for convenience, the behavior is expected to be the same across the G and DD phases.



Figure 5.1: A plot of the concentration of the HL chains, $\phi^{\text{HL}}(\mathbf{r})$, as a function of rescaled distance, \bar{d} , away from the center of a node for $\alpha = 1.4$ (red) and 1.67 (green). The plots were constructed using metastable P phases in the [111] direction (diagonal of the unit cell) for $f_{\rm A}^{\rm DBC} = 0.33$ and $\bar{\phi}^{\rm HL} \simeq 0.4$. The behavior of the $\phi^{\rm HL}(\mathbf{r})$ suggests that the HL chains are primarily confined in the nodes.

Based on arguments of packing frustration alone, we cannot explain the improved stability of the novel bicontinuous phases obtained by blending a second DBCP over a homopolymer. It is not expected that the degree to which the packing frustration is relieved will be the vastly different whether the additive is a homopolymer or a homopolymer-like DBCP since it is the G-forming DBCPs that are entropically frustrated. Instead we examine the effect of the additives on interfacial curvature. In Fig. 5.2, the mean curvature multiplied by the radius of gyration, $HR_g = H(N^{\text{DBC}}b/\sqrt{6})$, is shown for the AB interface of a P structure where $\bar{\phi}^{\text{homo}} \simeq 0.16$ in (a), and $\bar{\phi}^{\text{HL}} \simeq 0.16$ in (b). We briefly remind readers that in monodisperse systems, the local incompressibility together with the maximization of the conformational entropy will drive the AB interface to bend towards the minority domain. Consequently, the regions of lowest curvature for the bicontinuous



Figure 5.2: A plot depicting the product of mean curvature and radius of gyration, HR_g , on the AB interface ($\phi_A(\mathbf{r}) = 0.5$) for (a) $\bar{\phi}^{\text{homo}} \simeq 0.16$ and (b) $\bar{\phi}^{\text{HL}} \simeq 0.16$ with $\chi_{AB}N^{\text{DBC}} = 25$ and $\alpha = 2.32$. In (c), we show the volume fraction of the HL DBCPs, $\phi^{\text{HL}}(\mathbf{r})$, on the same interfacial surface shown in (b). The low-curvature areas coincide with the regions of high $\phi^{\text{HL}}(\mathbf{r})$, suggesting the local segregation of the HL chains modifies the interfacial mean curvature.

phases, circled in Fig. 5.2 for the P morphology, is entropically unfavorable for Gforming chains, being curved instead towards the majority B domain. It follows from $H_{\min}^{\text{HL}} < H_{\min}^{\text{homo}}$ that these areas are flatter in the case of $\bar{\phi}^{\text{HL}} \simeq 0.16$. We would suggest that the flattening of the interface is what leads to the enhanced stability of the various bicontinuous phases. The flattened regions will have curvature that is closer to what is preferred by the G-forming DBCPs as dictated by local incompressibility and entropy maximization. As a result, the G-forming chains, found at these locations, is able to better maximize, or increase, their conformational entropy compared to without the flattening effect.

The difference in interfacial curvature discussed above can be linked to the local segregation of the two DBCPs on the AB interface itself. In Fig. 5.2(c), we plot $\phi^{\text{HL}}(\boldsymbol{r})$



Figure 5.3: A plot of the volume fraction of HL chains, $\phi^{\text{HL}}(\mathbf{r})$, as a function of rescaled distance, \bar{d} , away from the center of a node, depicted by the solid lines, and radially outwards from a strut, indicated by the dashed lines. The different colors are used to differentiate between $\bar{\phi}^{\text{HL}} = 0.2$ (red), 0.3 (green), and 0.4 (blue). The plot was constructed using a set of P phases with $f_A^{\text{DBC}} = 0.34$, $f_A^{\text{HL}} = 0.95$, $\chi_{\text{AB}}N^{\text{DBC}} = 22.5$, and $\alpha = 2.32$. After the P phase is stabilized at $\bar{\phi}^{\text{HL}} = 0.2$, the further addition of the HL DBCPs will rapidly increase the additive concentration in the struts, suggesting the nodes are saturated.

wherever $\phi_A(\mathbf{r}) = 0.5$ for the same P phase depicted in (b). There is a clear gradient in the concentration on the interface, consistent with the notion that the G-forming and HL chains are locally segregated. Furthermore, the areas where the additive concentration is the greatest coincides with the regions of lowered mean curvature. We conclude from this correlation that the HL DBCPs perform two functions as an additive. First of all, similar to homopolymer, the HL DBCPs act as a "space filler" relieving the packing frustration at the nodes. Secondly, the HL DBCPs would be localized at the AB interfaces acting as co-surfactants to modify the interfacial property. In particular, the larger A-blocks results in a flatter AB interface.

The formation of the DD and P phases from the G morphology could be attributed to the saturation of HL DBCPs in the nodes. In Fig. 5.3, the additive concentration is depicted as a function of two quantities. The first is the distance, \bar{d} , away from the center of a node, represented by the solid lines. The second is \bar{d} radially outwards from the center of a strut, corresponding to the dashed lines. After stabilizing the P phase at $\bar{\phi}^{\text{HL}} = 0.2$, increasing the average additive concentration leaves the nodal volume fraction relatively unchanged, whereas the amount of additives in the struts rapidly grows. The observed trend supports the idea that the nodes can be saturated with additives, and any additional HL DBCPs is forced to the struts. Since the nodes are bulkier than the struts, chains found in the strut regions experiences a larger degree of confinement than those in the nodes. The asymmetry in confinement should subsequently lead to a decrease in the conformational entropy of the HL chains. We deduce that the equilibrium phase evolves to bicontinuous structures with relatively larger nodes as a means of circumventing the entropy loss. The proposed evolution will allow a greater fraction of HL DBCPs to be accommodated in the nodes than in the struts.

It was noted previously that deviations from a constant mean curvature (CMC) structure results in excess interfacial surface area, which is enthalpically unfavorable. In Fig. 5.4, we plot the product, HR_g , on the AB interface for each of the three considered bicontinuous phases. For each interface, we have also calculated the associated area-averaged deviation from CMC,

$$\sigma = \sqrt{\frac{1}{A} \int dA H^2 - \langle H \rangle^2} = \sqrt{\frac{1}{A} \int dA H^2 - \left(\frac{1}{A} \int dA H\right)^2}.$$
 (5.1)

Here, A is the surface area of the interface. As the bulkiness of the nodes (relative to the struts) grows from $G \rightarrow DD \rightarrow P$, we observe that the deviation, σ , becomes increasingly larger, corresponding to progessively more excess surface area. It follows



Figure 5.4: A plot depicting the product of mean curvature and radius of gyration, HR_g , of the AB interface ($\phi_A(\mathbf{r}) = 0.5$) for (a) the G phase, (b) the DD phase, and (c) P phase with $\bar{\phi}^{\text{HL}} \simeq 0.2$, $\chi_{\text{AB}}N^{\text{DBC}} = 22.5$, and $\alpha = 2.32$. The deviation from constant mean curvature increases as one moves from $G \rightarrow \text{DD} \rightarrow \text{P}$ phase.

that there is a correlation between the relative size of the nodes and the deviation from a CMC structure, which in turn gives rise to a competition between two opposing factors in the bicontinuous phases. One is the minimization of the interfacial surface area, and the other, discussed earlier, is the attempt to maximize the accepted concentration of HL DBCPs in the nodes.

The progression of bicontinuous structures from relatively more compact nodes to less compact ones, and the subsequent regression to morphologies with smaller junctions predicted in our blends (c.f. Figs. 4.1, 4.3, and 4.5) could be now understood by the following considerations. Upon first introducing the HL chains to the melt, saturation in the nodes triggers the equilibrium structure to evolve to bicontinuous phases with bulkier junctions. The progression ceases when the enthalpic cost for increasing the excess interfacial surface area, which grows with each transition, outweighs the resulting conformational entropy gain. Continuing to increase $\bar{\phi}^{\text{HL}}$ now causes the fraction of HL DBCPs to grow more rapidly in the struts than in the nodes. Once the additive concentration between the two regions are the same, the confinement asymmetry is reduced in order to maximize the total conformational entropy. Thus, the equilibrium state reverts to bicontinuous structures with smaller differences in bulkiness between the junctions and the struts (i.e. smaller nodes). This also decreases the enthalpic contribution to the free energy due to lower deviations from a CMC structure.

Lastly, from the discussions presented above, it follows that bicontinuous phases with relatively larger nodes could be stabilized by reducing the enthalpic cost for excess surface area. Conversely, doing the oppposite should decrease the relative stability of such structures, and favor the formation of morphologies with less excess interfacial surface area. This line of argument is consistent with the phase behaviour observed in Fig. 4.5. Here, the segregation strength can be seen as a means of controlling the effectiveness of the tradeoff between interfacial enthalpy and nodal conformational entropy. Accordingly, we find the P phase, stable for lower values of $\chi_{AB}N^{DBC}$, is replaced by a narrowing region of the DD morphology upon increasing the segregation strength.

Chapter 6

Conclusion

We have studied the formation of various bicontinuous phases in binary mixtures of DBCPs. The stabilization of the DD and P phases is achieved in G-forming DBCPs, $f_{\rm A}^{\rm HL} = 0.33$ to 0.34, blended with a homopolymer-like DBCP possessing a relatively short B block, $f_{\rm A}^{\rm HL} = 0.95$. Despite the slight difference in additives, the occurrence of these novel bicontinuous phases is not observed in homopolymer-DBCP systems for a similar set of parameters. The homopolymer blends instead macro-phase separates into a homopolymer-rich disordered phase, and a G or H morphology. We argued from this behavior that the B monomers of the HL DBCPs hinders the onset of macro-phase separation, allowing the DD and P phases to be stabilized despite the significant chain length asymmetry ($\alpha \approx 1.67$ to 2.32).

The stability region of the DD morphology is moreover larger than that found so far in the case of a homopolymer additive. We attribute this enhanced stability to the local segregation of the two DBCPs on the AB interface. The mean curvature where the HL chains are localized is modified such that the conformational entropy of the G-forming DBCPs is increased. In addition, indirect evidence indicates the alleviation of packing frustration. We lastly postulate the appearance of the DD and P phases is due to the entropy gain associated with bulkier nodes as one moves from $G \rightarrow DD \rightarrow P$ outweighing the enthalpic penalty corresponding to larger deviations from a constant mean curvature structure.

In the current thesis, we have considered the effects of segregation strength, chain length ratio, blending, and chemical composition of the G-forming DBCPs on the relative stability of the novel bicontinuous phases. The possibility of optimizing the molecular architecture of the HL DBCPs remains unexplored, which could perhaps give rise to more complex bicontinuous structures, such as the Neovius morphology [67], or further increase the relative stability of the DD or P phases. We have also restricted our attention to binary blends. One possible future work is to therefore consider continuous polydispersity. Polydispersed systems drawing its chain lengths from distributions, such as the Schulz [68], or the Poisson distribution, will be more reflective of the melts procured in experimental settings via typical polymerization processes. Under these realistic assumptions, any predictions made on the formation of the novel bicontinuous phases will be more experimentally accessible for verification.

Appendix A

Initial Ansatz for Pseudo-spectral Method

In this appendix, the initial concentration, $\phi_{\rm A}^{(0)}(\boldsymbol{r})$, is listed for each of the candidate phases considered in the present work.

For a lamellar phase with its surface normal in the z-direction, we have

$$\phi_{\rm A}^{(0)}(\mathbf{r}) = \Phi + (1 - \Phi)\cos(qz), \tag{A.1}$$

where $q = 2\pi/L$, Φ is the expected average A-monomer volume fraction, and L is the assumed periodicity.

The initial ansatz for the hexagonally-packed cylindrical phase reads

$$\phi_{\rm A}^{(0)}(\boldsymbol{r}) = \cos\left(q\frac{2y}{\sqrt{3}}\right) + \cos\left[q\left(z + \frac{y}{\sqrt{3}}\right)\right] + \cos\left[q\left(z - \frac{y}{\sqrt{3}}\right)\right],\tag{A.2}$$

where it is assumed that $L_y = \sqrt{3}L_z = \sqrt{3}L$ and its axis lies in the *x*-direction.

For body-centered packed spherical phase belonging to the space group, $(Im\bar{3}m)$, the initial guess is given by

$$\phi_{\rm A}^{(0)}(\boldsymbol{r}) = \frac{1}{2} + \frac{1}{2} \sum_{i=0}^{2} \cos\left[q\left(x_i - x_{\overline{i+1}}\right)\right],\tag{A.3}$$

where $\mathbf{r} = (x, y, z) = (x_0, x_1, x_2)$ and the line above the subscripts denotes the modulo operation with modulus 3, $\overline{i} = i \pmod{3}$.

For the double-gyroid phase, we construct the initial ansatz from its space group, $(Ia\bar{3}d)$, as

$$\phi_{A}^{(0)}(\boldsymbol{r}) = \frac{1}{6} + \frac{1}{10} \Biggl\{ \sum_{i=0}^{2} \cos \left[q \left(2x_{i} + x_{\overline{i+1}} + x_{\overline{i+2}} \right) \right] - \cos \left[q \left(-2x_{i} + x_{\overline{i+1}} + x_{\overline{i+2}} \right) \right] - \cos \left[q \left(2x_{i} + x_{\overline{i+1}} - x_{\overline{i+2}} \right) \right] + \cos \left[q \left(2x_{i} - x_{\overline{i+1}} + x_{\overline{i+2}} \right) \right] \Biggr\},$$
(A.4)

while the starting guess for the double-diamond morphology based its space group, $(Pn\bar{3}m)$, reads

$$\phi_{\mathbf{A}}^{(0)}(\boldsymbol{r}) = \frac{3}{4} + \frac{1}{24} \sum_{i=0}^{2} g_{110}(x_i, x_{\overline{i+1}}) + \frac{1}{2} g_{111}(x_i, x_{\overline{i+1}}, x_{\overline{i+2}}), \quad (A.5)$$

where

$$g_{110}(x_0, x_1) = \cos \left[q(x_0 + x_1) \right] + \cos \left[q(x_0 - x_1) \right],$$

$$g_{111}(x_0, x_1, x_2) = \sin \left[q(x_0 + x_1 + x_2) \right] - \sin \left[q(-x_0 + x_1 + x_2) \right]$$
(A.6)

$$- \sin \left[q(x_0 - x_1 + x_2) \right] - \sin \left[q(x_0 + x_1 - x_2) \right].$$

Lastly, we have the "plumber's nightmare" phase belonging to the same space

group as the S morphology, $(Im\bar{3}m)$, for which the initial ansatz is

$$\phi_{\rm A}^{(0)}(\boldsymbol{r}) = \frac{8}{10} + \frac{1}{30} \sum_{i=0}^{2} \cos\left(2qx_i\right) + \frac{1}{2}g_{110}(x_i, x_{\overline{i+1}}). \tag{A.7}$$

Appendix B

Pseudo-Spectral Method

The pseudo-spectral method [1] allows one to approximately solve the modified diffusion equation,

$$\frac{\partial q(\boldsymbol{r},s)}{\partial s} = \nabla^2 q(\boldsymbol{r},s) - \omega(\boldsymbol{r})q(\boldsymbol{r},s), \quad q(\boldsymbol{r},0) = 1,$$
(B.8)

where $q(\mathbf{r}, s)$ is the desired propagator, and $\omega(\mathbf{r})$ is an arbitrary potential. Below, we present the algorithm for the pseudo-spectral method used in the current work.

We begin by discretizing space into $M_x \times M_y \times M_z$ points such that the spatial step size in the γ -direction, for $\gamma \in \{x, y, z\}$, is given by $\Delta \gamma = L_{\gamma}/M_{\gamma}$, where L_{γ} is the length in the same direction. Furthermore, we discretize the number of statistical segments or contour length, N as defined in the main text, into $M_s + 1$ points, so that the contour step size is $\Delta s = N/M_s$. The extra point is required for $s_0 = 0\Delta s = 0$. Under the given discretization scheme, the propagator at contour step $s_n = n\Delta s$ for $n \in \{0 \le n \le M_s | n \in \mathbb{N}\}$ is now represented by an $M_x \times M_y \times M_z$ array, q^n , with

$$(\boldsymbol{q}^n)_{uvw} = q(\boldsymbol{r}_{uvw}, s_n),\tag{B.9}$$

where $\boldsymbol{r}_{uvw} = (u\Delta x, v\Delta y, w\Delta z), \ u \in \{0 \le u < M_x | u \in \mathbb{N}\}, \ v \in \{0 \le v < M_y | v \in \mathbb{N}\},\$ and $w \in \{0 \le w < M_z | w \in \mathbb{N}\}.$

Suppose now we have q^n in hand. It is always possible to start with n = 0, where $(q^0)_{uvw} = 1 \forall u, v, w$. The algorithm below can then be followed to determine q^{n+1} :

1. We first apply the potential contribution, $\omega(\mathbf{r})$, to \mathbf{q}^n , yielding

$$\left(\boldsymbol{q}_{\frac{1}{3}}^{n}\right)_{uvw} = \exp\left(-\omega(\boldsymbol{r}_{uvw})\frac{\Delta s}{2}\right)(\boldsymbol{q}^{n})_{uvw}.$$
 (B.10)

2. Next, the Fourier cofficients of $\left(\boldsymbol{q}_{\frac{1}{3}}^{n}\right)$ are required. Thus, we apply a fast Fourier transform (FFT) to $\boldsymbol{q}_{\frac{1}{3}}^{n}$, which amounts to

$$\left(\boldsymbol{p}_{\frac{1}{3}}^{n}\right)_{uvw} = \frac{1}{M_{x}M_{y}M_{z}} \sum_{l=0}^{M_{x}-1} \sum_{m=0}^{M_{y}-1} \sum_{n=0}^{M_{z}-1} \left(\boldsymbol{q}_{\frac{1}{3}}^{n}\right)_{lmn} \exp\left[-2\pi i \left(\frac{ul}{M_{x}} + \frac{vm}{M_{y}} + \frac{wn}{M_{z}}\right)\right].$$
(B.11)

3. The diffusion contribution, ∇^2 , is now accounted for via

$$\left(\boldsymbol{p}_{\frac{2}{3}}^{n}\right)_{uvw} = \exp\left[-4\pi^{2}\Delta s\left(\frac{K_{x}(u)^{2}}{M_{x}^{2}} + \frac{K_{y}(v)^{2}}{M_{y}^{2}} + \frac{K_{z}(w)^{2}}{M_{z}^{2}}\right)\right]\left(\boldsymbol{p}_{\frac{1}{3}}^{n}\right)_{uvw}, \quad (B.12)$$

where

$$K_{\gamma}(t) = \begin{cases} t & 0 \le t < \frac{M_{\gamma}}{2} + 1\\ M_{\gamma} - t & \frac{M_{\gamma}}{2} \le t < M_{\gamma} \end{cases}$$
(B.13)

The purpose of $K_{\gamma}(t)$ is to conform with the FFT-standard form used by common FFT packages, such as FFTW3 [69].

4. We apply an inverse FFT to $\left(\boldsymbol{p}_{\frac{2}{3}}^{n}\right)$, which reads

$$\left(\boldsymbol{q}_{\frac{2}{3}}^{n}\right)_{uvw} = \sum_{l=0}^{M_{x}-1} \sum_{m=0}^{M_{y}-1} \sum_{n=0}^{M_{z}-1} \left(\boldsymbol{p}_{\frac{2}{3}}^{n}\right)_{lmn} \exp\left[+2\pi i \left(\frac{ul}{M_{x}} + \frac{vm}{M_{y}} + \frac{wn}{M_{z}}\right)\right]. \quad (B.14)$$

5. At last, we obtain q^{n+1} by applying the potential contribution once more as in Step 1.,

$$(\boldsymbol{q}^{n+1})_{uvw} = \exp\left(-\omega(\boldsymbol{r}_{uvw})\frac{\Delta s}{2}\right)\left(\boldsymbol{q}_{\frac{2}{3}}^{n}\right)_{uvw}.$$
 (B.15)

In applying the potential and diffusion contributions separately as opposed to jointly, we have succeeded in solving $q(\mathbf{r}, s)$ to second order accuracy in s, i.e. the associated corrections to $q(\mathbf{r}, s)$ are of order $O(\Delta s^3)$ [1].

Appendix C

Simpsons Rule

The numerical integration method used in the current work is the Simpsons Rule for both even and odd number of intervals [70]. Given M + 1 > 6 data points, $\{(x_i, y_i)\}_{i=0}^M$, equally spaced in x, the integration rule reads

$$\int_{x_0}^{x_M} \mathrm{d}x \, y(x) \approx \Delta x \left(\frac{9}{24} y_0 + \frac{28}{24} y_1 + \frac{23}{24} y_1 + \sum_{i=3}^{M-3} y_i + \frac{23}{24} y_{M-2} + \frac{28}{24} y_{M-1} + \frac{9}{24} y_M \right), \tag{C.16}$$

where $\Delta x = x_i - x_{i-1}$. One small computational advantage offered by Eq. (C.16) over the even Simpsons Rule is that the integration weights are all equal to 1, except for the first and last three points. Moreover, periodic boundaries are frequently assumed and thus, only M needed data points are at hand. Under this assumption, Eq. (C.16) can be rewritten as

$$\int_{x_0}^{x_M} \mathrm{d}x \, y(x) \approx \Delta x \left(\frac{18}{24} y_0 + \frac{28}{24} y_1 + \frac{23}{24} y_1 + \sum_{i=3}^{M-2} y_i + \frac{23}{24} y_{M-2} + \frac{28}{24} y_{M-1} \right), \quad (C.17)$$

where we have made use of the periodicity, $y_M = y(x_M) = y(x_0) = y_0$.

Appendix D

Anderson Mixing

In this appendix, we detail our implementation of Anderson mixing in the context of SCFT. This numerical technique was pioneered by Anderson [71]. Anderson mixing was first applied to SCFT by Schmid in their study of liqid monolayers [72], and was further developed for polymeric systems by Thompson [65]. One advantage over the simple mixing scheme presented in Section 3 that is offered by Anderson mixing is a faster rate of convergence towards the desired solutions in most cases.

On one hand, simple mixing uses solely the current iteration's input and output fields, $\omega_{\beta}^{(n,\text{in})}(\mathbf{r})$ and $\omega_{\beta}^{(n,\text{out})}(\mathbf{r})$, to construct the next set, $\omega_{\beta}^{(n+1,\text{in})}(\mathbf{r})$. On the other, Anderson mixing determines $\omega_{\beta}^{(n+1,\text{in})}(\mathbf{r})$ using an optimal combination of input and output fields spanning a number of previous trials. Thus, when the history of input fields show steady signs of convergence, then the convergence process is readily expendited through Anderson mixing. Conversely, when the deviations of the fields from one iteration in the past from the next is large, then Anderson mixing performs rather poorly, frequently yielding new inputs that are farther away from the desired solutions than before. For these reasons, simple mixing is often first used to ensure a history of well-behaved input fields for numerical stability, before switching to Anderson mixing for a faster rate of convergence.

Suppose we are at the n^{th} iteration of the procedure outlined in Section. 3. We define the deviation functions associated with the monomer species, β , as

$$d_{\beta}^{(n)} = d_{\beta}^{(n)}(\boldsymbol{r}) = \omega_{\beta}^{(n,\text{out})} - \omega_{\beta}^{(n,\text{in})}, \qquad (D.18)$$

where $\omega_{\beta}^{(n,\text{in})} = \omega_{\beta}^{(n,\text{in})}(\boldsymbol{r})$ and $\omega_{\beta}^{(n,\text{out})} = \omega_{\beta}^{(n,\text{out})}(\boldsymbol{r})$. The next set of input fields are given by

$$\begin{split} \omega_{\beta}^{(n+1,\text{in})} &= \Lambda^{l} \omega_{\beta}^{(n,\text{in})} + (1 - \Lambda^{l}) \omega_{\beta}^{(n,\text{out})} \\ &- \sum_{j=1}^{l} A_{j} \left[\Lambda^{l} \left(\omega_{\beta}^{(n,\text{in})} - \omega_{\beta}^{(n-j,\text{in})} \right) + (1 - \Lambda^{l}) \left(\omega_{\beta}^{(n,\text{out})} - \omega_{\beta}^{(n-j,\text{out})} \right) \right] \\ &= \left(1 - \sum_{j=1}^{l} A_{j} \right) \left(\omega_{\beta}^{(n,\text{in})} + (1 - \Lambda^{l}) d_{\beta}^{(n)} \right) + \sum_{j=1}^{l} \left(\omega_{\beta}^{(n-j,\text{in})} + (1 - \Lambda^{l}) d_{\beta}^{(n-j)} \right) \\ &\qquad (D.19) \end{split}$$

where $l = \min(M_{\text{AM}}, n)$ and M_{AM} is the current and maximum number, respectively, of previous iterations to consider, Λ governs the relative contribution of input fields to $\omega_{\beta}^{(n+1,\text{in})}$, while A_j are the coefficients belonging to the vector \boldsymbol{A} satisfying

$$\mathbb{U}\boldsymbol{A} = \boldsymbol{D}.\tag{D.20}$$

Here, \mathbb{U} is $l \times l$ symmetric matrix,

$$(\mathbb{U})_{jk} = \sum_{\beta=A,B} \int \mathrm{d}\boldsymbol{r} \, \left(d_{\beta}^{(n)} - d_{\beta}^{(n-j)} \right) \left(d_{\beta}^{(n)} - d_{\beta}^{(n-k)} \right) \tag{D.21}$$

and \boldsymbol{D} is a vector of length l,

$$\left(\boldsymbol{D}\right)_{j} = \sum_{\beta=\mathrm{A,B}} \int \mathrm{d}\boldsymbol{r} \, d_{\beta}^{(n)} \left(d_{\beta}^{(n)} - d_{\beta}^{(n-j)}\right). \tag{D.22}$$

In our implementation of Anderson mixing, we set $\Lambda = 0.9$ and $M_{\rm AM} = 30$. Furthermore, A is obtained via LU factorization [73]. Note that U may not be invertible when the history of input and output fields are poorly behaved (i.e. an optimal combination cannot be found). We see from Eq. (3.3) that $\omega_{\beta}^{(n,in)}$ and $\omega_{\beta}^{(n,out)}$ contributes to $\omega_{\beta}^{(n+1,in)}$ in the same manner for every step using simple mixing. For Anderson mixing however, the contributions of the input and output fields from one particular past trial to $\omega_{\beta}^{(n+1,in)}$ can differ from one iteration to another, being governed by the magnitude of A_j . Thus, Anderson mixing is able to correct for the occasional misbehaved or "bad" step [65], whereas simple mixing cannot.

Appendix E

Quadratic Fitting

Given a set of three points, $\{(x_i, y_i)\}_{i=0}^2$, the corresponding fitting coefficients of the quadratic form, $y(x) = px^2 + qx + r$, reads

$$p = \frac{1}{d} \sum_{i=0}^{2} x_i (y_{\overline{i+2}} - y_{\overline{i+1}}), \qquad d = \prod_{i=0}^{2} (x_i - x_{\overline{i+1}}), \qquad (E.23)$$
$$q = \sum_{i=0}^{2} x_i^2 (y_{\overline{i+1}} - y_{\overline{i+2}}), \qquad r = \sum_{i=0}^{2} x_i x_{\overline{i+1}} (x_i - x_{\overline{i+1}}) y_{\overline{i+2}},$$

where again the line above the subscripts denotes the modulo operation with modulus 3, $\bar{i} = i \pmod{3}$.

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