

Field-Theoretic Simulations of Binary Blends of Complementary Diblock Copolymers

by

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Author's Declaration

I hereby declare that I am the sole author of this thesis. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners.

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Abstract

The phase behavior of binary blends of AB diblock copolymers of compositions f and $1 - f$ is examined using field-theoretic simulations. Highly asymmetric compositions (i.e., $f \approx 0$) behave like homopolymer blends macrophase separating into coexisting A- and B-rich phases as the segregation is increased, whereas more symmetric diblocks (i.e., $f \approx 0.5$) microphase separate into an ordered lamellar phase. In self-consistent field theory, these behaviors are separated by a Lifshitz critical point at $f = 0.2113$. However, its lower critical dimension is believed to be four, which implies that the Lifshitz point should be destroyed by fluctuations. Consistent with this, it is found to transform into a tricritical point. Furthermore, the highly swollen lamellar phase near the mean-field Lifshitz point disorders into a bicontinuous microemulsion ($B\mu E$), consisting of large, interpenetrating A- and B-rich microdomains. A $B\mu E$ has been previously reported in ternary blends of AB diblock copolymers with its parent A- and B-type homopolymers, but in that system the homopolymers have a tendency to macrophase separate. Our alternative system for creating $B\mu E$ is free of this macrophase separation.

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Dedication

This is dedicated to my parents for nurturing in me a love of asking questions.

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Chapter 1

Introduction

1.1 Microemulsion

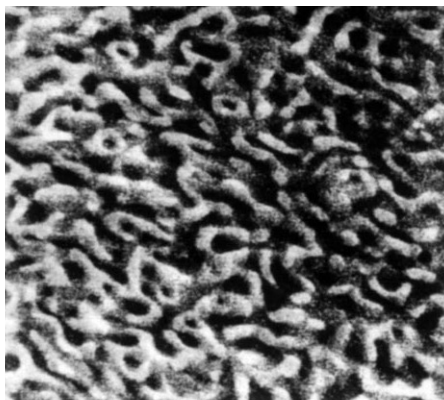


Figure 1.1: Microscopic image of a microemulsion created by a blend of poly(ethylene) and poly(ethylenepropylene) from [1]. The blend is compatibilized by adding diblocks to reach a homopolymer concentration of $\phi_h = 0.9$.

Bicontinuous microemulsion (B μ E) is a well-known phase in lyotropic liquid crystals formed from water, oil, and surfactant [2]. The surfactant acts to reduce the tension of the interface between the water and oil. When the tension of the interface approaches zero, the system can lower its free energy by taking a configuration where the two domains form a random network of interpenetrating water- and oil-rich regions separated by a monolayer

of surfactant. This random network is stabilized by the fact that it has higher configurational entropy than a periodic phase. Analogous behavior to this has been found in similar three-component polymeric systems [1], where an immiscible blend of A- and B-type homopolymers are compatibilized by a symmetric AB diblock copolymer. B μ E is an interesting system in polymers because it provides a means of blending polymers of different chemistries in order to vary material properties [3]. The fact that microemulsions have bicontinuous domains has led to them being proposed for high-tech applications such as nanoporous functional materials [4, 5], solar cells [6, 7], fuel cells [8], and rechargeable batteries [8, 9].

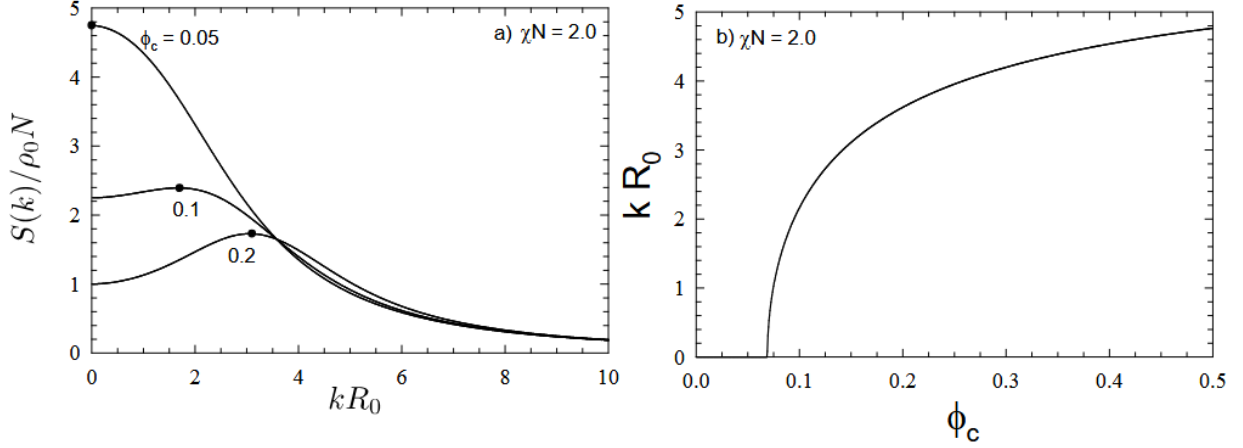


Figure 1.2: (a) Random-phase approximation structure function $S(k)$ of the three-component polymer blend. A series of blends with different ϕ_c are plotted, calculated at a segregation of $\chi N = 2$. (b) The peak position, k^* , as a function of ϕ_c , which is independent of χN in this approximation.

The formation of B μ E is related to the existence of an isotropic Lifshitz critical point in the self-consistent field theory (SCFT) phase diagram [10] shown in Fig. 1.3(c). At the Lifshitz point, the peak wavevector, k^* , in the disordered-state structure function, $S(k)$, moves from $k^* > 0$ to $k^* = 0$ as the copolymer concentration is decreased, as seen in Fig. 1.2. When $k^* > 0$, a disordered (DIS) melt will microphase separate into a lamellar (LAM) microstructure of period $D = 2\pi/k^*$ at the transition, and similarly, when $k^* = 0$, it macrophase separates into coexisting A- and B-rich (A+B) phases. In SCFT, the A+B and LAM regions are separated by three-phase A+B+LAM coexistence [1]. As the Lifshitz point is approached, the lamellar period diverges towards infinity as k^* approaches zero. The period of the lamellae cannot become macroscopic, and so the highly-swollen LAM

phase disorders into a B μ E [11]. The region where this B μ E replaces the Lifshitz point is what we would expect from the lower critical dimension of a Lifshitz point being four [12, 13]. Given that the critical dimension exceeds the three dimensions of our melt, the Lifshitz point will be destroyed by fluctuations [14]. This has already been observed in experiments by Bates et al. [1] for polyethylene (PE) and poly(ethylene-propylene) (PEP). They found that the Lifshitz point along with the A+B+LAM coexistence was replaced by a channel of B μ E extending towards low temperature ($T \rightarrow 0$) as can be seen in Fig. 1.3(a). Other chemical systems have been studied with similar conclusions about the topology of the phase diagram [15, 16, 17, 18, 3, 19, 20, 21, 22].

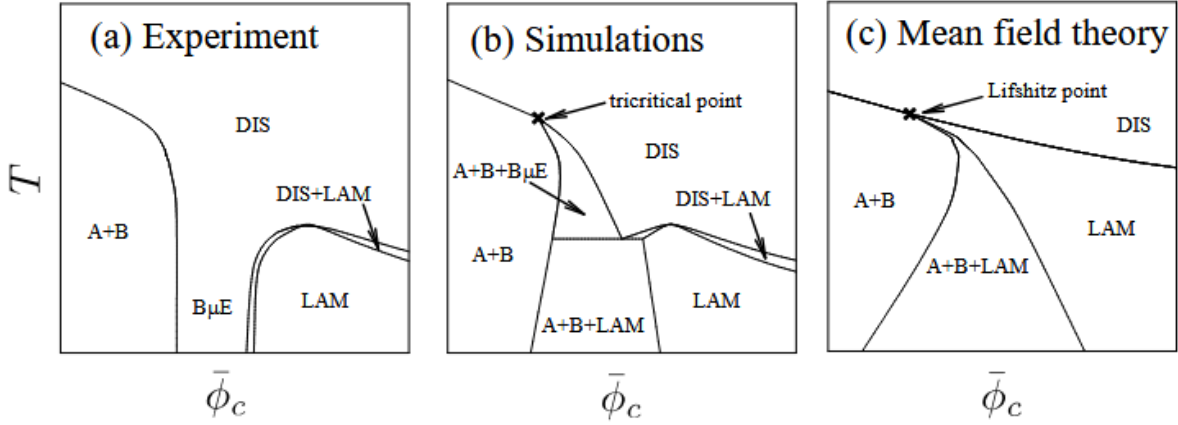


Figure 1.3: Schematic (a) experimental [11, 1], (b) FTSs [23, 24, 25], and Mean field SCFT [10] phase diagrams plotted in terms of copolymer volume fraction, ϕ_c , and temperature, T . The labels A, B, LAM, DIS, and B μ E denote A-homopolymer-rich, B-homopolymer-rich, lamellar, disordered, and bicontinuous microemulsion, respectively.

Theoretical calculations of the phase diagram from field-theoretic simulations (FTSs), Fig. 1.3(b), have also found that the Lifshitz point is destroyed by fluctuations [23, 24, 25]. They found that the B μ E channel seen in experiments is unstable and should macrophase separate into a three-phase coexistence. This phase separation is caused by the weakness of the long-range attraction that exists between the diblock monolayers separating the lamellae [26, 27, 28]. As homopolymer is added, the period of the LAM phase swells until it reaches the preferred separation of the monolayers. After this point any additional homopolymer macrophase separates forming two coexisting homopolymer-rich phases. This leads to the A+B+LAM coexistence predicted by SCFT [29] and similarly

to the A+B+B μ E coexistence observed in FTSS [24, 25]. The coexistence between B μ E and homopolymer-rich phases was later found in experiments [9, 22]. The phase diagram still contains a single-phase B μ E region, but the problem is that it may be difficult to distinguish from the A+B+B μ E coexistence region due to the difference in time scales involved in the formation of the B μ E and phase separation of the homopolymers. A pure B μ E morphology can potentially be created in either region, but its long-term stability will be limited if the system parameters correspond to the coexistence region. For some chemistries, one solution is to stabilize the B μ E structure by cross-linking one or both of the polymer components [4, 22]. Alternatively, one could just use another system for which this type of macrophase separation is prohibited.

A system consisting of only two components would prohibit three-phase coexistence. Inspired by this, we will study a melt of two complementary diblocks, one with volume fraction f and the other with volume fraction $1 - f$. A 50/50 blend of these two polymers will always have an even monomer composition i.e., same amount of A and B monomers. This blend has the same general type of phase behaviour as the three-component melt. When $f = 0$ or 1 , we have a blend of two homopolymers with a second-order transition to a macrophase separated state and a peak wavevector at $k^* = 0$. However, when $f = 0.5$, the two diblocks become equivalent and therefore we get a symmetric single-component diblock melt with $k^* > 0$ which microphase separates into the LAM phase. As we will see later in this work, there exists an intermediate f where k^* becomes non-zero producing a Lifshitz point. However, due to the fact that the melt is a blend of only two components, there cannot exist a region of three-phase coexistence. Thus, this system has the potential to form a large region of stable B μ E. Encouraged by the potential of a stable polymeric microemulsion, we study the phase behaviour of this system.

1.2 Polymers

Polymers are long chains of repeating units called monomers linked together by covalent bonds. These units are compounds like isoprene, propylene, or styrene, but in the interest of generality, we will just refer to them as A and B . The monomers are generally able to rotate freely around the bond. This means that the number of configurations of the polymer is very large [30]. This configuration entropy of the polymer is an important quantity we need to calculate. One simple model for polymers is the freely-jointed chain model. Instead of restricting the azimuthal angle between adjacent monomers to a fixed value, as it would be for carbon-carbon bonds, we allow the bonds to take any angle. We can think of this as a coarse-graining step where we group a number of monomers into

a single effective segment by averaging over the degrees of freedom. We can now allow arbitrary angles between our segments [30]. We can represent the statistics of the polymer by a probability distribution, $P_1(\mathbf{r}_N, N)$, over the configuration of the polymer, where the variables are N , the total number of segments, and $\mathbf{r}_N$, the position of the N^{th} segment.

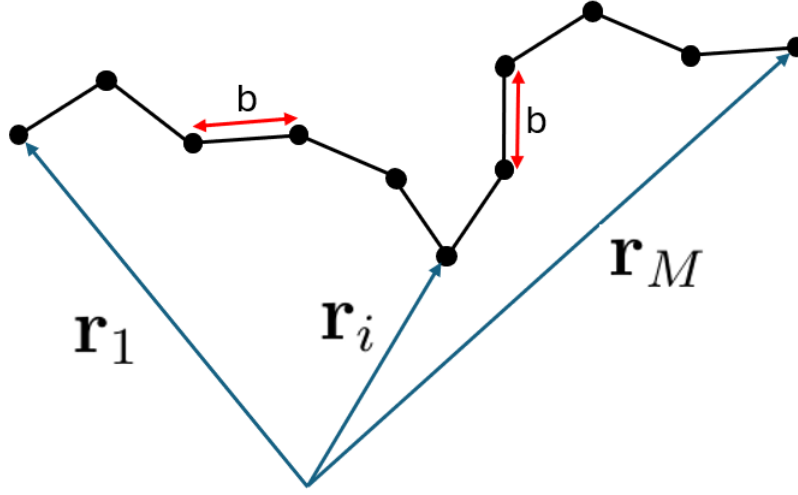


Figure 1.4: Diagram of freely jointed chain model.

To calculate this distribution, we can start at one end of the polymer by specifying the segment distribution $P_1(\mathbf{r}_1)$. We can then build up the chain by sequentially adding segments to the end of the chain. We know that the distribution is uniform with a fixed bond length b , so it has the form

$$P_2(\mathbf{r}_{i+1}, \mathbf{r}_i) = \frac{\delta(\|\mathbf{x}_i\| - b)}{4\pi b^2}, \quad (1.1)$$

where we have defined the bond vector $\mathbf{x}_i = \mathbf{r}_{i+1} - \mathbf{r}_i$. One important observable is the end-to-end length of the chain, which can be calculated directly from

$$\mathbf{R} = \mathbf{r}_N - \mathbf{r}_1 = \sum_{i=1}^{N-1} \mathbf{x}_i. \quad (1.2)$$

We can calculate the average length directly by symmetry to find $\langle \mathbf{R} \rangle = \mathbf{0}$. The second

moment is then

$$R_0^2 = \langle \mathbf{R} \cdot \mathbf{R} \rangle = \sum_{i=1}^{N-1} \sum_{j=1}^{N-1} \langle \mathbf{x}_i \cdot \mathbf{x}_j \rangle = \sum_{i=1}^{N-1} \sum_{j=1}^{N-1} b^2 \delta_{i,j} = b^2(N-1). \quad (1.3)$$

We use the fact that vectors between monomers are independently distributed, and thus $\langle \mathbf{x}_i \cdot \mathbf{x}_j \rangle = b^2 \delta_{i,j}$. This tells us that $R_0 = b\sqrt{N-1}$ so that we can use this to classify the length of the polymer, the so-called average end-to-end vector.

Next we solve the distribution of the i^{th} monomer by solving a recurrence relationship that comes from building the chain up to the full length N step by step.

$$P_1(\mathbf{r}_{i+1}, i+1) = \int d\mathbf{r}_i P_2(\mathbf{x}_i) P_1(\mathbf{r}_i, i) = \frac{1}{4\pi b^2} \int d\mathbf{r}_i \delta(\|\mathbf{r}_{i+1} - \mathbf{r}_i\| - b) P_1(\mathbf{r}_i, i). \quad (1.4)$$

For those familiar with stochastic processes, this is the Chapman–Kolmogorov equation [31, 32]. We can solve Eq. 1.4 in Fourier (frequency) space using the Fourier transform $f(\mathbf{k}) = \int d\mathbf{x} e^{-i\mathbf{k} \cdot \mathbf{x}} f(\mathbf{r})$

$$\begin{aligned} P_1(\mathbf{k}, i+1) &= \frac{1}{4\pi b^2} \left(\int d\mathbf{x} e^{-i\mathbf{k} \cdot \mathbf{x}} \delta(\|\mathbf{x}\| - b) \right) P_1(\mathbf{k}, i) \\ &= \text{sinc}(b\|\mathbf{k}\|) P_1(\mathbf{k}, i), \end{aligned} \quad (1.5)$$

where we used the fact that the delta function constrains $\mathbf{x}$ to a sphere of radius b and this gives $\int d\mathbf{x} e^{-i\mathbf{k} \cdot \mathbf{x}} \delta(\|\mathbf{x}\| - b) = 4\pi b^2 \text{sinc}(b\|\mathbf{k}\|)$ with $\text{sinc}(x) = \sin(x)/x$. The result is a simple equation to solve, with an initial condition $P_1(\mathbf{k}, 1)$. The solution is

$$P_1(\mathbf{k}, N) = \text{sinc}^N(b\|\mathbf{k}\|) P_1(\mathbf{k}, 1). \quad (1.6)$$

With this, we have now solved for the distribution of the chain. The final step is to transform back to real space, which requires the evaluation of several convolutions.

There is a useful simplification that occurs if we coarse-grain the chain by grouping l segments together to get

$$P_1(\mathbf{k}, N) = \left(\text{sinc}^l(b\|\mathbf{k}\|) \right)^{\frac{N}{l}} P_1(\mathbf{k}, 1). \quad (1.7)$$

To simplify this note that for small x we can Taylor expand $\text{sinc}(x) \approx 1 - \frac{1}{6}x^2$ this lets us write

$$\text{sinc}^l(b\|\mathbf{k}\|) \approx \left(1 - \frac{1}{6}b^2\|\mathbf{k}\|^2 \right)^l \approx e^{-\frac{1}{6}b^2l\|\mathbf{k}\|^2}. \quad (1.8)$$

Putting this back into Eq. 1.7 gives

$$P_1(\mathbf{k}, N) = e^{-\frac{1}{6}b^2N\|\mathbf{k}\|^2} P_1(\mathbf{k}, 1). \quad (1.9)$$

This shows that as the number of monomers we group into a coarse-grained segment increases the correlations between segments become Gaussian. This is what one might expect from the central limit theorem. These Gaussian correlations motivate us to study a model with explicit Gaussian correlations, the so-called bead-spring model.

1.3 Bead-Spring Polymer in a Field

As we saw in the previous section, the correlation along the chain becomes Gaussian as the size of the coarse-grained segments get larger. This is a general feature of all non-interacting chain models [30, 32, 33, 34]. This is due to the fact that if we coarse grain the chain over l degrees of freedom, we get a sum of l random variables. The central limit theorem says that the distribution of this sum must converge to a Gaussian. This means in the limit we get a model with perfectly Gaussian correlations between adjacent segments, a so-called bead-spring model. After this process, we now have a polymer with N coarse-grained segments (or beads) that have Gaussian correlations between them of the form

$$P_2(\mathbf{r}_{i+1}, \mathbf{r}_i) = \left(\frac{3}{2\pi a^2}\right)^{3/2} e^{-\frac{3}{2a^2}\|\mathbf{r}_{i+1}-\mathbf{r}_i\|^2}. \quad (1.10)$$

This is where the name bead-spring model comes from, and why we can think of the polymer as a long chain of beads connected by harmonic springs. The spring force comes from the entropic need to have segments be Gaussian correlated. We have seen this arise naturally from coarse-graining the polymer. To see this, imagine you have a polymer chain with two fixed points $\mathbf{r}_i$ and $\mathbf{r}_j$. The entropic interaction gives a free energy that is a function of only the distance between the points, $U(\|\mathbf{r}_i - \mathbf{r}_j\|)$. Now this energy must have a minimum at the equilibrium spacing between the points denoted L . We can expand the free energy around the minimum to get $U(\|\mathbf{r}_i - \mathbf{r}_j\|) = U(L) + \frac{1}{2}U'(L)\|\mathbf{r}_i - \mathbf{r}_j\|^2$.

This shows that for any chain near its equilibrium configuration, the change in entropic free energy due to small displacements behaves like a harmonic spring,

$$\frac{E(\mathbf{r}_{i+1}, \mathbf{r}_i)}{k_B T} = \frac{3}{2a^2}\|\mathbf{r}_{i+1} - \mathbf{r}_i\|^2, \quad (1.11)$$

where k_B is Boltzmann constant and T is the temperature of the system. We can calculate the average length of one spring as

$$\langle r^2 \rangle = \left(\frac{3}{2\pi a^2}\right)^{3/2} \int d\mathbf{r} r^2 e^{-\frac{3}{2a^2}r^2} = a^2, \quad (1.12)$$

so we see that the statistical segment length a is the average distance between monomers.

Commonly, we want to study polymers in some environment. A simple approach is to add an external field, $W(\mathbf{r})$. Note that we choose the units of W to correspond to a dimensionless energy per bead. With this we can calculate the total energy of the polymer in a field $W(\mathbf{r})$ with the Hamiltonian

$$\frac{H(\{\mathbf{r}_i\}; [W])}{k_B T} = \frac{3}{2a^2} \sum_{i=1}^{N-1} \|\mathbf{r}_{i+1} - \mathbf{r}_i\|^2 + \sum_{i=1}^N W_i(\mathbf{r}_i). \quad (1.13)$$

Now we want to do the statistical mechanics of the bead-spring polymer in a field. We start with the partition function for a single chain in a field $W(\mathbf{r})$,

$$\begin{aligned} Q(N; [W]) &= \frac{1}{V} \int \left(\prod_{i=1}^N d\mathbf{r}_i \right) e^{-\frac{H(\{\mathbf{r}_i\}; [W])}{k_B T}} \\ &= \frac{1}{V} \int \left(\prod_{i=1}^N d\mathbf{r}_i \right) e^{-\frac{3}{2a^2} \sum_{i=1}^{N-1} \|\mathbf{r}_{i+1} - \mathbf{r}_i\|^2 - \sum_{i=1}^N W_i(\mathbf{r}_i)}. \end{aligned} \quad (1.14)$$

Next, we define the chain propagator such that it is the distribution of the N^{th} bead,

$$q(\mathbf{r}_N, N; [W]) = \frac{1}{V} \int \prod_{i=1}^{N-1} \left(\frac{3}{2a^2\pi} \right)^{\frac{3}{2}} d\mathbf{r}_i e^{-\frac{3}{2a^2} \sum_{i=1}^{N-1} \|\mathbf{r}_{i+1} - \mathbf{r}_i\|^2 - \sum_{i=1}^N W_i(\mathbf{r}_i)}. \quad (1.15)$$

This means that we can calculate the single-chain partition function from the normalization of the chain propagator as $Q(N; [W]) = \frac{1}{V} \int d\mathbf{r}_N q(\mathbf{r}_N, N; [W])$. To proceed, we need a way to solve for the chain propagator. First, note that we can reorder the integrals by factoring out the integral over $\mathbf{r}_{N-1}$ to get

$$\begin{aligned} q(\mathbf{r}_N, N; [W]) &= e^{-W_N(\mathbf{r}_N)} \int \left(\frac{3}{2a^2\pi} \right)^{\frac{3}{2}} d\mathbf{r}_{N-1} e^{-\frac{3}{2a^2} \|\mathbf{r}_N - \mathbf{r}_{N-1}\|^2} \times \\ &\quad \int \prod_{i=1}^{N-2} \left(\frac{3}{2a^2\pi} \right)^{\frac{3}{2}} d\mathbf{r}_i e^{-\frac{3}{2a^2} \sum_{i=1}^{N-2} \|\mathbf{r}_{i+1} - \mathbf{r}_i\|^2 - \sum_{i=1}^{N-1} W_i(\mathbf{r}_i)}. \end{aligned} \quad (1.16)$$

However, we know that the last series of integrals is just the definition of the single-chain propagator [35, 36],

$$q(\mathbf{r}_{N-1}, N-1; [W]) = \int \prod_{i=1}^{N-2} \left(\frac{3}{2a^2\pi} \right)^{\frac{3}{2}} d\mathbf{r}_i e^{-\frac{3}{2a^2} \sum_{i=1}^{N-2} \|\mathbf{r}_{i+1} - \mathbf{r}_i\|^2 - \sum_{i=1}^{N-1} W_i(\mathbf{r}_i)}. \quad (1.17)$$

Therefore, we obtain a recurrence relationship for $q(\mathbf{r}_N, N; [W])$ of the form

$$q(\mathbf{r}_N, N; [W]) = e^{-W_N(\mathbf{r}_N)} \int d\mathbf{r}_{N-1} \left(\frac{3}{2a^2\pi} \right)^{\frac{3}{2}} e^{-\frac{3}{2a^2} \|\mathbf{r}_N - \mathbf{r}_{N-1}\|^2} q(\mathbf{r}_{N-1}, N-1; [W]). \quad (1.18)$$

To simplify, we define the functions

$$\begin{aligned} h(\mathbf{r}; [W]) &= e^{-W(\mathbf{r})}, \\ g(\mathbf{R}) &= \left(\frac{3}{2a^2\pi} \right)^{\frac{3}{2}} e^{-\frac{3}{2a^2} \|\mathbf{R}\|^2}. \end{aligned} \quad (1.19)$$

Inserting these definitions in Eq. 1.18 gives

$$q(\mathbf{r}_N, N; [W]) = h(\mathbf{r}_N; [W]) \int d\mathbf{r}_{N-1} g(\mathbf{r}_N - \mathbf{r}_{N-1}) q(\mathbf{r}_{N-1}, N-1; [W]). \quad (1.20)$$

Note that the integral is a convolution, and so it is a simple multiplication in Fourier space. We can use the Fourier transform to get

$$q(\mathbf{r}_N, N; [W]) = h(\mathbf{r}_N; [W]) \mathcal{F}^{-1}[g(\mathbf{k}) q(\mathbf{k}, N-1; [W])], \quad (1.21)$$

where the Fourier transform of $g(\mathbf{r})$ is $g(\mathbf{k}) = \exp\left(-\frac{a^2}{6} \|\mathbf{k}\|^2\right)$. In general the above equation must be solved numerically [37, 36], however, in the special case that $W(\mathbf{r}) = 0$ so that $h(\mathbf{r}) = 1$, we can solve it exactly to get

$$q(\mathbf{k}, N; [0]) = g(\mathbf{k})^{N-1} = \exp\left(-\frac{a^2(N-1)}{6} \|\mathbf{k}\|^2\right) q(\mathbf{k}, 1; [0]). \quad (1.22)$$

Without loss of generality we can fix the tail of the polymer at $\mathbf{r}_1 = \mathbf{0}$ so that $q(\mathbf{k}, 1; [0]) = 1$, then in real space we get

$$q(\mathbf{r}_N, N; [0]) = \left(\frac{3}{2a^2(N-1)\pi} \right)^{\frac{3}{2}} \exp\left(-\frac{3}{2a^2(N-1)} \|\mathbf{r}_N\|^2\right). \quad (1.23)$$

Note that the average end-to-end distance of the polymer can be calculated from this as

$$R_0^2 = \langle ||\mathbf{r}_N - \mathbf{r}_1||^2 \rangle = \langle ||\mathbf{r}_N||^2 \rangle = \langle \mathbf{r}_N \cdot \mathbf{r}_N \rangle, \quad (1.24)$$

where we have fixed $\mathbf{r}_1 = \mathbf{0}$. Evaluating the integral in Eq. 1.24 yields

$$\begin{aligned} R_0^2 &= \frac{1}{Q(N; [0])} \int d\mathbf{r}_N (\mathbf{r}_N \cdot \mathbf{r}_N) \exp\left(-\frac{3}{2a^2(N-1)} \mathbf{r}_N \cdot \mathbf{r}_N\right) \\ &= \sum_{i=1}^3 \frac{1}{3} a^2 (N-1) = a^2 (N-1). \end{aligned} \quad (1.25)$$

In the limit $N \rightarrow \infty$, we recover the expected result of $R_0^2 = a^2 N$.

Another important thing to calculate is the probability of going from a point $\mathbf{r}_1$ to $\mathbf{r}_2$, which can be calculated as

$$\begin{aligned} \langle \delta(\mathbf{r}_j - \mathbf{r}_2) \delta(\mathbf{r}_i - \mathbf{r}_1) \rangle_0 &= \langle \delta(\mathbf{r}_j - \mathbf{r}_2 + \mathbf{r}_1) \delta(\mathbf{r}_i) \rangle_0 \\ &= \frac{1}{V^2 Q[N; 0]} q(\mathbf{r}_2 - \mathbf{r}_1, |j - i| + 1; [0]) \\ &= \frac{1}{V^2} \exp\left(-\frac{3}{2a^2|j - i|} |\mathbf{r}_2 - \mathbf{r}_1|^2\right). \end{aligned} \quad (1.26)$$

This follows from the fact that the propagator is isotropic. Now we can see that we can interpret the propagator as the probability of a chain of length $|j - i|$ going from point $\mathbf{r}_1$ to point $\mathbf{r}_2$.

1.4 Symmetric Blend of Diblocks

The system we are considering, for the creation of microemulsion, is a binary blend of diblock copolymers. This is a melt of two diblocks labeled $\alpha = 1$ and $\alpha = 2$. Each diblock has two blocks made of different chemistries labeled $\kappa = A$ and $\kappa = B$, and each block has a number of monomers $N_{\kappa, \alpha}$. We label the location of the s^{th} monomer on the i^{th} polymer as $\mathbf{r}_{i, s}$.

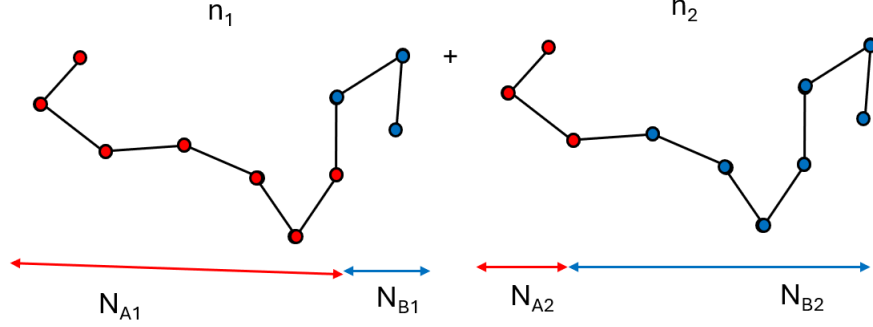


Figure 1.5: Diagram of a blend of n_1 polymers of type 1 and n_2 polymers of type 2. In the diagram the type 1 polymers have $N_{A1} = 7$ monomers of type A, and $N_{B1} = 3$ monomers of type B. Now the blend is complementary, so we can see that we have n_2 polymers of type 2 and each has $N_{A2} = 3$ monomers of type A, and $N_{B2} = 7$ monomers of type B.

There is an interaction between the diblocks that comes from contacts between polymers, with associated energies ϵ_{AA} , ϵ_{BB} , and ϵ_{AB} depending on the types of monomers in contact. When the range of these interactions is small compared to the polymer length scale R_0 . Then the interactions are well approximated by delta functions checking if the centre of mass of the two beads are overlapping [30, 32]. With this, we can write the total internal energy of the melt by counting all the contacts, with sums over delta functions, and multiplying by the associated energy per contact ϵ_{ij} , which has units of energy times

density. This gives the total energy as

$$\begin{aligned}
U = & \frac{-1}{2\rho_0^2} \sum_{i,j=1}^{n_1} \left(\epsilon_{AA} \sum_{s,t=1}^{N_{A1}} \delta(\mathbf{r}_{i,s} - \mathbf{r}_{j,t}) + \epsilon_{BB} \sum_{s,t=1}^{N_{B1}} \delta(\mathbf{r}_{i,s+N_{A1}} - \mathbf{r}_{j,t+N_{A1}}) \right) \\
& - \frac{2\epsilon_{AB}}{2\rho_0^2} \left(\sum_{i,j=1}^{n_1} \sum_{s=1}^{N_{A1}} \sum_{t=1}^{N_{B1}} \delta(\mathbf{r}_{i,s} - \mathbf{r}_{j,t+N_{A1}}) + \sum_{i,j=1}^{n_2} \sum_{s=1}^{N_{A2}} \sum_{t=1}^{N_{B2}} \delta(\mathbf{r}_{i,s} - \mathbf{r}_{j,t+N_{A2}}) \right) \\
& - \frac{1}{2\rho_0^2} \sum_{i,j=1}^{n_2} \left(\epsilon_{AA} \sum_{s,t=1}^{N_{A2}} \delta(\mathbf{r}_{i,s} - \mathbf{r}_{j,t}) + \epsilon_{BB} \sum_{s,t=1}^{N_{B2}} \delta(\mathbf{r}_{i,s+N_{A2}} - \mathbf{r}_{j,t+N_{A2}}) \right) \\
& - \frac{2}{2\rho_0^2} \sum_{i=1}^{n_1} \sum_{j=1}^{n_2} \left(\epsilon_{AA} \sum_{s=1}^{N_{A1}} \sum_{t=1}^{N_{A2}} \delta(\mathbf{r}_{i,s} - \mathbf{r}_{j,t}) + \epsilon_{BB} \sum_{s=1}^{N_{B1}} \sum_{t=1}^{N_{B2}} \delta(\mathbf{r}_{i,s+N_{A1}} - \mathbf{r}_{j,t+N_{A2}}) \right) \\
& - \frac{2\epsilon_{AB}}{2\rho_0^2} \sum_{i=1}^{n_1} \sum_{j=1}^{n_2} \left(\sum_{s=1}^{N_{A1}} \sum_{t=1}^{N_{B2}} \delta(\mathbf{r}_{i,s} - \mathbf{r}_{j,t+N_{A2}}) + \sum_{s=1}^{N_{B1}} \sum_{t=1}^{N_{A2}} \delta(\mathbf{r}_{i,s+N_{A1}} - \mathbf{r}_{j,t}) \right).
\end{aligned} \tag{1.27}$$

We can simplify this sum by defining the number of contacts between a polymer of type $\alpha = 1, 2$ blocks $\kappa = A, B$ with a polymer of type $\beta = 1, 2$ blocks $\gamma = A, B$ as a function $u_{\kappa,\gamma;\alpha,\beta}$. For example, if we want $\kappa = A$, $\gamma = B$, $\alpha = 1$, and $\beta = 2$, then we get

$$u_{A,B;1,2} = \frac{-1}{2\rho_0^2} \sum_{i=1}^{n_1} \sum_{j=1}^{n_2} \sum_{s=1}^{N_{A1}} \sum_{t=1}^{N_{B2}} \delta(\mathbf{r}_{i,s} - \mathbf{r}_{j,t+N_{A2}}). \tag{1.28}$$

Substituting this in allows us write the internal energy as

$$\begin{aligned}
U = & \epsilon_{AA} u_{A,A;1,1} + \epsilon_{BB} u_{B,B;1,1} + \epsilon_{AB} u_{A,B;1,1} + \epsilon_{AB} u_{A,B;2,2} \\
& + \epsilon_{AA} u_{A,A;2,2} + \epsilon_{BB} u_{B,B;2,2} + 2\epsilon_{AA} u_{A,A;1,2} + 2\epsilon_{BB} u_{B,B;1,2} \\
& + 2\epsilon_{AB} u_{A,B;1,2} + 2\epsilon_{AB} u_{A,B;2,1}.
\end{aligned} \tag{1.29}$$

We still need to simplify this more. To do this, we define the concentrations of the different

blocks as

$$\begin{aligned}
\phi_{A1}(\mathbf{r}) &= \frac{1}{\rho_0} \sum_{i=1}^{n_1} \sum_{s=1}^{N_{A1}} \delta(\mathbf{r}_{i,s} - \mathbf{r}), \\
\phi_{B1}(\mathbf{r}) &= \frac{1}{\rho_0} \sum_{i=1}^{n_1} \sum_{t=N_{A1}+1}^N \delta(\mathbf{r}_{i,t} - \mathbf{r}), \\
\phi_{A2}(\mathbf{r}) &= \frac{1}{\rho_0} \sum_{j=1}^{n_2} \sum_{s=1}^{N_{A2}} \delta(\mathbf{r}_{j,s} - \mathbf{r}), \\
\phi_{B2}(\mathbf{r}) &= \frac{1}{\rho_0} \sum_{j=1}^{n_2} \sum_{t=N_{A2}+1}^N \delta(\mathbf{r}_{j,t} - \mathbf{r}).
\end{aligned} \tag{1.30}$$

Now, we use the identity $\delta(\mathbf{x} - \mathbf{y}) = \int d\mathbf{r} \delta(\mathbf{x} - \mathbf{r}) \delta(\mathbf{y} - \mathbf{r})$. This is just the sifting property of the delta function applied to another delta function. This allows us to simplify $u_{\kappa,\gamma;\alpha,\beta}$ in terms of the concentrations. Take for example

$$\begin{aligned}
u_{A,B;1,2} &= \frac{-1}{2\rho_0^2} \int d\mathbf{r} \sum_{i=1}^{n_1} \sum_{s=1}^{N_{A1}} \delta(\mathbf{r}_{i,s} - \mathbf{r}) \sum_{j=1}^{n_2} \sum_{t=1}^{N_{B2}} \delta(\mathbf{r} - \mathbf{r}_{j,t+N_{A2}}) \\
&= - \int d\mathbf{r} \phi_{A1}(\mathbf{r}) \phi_{B2}(\mathbf{r}).
\end{aligned} \tag{1.31}$$

In general, we get

$$u_{\kappa,\gamma;\alpha,\beta} = - \int d\mathbf{r} \phi_{\kappa\alpha}(\mathbf{r}) \phi_{\gamma\beta}(\mathbf{r}). \tag{1.32}$$

Now, we can substitute these density's back into Eq. 1.29 to re-express the total interaction energy as

$$\begin{aligned}
U &= - \int d\mathbf{r} \left(\epsilon_{AA} \phi_{A1}(\mathbf{r}) \phi_{A1}(\mathbf{r}) + \epsilon_{AA} \phi_{A1}(\mathbf{r}) \phi_{A2}(\mathbf{r}) + \epsilon_{AA} \phi_{A2}(\mathbf{r}) \phi_{A2}(\mathbf{r}) \right. \\
&\quad + \epsilon_{BB} \phi_{B1}(\mathbf{r}) \phi_{B1}(\mathbf{r}) + \epsilon_{BB} \phi_{B1}(\mathbf{r}) \phi_{B2}(\mathbf{r}) + \epsilon_{BB} \phi_{B2}(\mathbf{r}) \phi_{B2}(\mathbf{r}) \\
&\quad \left. + 2\epsilon_{AB} \phi_{A1}(\mathbf{r}) \phi_{B1}(\mathbf{r}) + 2\epsilon_{AB} \phi_{A2}(\mathbf{r}) \phi_{B2}(\mathbf{r}) + 2\epsilon_{AB} \phi_{A1}(\mathbf{r}) \phi_{B2}(\mathbf{r}) + 2\epsilon_{AB} \phi_{A2}(\mathbf{r}) \phi_{B1}(\mathbf{r}) \right).
\end{aligned} \tag{1.33}$$

If we define the total A concentration $\phi_A(\mathbf{r}) = \phi_{A1}(\mathbf{r}) + \phi_{A2}(\mathbf{r})$ and the total B concentration $\phi_B(\mathbf{r}) = \phi_{B1}(\mathbf{r}) + \phi_{B2}(\mathbf{r})$, we then obtain

$$U = - \int d\mathbf{r} \left(\frac{1}{2} \epsilon_{AA} \phi_A^2(\mathbf{r}) + \frac{1}{2} \epsilon_{BB} \phi_B^2(\mathbf{r}) + \epsilon_{AB} \phi_A(\mathbf{r}) \phi_B(\mathbf{r}) \right). \quad (1.34)$$

However, it is convenient to write this in a form involving the two concentrations

$$\begin{aligned} \phi_+(\mathbf{r}) &= \phi_A(\mathbf{r}) + \phi_B(\mathbf{r}), \\ \phi_-(\mathbf{r}) &= \phi_A(\mathbf{r}) - \phi_B(\mathbf{r}). \end{aligned} \quad (1.35)$$

Inverting these gives

$$\begin{aligned} \phi_A(\mathbf{r}) &= \frac{1}{2}(\phi_+(\mathbf{r}) + \phi_-(\mathbf{r})), \\ \phi_B(\mathbf{r}) &= \frac{1}{2}(\phi_+(\mathbf{r}) - \phi_-(\mathbf{r})). \end{aligned} \quad (1.36)$$

Now, plugging this into the energy and simplifying gives

$$\begin{aligned} U = - \int d\mathbf{r} \left(\frac{2\epsilon_{AB} + \epsilon_{AA} + \epsilon_{BB}}{8} \phi_+^2(\mathbf{r}) \right. \\ \left. + \frac{\epsilon_{AA} - \epsilon_{BB}}{8} \phi_+(\mathbf{r}) \phi_-(\mathbf{r}) + \frac{-2\epsilon_{AB} + \epsilon_{AA} + \epsilon_{BB}}{8} \phi_-^2(\mathbf{r}) \right). \end{aligned} \quad (1.37)$$

Let us define $\chi = \chi_{--} = \frac{2\epsilon_{AB} - \epsilon_{AA} - \epsilon_{BB}}{2\rho_0 k_B T}$ as the Flory-Huggins interaction parameter. We can see that the Flory-Huggins parameter is unitless as the units of the ϵ 's cancel the units of $\rho_0 k_B T$. Note that $\chi \propto 1/T$, so in the high temperature limit our interactions vanish. This is what we expect because the system should be dominated by the entropic free energy from the configurations of the polymer chains. We can also define the other parameters $\chi_{++} = \frac{2\epsilon_{AB} + \epsilon_{AA} + \epsilon_{BB}}{2\rho_0 k_B T}$ as well as $\chi_{-+} = \chi_{+-} = \frac{\epsilon_{AA} - \epsilon_{BB}}{4\rho_0 k_B T}$. Inserting the definitions into Eq. 1.37 gives

$$\frac{U}{k_B T} = - \rho_0 \int d\mathbf{r} \frac{1}{4} \begin{bmatrix} \phi_-(\mathbf{r}) & \phi_+(\mathbf{r}) \end{bmatrix} \begin{bmatrix} \chi_{--} & \chi_{-+} \\ \chi_{+-} & \chi_{++} \end{bmatrix} \begin{bmatrix} \phi_-(\mathbf{r}) \\ \phi_+(\mathbf{r}) \end{bmatrix}. \quad (1.38)$$

Let's define

$$\boldsymbol{\chi} = \begin{bmatrix} \chi_{--} & \chi_{-+} \\ \chi_{+-} & \chi_{++} \end{bmatrix} \quad (1.39)$$

,

$$\boldsymbol{\phi} = \begin{bmatrix} \phi_-(\mathbf{r}) \\ \phi_+(\mathbf{r}) \end{bmatrix} \quad (1.40)$$

Putting this all together we get a simplified version of the interaction of the form

$$\frac{U}{k_B T} = -\frac{\rho_0}{4} \int d\mathbf{r} \boldsymbol{\phi}^T \boldsymbol{\chi} \boldsymbol{\phi}. \quad (1.41)$$

With this, we have a simple form for the internal energy of the melt that comes from contact energies between the polymers. The next step is to find a simplified way to calculate the partition function [38], so that we can evaluate the thermal average of observables.

1.5 Particle-to-Field Transformation

From the previous section, we know that interactions occur between the A and B segments. To apply this to a melt, we need to write the partition function for a fixed number of polymers n . This corresponds to the canonical ensemble, which has the form

$$\mathcal{Z} = \int \prod_{\alpha=1}^{n_1} \prod_{\beta=1}^{n_2} \prod_{i=1}^N \prod_{j=1}^N \frac{d\mathbf{r}_{\beta,j} d\mathbf{r}_{\alpha,i} d\mathbf{p}_{\beta,j} d\mathbf{p}_{\alpha,i}}{n_1! n_2! h^{3(n_1 N + n_2 N)} V^{n_1 + n_2}} \delta[1 - \phi_+(\mathbf{r})] e^{-\frac{\mathcal{H}_p}{k_B T}}. \quad (1.42)$$

The factors of $1/n!$ account for the indistinguishability of the polymers, and the delta function enforces incompressibility. The constant h is Planck's constant, V is the volume of the system, and the Hamiltonian for the particle-based system is

$$\begin{aligned} \frac{\mathcal{H}_p}{k_B T} &= \frac{1}{2m} \sum_{\alpha=1}^{n_1} \sum_{i=1}^N \|\mathbf{p}_{\alpha,i}\|^2 + \frac{1}{2m} \sum_{\beta=1}^{n_2} \sum_{j=1}^N \|\mathbf{p}_{\beta,j}\|^2 \\ &+ \frac{3}{2a^2} \sum_{\alpha=1}^{n_1} \sum_{i=1}^{N-1} \|\mathbf{r}_{\alpha,i+1} - \mathbf{r}_{\alpha,i}\|^2 + \frac{3}{2a^2} \sum_{\beta=1}^{n_2} \sum_{j=1}^{N-1} \|\mathbf{r}_{\beta,j+1} - \mathbf{r}_{\beta,j}\|^2 \\ &- \rho_0 \int d\mathbf{r} \frac{1}{4} \boldsymbol{\phi}^T \boldsymbol{\chi} \boldsymbol{\phi}. \end{aligned} \quad (1.43)$$

Integrating over the momenta gives

$$\Lambda^{-3(n_1 N + n_2 N)} = \int \prod_{\alpha,\beta,i,j} \frac{d\mathbf{p}_{\beta,j} d\mathbf{p}_{\alpha,i}}{h^{3(n_1 N + n_2 N)}} e^{-\sum_{\alpha,i} \frac{\|\mathbf{p}_{\alpha,i}\|^2}{2mk_B T} - \sum_{\beta,j} \frac{\|\mathbf{p}_{\beta,j}\|^2}{2mk_B T}}, \quad (1.44)$$

where the constant Λ is

$$\Lambda^{-1} = \frac{1}{h} \int dp e^{-\frac{p^2}{2mk_B T}} = \sqrt{\frac{2\pi mk_B T}{h^2}}. \quad (1.45)$$

We now define a measure for the particle-based configurational integral

$$\tilde{\mathcal{D}}\Xi = \prod_{\alpha=1}^{n_1} \prod_{\beta=1}^{n_2} \prod_{i=1}^N \prod_{j=1}^N \frac{d\mathbf{r}_{\beta,j} d\mathbf{r}_{\alpha,i}}{V^{n_1+n_2}} e^{-\frac{3}{2a^2} \sum_{\alpha,i}^{n_1, N-1} \|\mathbf{r}_{\alpha,i+1} - \mathbf{r}_{\alpha,i}\|^2 - \frac{3}{2a^2} \sum_{\beta,j}^{n_2, N-1} \|\mathbf{r}_{\beta,j+1} - \mathbf{r}_{\beta,j}\|^2}. \quad (1.46)$$

Since Λ is a multiplicative constant, it only adds an unimportant constant to the free energy, and may be dropped. Rewriting the partition function in terms of this measure gives

$$\mathcal{Z} \propto \frac{1}{n_1! n_2!} \int \tilde{\mathcal{D}}\Xi e^{\rho_0 \int d\mathbf{r} \frac{1}{4} \phi^T \chi \phi} \delta[1 - \phi_+(\mathbf{r})]. \quad (1.47)$$

Applying the delta function enforces $\phi_+ = 1$, yielding

$$\mathcal{Z} \propto \frac{1}{n_1! n_2!} \int \tilde{\mathcal{D}}\Xi e^{\rho_0 \frac{1}{4} \int d\mathbf{r} (\chi_{--} \phi_-^2(\mathbf{r}) + (\chi_{-+} + \chi_{+-}) \phi_-(\mathbf{r}) + \chi_{++})} \delta[1 - \phi_+(\mathbf{r})]. \quad (1.48)$$

The integrals $\int d\mathbf{r} 1 = V$ and $\int d\mathbf{r} \phi_-(\mathbf{r}) = -(N_{A1} - N_{B1})n_1 - (N_{A2} - N_{B2})n_2$ are constants and can be dropped. Defining $\chi_{--} \equiv \chi$ and noting $\chi_{++} = \chi + (\epsilon_{AA} + \epsilon_{BB})/(\rho_0 k_B T)$, we retain only terms proportional to χ , simplifying the partition function to

$$\mathcal{Z} \propto \frac{1}{n_1! n_2!} \int \tilde{\mathcal{D}}\Xi e^{\rho_0 \frac{1}{4} \int d\mathbf{r} (\chi \phi_-^2(\mathbf{r}) + 1)} \delta[1 - \phi_+(\mathbf{r})]. \quad (1.49)$$

Next, we perform a Hubbard–Stratonovich transformation (shown in the Appendix A) to linearize the interaction [32, 36, 39, 40]

$$e^{\frac{\chi \rho_0}{4} \int d\mathbf{r} \phi_-^2(\mathbf{r})} \propto \int \mathcal{D}W_- e^{-\int d\mathbf{r} \frac{W_-^2(\mathbf{r})}{\chi \rho_0} + \int d\mathbf{r} \phi_-(\mathbf{r}) W_-(\mathbf{r})}. \quad (1.50)$$

The delta function can be expanded as its Fourier transform

$$\delta[1 - \phi_+(\mathbf{r})] \propto \int \mathcal{D}W_+ e^{-i \int d\mathbf{r} (1 - \phi_+(\mathbf{r})) W_+(\mathbf{r})}. \quad (1.51)$$

Substituting these transformations into Eq. 1.49 gives

$$\mathcal{Z} \propto \frac{1}{n_1! n_2!} \int \mathcal{D}W_+ \mathcal{D}W_- \tilde{\mathcal{D}}\Xi e^{-i \int d\mathbf{r} (1 - \phi_+(\mathbf{r})) W_+(\mathbf{r}) - \int d\mathbf{r} \frac{W_-^2(\mathbf{r})}{\chi \rho_0} + \int d\mathbf{r} \phi_-(\mathbf{r}) W_-(\mathbf{r}) + \frac{\rho_0 \chi}{4}}. \quad (1.52)$$

Regrouping all terms containing $\phi_{\pm}$ into a single factor gives

$$Q_{\text{total}} = \int \tilde{\mathcal{D}}\Xi e^{\int d\mathbf{r} (i\phi_+(\mathbf{r})W_+(\mathbf{r}) - \phi_-(\mathbf{r})W_-(\mathbf{r}))}. \quad (1.53)$$

We now express the densities in terms of microscopic polymer configurations by defining

$$\gamma_{\kappa,s} = \begin{cases} 1, & s \leq N_{\kappa}, \\ -1, & s > N_{\kappa}. \end{cases} \quad (1.54)$$

Substituting this and using the sifting property of the delta function yields

$$\begin{aligned} Q_{\text{total}} = & \frac{1}{V^{n_1+n_2}} \prod_{\alpha=1}^{n_1} \left(\int \prod_{i=1}^N d\mathbf{r}_{\alpha,i} e^{-\frac{3}{2a^2} \sum_{i=1}^{N-1} \|\mathbf{r}_{\alpha,i+1} - \mathbf{r}_{\alpha,i}\|^2 - \frac{1}{\rho_0} \sum_{s=1}^N (-iW_+(\mathbf{r}_{\alpha,s}) + \gamma_{1,s}W_-(\mathbf{r}_{\alpha,s}))} \right) \\ & \times \prod_{\beta=1}^{n_2} \left(\int \prod_{i=1}^N d\mathbf{r}_{\beta,i} e^{-\frac{3}{2a^2} \sum_{i=1}^{N-1} \|\mathbf{r}_{\beta,i+1} - \mathbf{r}_{\beta,i}\|^2 - \frac{1}{\rho_0} \sum_{s=1}^N (-iW_+(\mathbf{r}_{\beta,s}) + \gamma_{2,s}W_-(\mathbf{r}_{\beta,s}))} \right). \end{aligned} \quad (1.55)$$

Each factor corresponds to an independent single-chain partition function of the form

$$Q_{\kappa}[W_+, W_-] = \frac{1}{V} \int \prod_{i=1}^N d\mathbf{r}_i e^{-\frac{3}{2a^2} \sum_{i=1}^{N-1} \|\mathbf{r}_{i+1} - \mathbf{r}_i\|^2 - \sum_{s=1}^N (W_+(\mathbf{r}_s) + \gamma_{\kappa,s}W_-(\mathbf{r}_s))}. \quad (1.56)$$

Thus, the total product becomes

$$Q_{\text{total}} = Q_1^{n_1} \left[-\frac{iW_+}{\rho_0}, \frac{W_-}{\rho_0} \right] Q_2^{n_2} \left[-\frac{iW_+}{\rho_0}, \frac{W_-}{\rho_0} \right]. \quad (1.57)$$

Substituting this back, the partition function is

$$\mathcal{Z} \propto \int \mathcal{D}W_+ \mathcal{D}W_- \frac{Q_1^{n_1} \left[-\frac{iW_+}{\rho_0}, \frac{W_-}{\rho_0} \right] Q_2^{n_2} \left[-\frac{iW_+}{\rho_0}, \frac{W_-}{\rho_0} \right]}{n_1! n_2!} e^{-\int d\mathbf{r} \left(\frac{W_-^2(\mathbf{r})}{\chi \rho_0} - iW_+(\mathbf{r}) + \frac{\rho_0 \chi}{4} \right)}. \quad (1.58)$$

Using Stirling's approximation $\ln(n!) \approx n \ln n - n$, we define the effective Hamiltonian

$$\begin{aligned} \frac{\mathcal{H}}{k_B T} = & -n_1 \ln \left(\frac{Q_1 \left[-\frac{iW_+}{\rho_0}, \frac{W_-}{\rho_0} \right]}{n_1} \right) - n_2 \ln \left(\frac{Q_2 \left[-\frac{iW_+}{\rho_0}, \frac{W_-}{\rho_0} \right]}{n_2} \right) \\ & + n + \int d\mathbf{r} \left(\frac{W_-^2(\mathbf{r})}{\chi \rho_0} - iW_+(\mathbf{r}) + \frac{\rho_0 \chi}{4} \right). \end{aligned} \quad (1.59)$$

Dropping the constant term proportional to n and rescaling the fields as $W_+ \rightarrow i\rho_0 W_+$ and $W_- \rightarrow \rho_0 W_-$ gives

$$\frac{\mathcal{H}}{k_B T} = -n_1 \ln \left(\frac{Q_1[W_+, W_-]}{n_1} \right) - n_2 \ln \left(\frac{Q_2[W_+, W_-]}{n_2} \right) + \rho_0 \int d\mathbf{r} \left(\frac{W_-^2(\mathbf{r})}{\chi} - W_+(\mathbf{r}) + \frac{\chi}{4} \right). \quad (1.60)$$

This is the Hamiltonian functional for the polymer melt in the canonical ensemble. We can define the energy of a canonical melt of non-interacting polymers as

$$\frac{\mathcal{H}_{can}^Q}{k_B T} = -n_1 \ln \left(\frac{Q_1}{n_1} \right) - n_2 \ln \left(\frac{Q_2}{n_2} \right), \quad (1.61)$$

where we have dropping the explicit dependence of $Q_\kappa[W_+, W_-]$ on $W_\pm$. Then the total Hamiltonian can be expressed as

$$\frac{\mathcal{H}}{k_B T} = \frac{\mathcal{H}_{can}^Q}{k_B T} + \rho_0 \int d\mathbf{r} \left(\frac{W_-^2(\mathbf{r})}{\chi} - W_+(\mathbf{r}) + \frac{\chi}{4} \right). \quad (1.62)$$

We have performed an exact mathematical transformation from a particle-based polymer theory, in which the partition function is expressed as an integral over the coordinates of the beads $\mathbf{r}_{\alpha,i}$, to a field-based theory, where the partition function is evaluated as an integral over all possible configurations of the fields $W_\pm(\mathbf{r})$. The field $W_-(\mathbf{r})$ is a composition field that couples to the local composition $\hat{\phi}_-(\mathbf{r})$, while the field $W_+(\mathbf{r})$ is a pressure field that couples to the local monomer density $\hat{\phi}_+(\mathbf{r})$.

This transformation divides the Hamiltonian into two parts. The first part, $\frac{\mathcal{H}_{can}^Q}{k_B T}$, represents the free energy of a melt of n non-interacting diblock copolymers subjected to the fields W_+ and W_- . The second part represents the energy of the fields themselves. This field contribution to the Hamiltonian has the same form for all systems of incompressible AB block copolymers governed by our interaction model [36, 32]. Consequently, when we consider a different ensemble in the next section, the field contribution to the Hamiltonian will remain unchanged.

1.6 Semi-Grand Canonical Ensemble

In the Section 1.5, we obtained the canonical partition function, which has fixed values for n_1 and n_2 ,

$$\mathcal{Z}_{can}(n_1, n_2) \propto \int \mathcal{D}W_+ \mathcal{D}W_- e^{-\frac{\mathcal{H}}{k_B T}}. \quad (1.63)$$

However, one of the main phases of interest is a coexistence phase. For these phases, it is better to use an ensemble that allows the system to dynamically control the concentrations of species 1 and 2. A fully grand-canonical ensemble would allow both n_1 and n_2 to fluctuate. Here we introduce a semi-grand ensemble by summing over n_1 (at fixed $n = n_1 + n_2$) [23], where $z = e^{\mu/k_B T}$ is the fugacity and μ is an exchange chemical potential

$$\mathcal{Z}_{\text{SG}} = \sum_{n_1=0}^n z^{n_1} \mathcal{Z}_{\text{can}}(n_1, n - n_1). \quad (1.64)$$

This semi-grand ensemble keeps the total number of polymers in the melt n constant, but allows the relative number of the two types of polymers to fluctuate by fixing $n_2 = n - n_1$. Substituting the canonical partition function before applying Stirling's approximation gives

$$\mathcal{Z}_{\text{SG}} = \int \mathcal{D}W_+ \mathcal{D}W_- e^{-\rho_0 \int d\mathbf{r} \left(\frac{W_-^2(\mathbf{r})}{\chi} - W_+(\mathbf{r}) + \frac{\chi}{4} \right)} \sum_{n_1=0}^n \frac{(zQ_1)^{n_1} (Q_2)^{n-n_1}}{n_1! (n - n_1)!}. \quad (1.65)$$

Using the binomial identity $(x + y)^n = n! \sum_{i=0}^n \frac{x^i}{i!} \frac{y^{n-i}}{(n-i)!}$ we obtain

$$\mathcal{Z}_{\text{SG}} = \int \mathcal{D}W_+ \mathcal{D}W_- e^{-\rho_0 \int d\mathbf{r} \left(\frac{W_-^2(\mathbf{r})}{\chi} - W_+(\mathbf{r}) + \frac{\chi}{4} \right)} \frac{(zQ_1 + Q_2)^n}{n!}. \quad (1.66)$$

Moving the prefactor into the exponential and applying Stirling's approximation $\ln n! \approx n \ln n - n$ yields

$$\mathcal{Z}_{\text{SG}} = \int \mathcal{D}W_+ \mathcal{D}W_- e^{n \ln(zQ_1 + Q_2) - \rho_0 \int d\mathbf{r} \left(\frac{W_-^2(\mathbf{r})}{\chi} - W_+(\mathbf{r}) + \frac{\chi}{4} \right)}. \quad (1.67)$$

Therefore, the field-theoretic Hamiltonian for the semi-grand canonical ensemble is

$$\frac{\mathcal{H}}{k_B T} = -n \ln(zQ_1 + Q_2) + \rho_0 \int d\mathbf{r} \left(\frac{W_-^2(\mathbf{r})}{\chi} - W_+(\mathbf{r}) + \frac{\chi}{4} \right). \quad (1.68)$$

This is the Hamiltonian functional for the polymer melt in the semi-grand canonical ensemble. We can define the energy of a semi-grand canonical melt of non-interacting polymers as

$$\frac{\mathcal{H}_{\text{SG}}^Q}{k_B T} = -n \ln(zQ_1 + Q_2). \quad (1.69)$$

Then the total Hamiltonian can be expressed as

$$\frac{\mathcal{H}}{k_B T} = \frac{\mathcal{H}_{\text{SG}}^Q}{k_B T} + \rho_0 \int d\mathbf{r} \left(\frac{W_-^2(\mathbf{r})}{\chi} - W_+(\mathbf{r}) + \frac{\chi}{4} \right). \quad (1.70)$$

Chapter 2

Mean-Field Theory

Now that we have a field-theoretic representation of our system, we want a way to calculate its phase behavior. A common approach is self-consistent field theory (SCFT), which applies the saddle-point (mean-field) approximation to the partition function. In this approximation, the functional integral is dominated by the Boltzmann weight evaluated at the saddle-point fields w_+ and w_-

$$\mathcal{Z} \propto \int \mathcal{D}w_+ \mathcal{D}w_- e^{-\mathcal{H}[w_+, w_-]/k_B T} \approx e^{-\mathcal{H}[w_+, w_-]/k_B T}. \quad (2.1)$$

The saddle-point fields are obtained by extremizing the Boltzmann weights, however this is equivalent to extremizing the Hamiltonian yielding

$$0 = \frac{\mathcal{D}}{\mathcal{D}w_+(\mathbf{r})} \frac{\mathcal{H}[w_+, w_-]}{k_B T}, \quad 0 = \frac{\mathcal{D}}{\mathcal{D}w_-(\mathbf{r})} \frac{\mathcal{H}[w_+, w_-]}{k_B T}. \quad (2.2)$$

Using the Hamiltonian for the canonical ensemble derived in the previous chapter,

$$\frac{\mathcal{H}}{k_B T} = -n_1 \ln \left(\frac{Q_1[w_+, w_-]}{n_1} \right) - n_2 \ln \left(\frac{Q_2[w_+, w_-]}{n_2} \right) + \rho_0 \int d\mathbf{r} \left(\frac{w_-^2(\mathbf{r})}{\chi} - w_+(\mathbf{r}) + \frac{\chi}{4} \right), \quad (2.3)$$

the functional derivatives give

$$\begin{aligned} 0 &= \frac{\mathcal{D}}{\mathcal{D}w_+(\mathbf{r})} [-n_1 \ln Q_1 - n_2 \ln Q_2] - \rho_0, \\ 0 &= \frac{\mathcal{D}}{\mathcal{D}w_-(\mathbf{r})} [-n_1 \ln Q_1 - n_2 \ln Q_2] + \rho_0 \frac{2w_-(\mathbf{r})}{\chi}. \end{aligned} \quad (2.4)$$

Solving for the density $\phi_{\pm}(\mathbf{r})$, we find

$$\begin{aligned}\rho_0 \phi_+(\mathbf{r}) &= \frac{\mathcal{D}}{\mathcal{D}w_+(\mathbf{r})} [-n_1 \ln Q_1 - n_2 \ln Q_2], \\ \rho_0 \phi_-(\mathbf{r}) &= \frac{\mathcal{D}}{\mathcal{D}w_-(\mathbf{r})} [-n_1 \ln Q_1 - n_2 \ln Q_2],\end{aligned}\tag{2.5}$$

where the incompressible melt density is $\rho_0 = nN/V$, and we obtain the mean-field (SCFT) equations

$$\begin{aligned}\phi_+(\mathbf{r}) &= 1, \\ \phi_-(\mathbf{r}) &= -\frac{2}{\chi} w_-(\mathbf{r}).\end{aligned}\tag{2.6}$$

To close the system, the densities $\phi_{\pm}(\mathbf{r})$ are computed from the single-chain partition functions $Q_{\kappa}[w_+, w_-]$ via their propagators. In practice, one solves the SCFT equations iteratively for $w_{\pm}(\mathbf{r})$ and $\phi_{\pm}(\mathbf{r})$ until self-consistency is reached. While this can be done numerically, several useful analytic approximations are available that will let us find most of the phase boundaries without having to perform the full numerical SCFT.

2.1 Constant-Field Approximation

We start from the single-chain partition function

$$Q_{\kappa} = \frac{1}{V} \int \prod_{i=1}^N d\mathbf{r}_i \exp \left[-\frac{3}{2a^2} \sum_{i=1}^{N-1} \|\mathbf{r}_{i+1} - \mathbf{r}_i\|^2 - \sum_{s=1}^N (w_+(\mathbf{r}_s) + \gamma_{\kappa,s} w_-(\mathbf{r}_s)) \right]. \tag{2.7}$$

Here, $\kappa = 1, 2$ labels the polymer species, and $\gamma_{\kappa,s} = \pm 1$ indicates the sign associated with the monomers along chain type κ .

In the simplest case, w_+ and w_- are spatially uniform. Writing the single-chain partition function in terms of these constant fields gives

$$\begin{aligned}Q_{\kappa}[w_+, w_-] &= \frac{1}{V} e^{-N(w_+ + (1-2f_{\kappa})w_-)} \int \prod_{i=1}^N d\mathbf{r}_i \exp \left[-\frac{3}{2a^2} \sum_{i=1}^{N-1} \|\mathbf{r}_{i+1} - \mathbf{r}_i\|^2 \right] \\ &= e^{-N(w_+ + (1-2f_{\kappa})w_-)} Q_{\kappa}[0, 0],\end{aligned}\tag{2.8}$$

where $Q_\kappa[0, 0]$ denotes the Gaussian single-chain partition function in zero fields, and $f_\kappa = \frac{N_{A\kappa}}{N}$ is the volume fraction of a polymer of type κ . Without loss of generality, we can normalize $Q_\kappa[w_+, w_-]$ so that $Q_\kappa[0, 0] = 1$. To use this in the mean-field (MF) equations, we need

$$\ln Q_\kappa = -N[w_+ + (1 - 2f_\kappa)w_-]. \quad (2.9)$$

With incompressibility and $\rho_0 = nN/V$, the concentrations are

$$\begin{aligned} \phi_+ &= \frac{n_1 + n_2}{n}, \\ \phi_- &= 1 - \frac{2}{n}(n_1 f_1 + n_2 f_2). \end{aligned} \quad (2.10)$$

The SCFT equations are then

$$\begin{aligned} \frac{n_1 + n_2}{n} &= 1, \\ w_- &= -\frac{\chi}{2} \left(1 - \frac{2}{n}(f_1 n_1 + f_2 n_2) \right). \end{aligned} \quad (2.11)$$

Next, we evaluate the free energy for the uniform fields by substituting these results into the Hamiltonian

$$\begin{aligned} \frac{\mathcal{F}}{k_B T} &= n_1 \ln n_1 + n_2 \ln n_2 + n_1 N w_+ + n_1 N (1 - 2f_1) w_- \\ &\quad + n_2 N w_+ + n_2 N (1 - 2f_2) w_- + N n \left(\frac{w_-^2}{\chi} - w_+ + \frac{\chi}{4} \right). \end{aligned} \quad (2.12)$$

Substituting the SCFT expression for w_- and simplifying gives

$$\frac{\mathcal{F}}{k_B T} = n_1 \ln n_1 + n_2 \ln n_2 - \frac{N n}{\chi} w_-^2 + \frac{\chi N n}{4}. \quad (2.13)$$

In terms of the parameters,

$$\frac{\mathcal{F}}{k_B T} = n_1 \ln n_1 + n_2 \ln n_2 + N n \chi \left(\frac{1}{n}(f_1 n_1 + f_2 n_2) \right) \left(1 - \frac{1}{n}(f_1 n_1 + f_2 n_2) \right). \quad (2.14)$$

The interaction term has the familiar $\phi_A(1 - \phi_A)$ form, where $\phi_A = (f_1 n_1 + f_2 n_2)/n$. To proceed, we define the order parameter

$$\hat{\Psi}_1 = \frac{n_1 - n_2}{n}. \quad (2.15)$$

Enforcing incompressibility ($n_1 + n_2 = n$) gives

$$\frac{n_1}{n} = \frac{1 + \hat{\Psi}_1}{2}, \quad \frac{n_2}{n} = \frac{1 - \hat{\Psi}_1}{2}. \quad (2.16)$$

In terms of the order parameter, the free energy per molecule becomes

$$\begin{aligned} \frac{\mathcal{F}}{nk_B T} &= \frac{1 + \hat{\Psi}_1}{2} \ln \left(\frac{1 + \hat{\Psi}_1}{2} \right) + \frac{1 - \hat{\Psi}_1}{2} \ln \left(\frac{1 - \hat{\Psi}_1}{2} \right) \\ &+ N\chi \left(f_1^{\frac{1+\hat{\Psi}_1}{2}} + f_2^{\frac{1-\hat{\Psi}_1}{2}} \right) \left(1 - f_1^{\frac{1+\hat{\Psi}_1}{2}} - f_2^{\frac{1-\hat{\Psi}_1}{2}} \right), \end{aligned} \quad (2.17)$$

where a constant term $\ln n$ has been omitted. This function has one minimum when χN is small and two local minima when χN is large, corresponding to coexistence between a phase rich in polymer type 1 ($\hat{\Psi}_1 > 0$) and a phase rich in polymer type 2 ($\hat{\Psi}_1 < 0$).

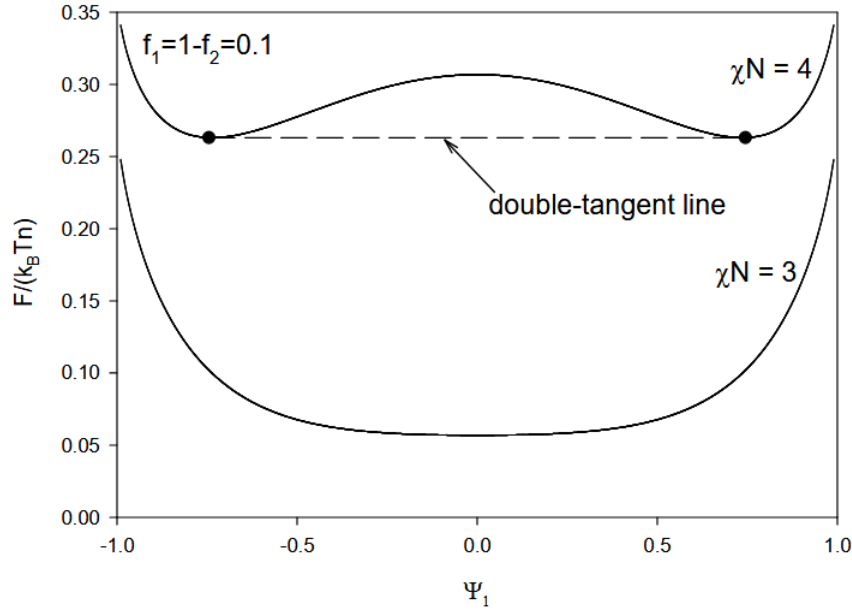


Figure 2.1: Plot of the free energy as a function of $\hat{\Psi}_1$ for $f_1 = 1 - f_2 = 0.1$ with two curves at different values of χN . The curve at $\chi N = 3$ is below the spinodal and so has only a single minimum at $\hat{\Psi}_1$. The other curve evaluated at $\chi N = 4$ is above the spinodal and so has two minima. The dashed line shows the free energy of a coexistence between the two minima, showing that this mixed state is more stable than a single phase state.

The spinodal, which is the point where the homogeneous phase becomes unstable with respect to macrophase separation, occurs when the curvature of $\mathcal{F}$ becomes zero at $\hat{\Psi}_1 = 0$. This is the point in χN when the system goes from having one minimum to having multiple. At this point the curvature at $\hat{\Psi}_1 = 0$ vanishes, giving the condition

$$\left. \frac{d^2}{d\hat{\Psi}_1^2} \frac{\mathcal{F}}{k_B T} \right|_{\hat{\Psi}_1=0} = 0. \quad (2.18)$$

The first and second derivatives are

$$\begin{aligned} \frac{d}{d\hat{\Psi}_1} \frac{\mathcal{F}}{k_B T} &= \frac{1}{2} \ln \left(\frac{1 + \hat{\Psi}_1}{2} \right) - \frac{1}{2} \ln \left(\frac{1 - \hat{\Psi}_1}{2} \right) \\ &\quad + N\chi \left(\frac{f_1 - f_2}{2} \right) \left[1 - \left(f_1^{\frac{1+\hat{\Psi}_1}{2}} + f_2^{\frac{1-\hat{\Psi}_1}{2}} \right) \right] \\ &\quad - N\chi \left(f_1^{\frac{1+\hat{\Psi}_1}{2}} + f_2^{\frac{1-\hat{\Psi}_1}{2}} \right) \left(\frac{f_1 - f_2}{2} \right), \end{aligned} \quad (2.19)$$

$$\frac{d^2}{d\hat{\Psi}_1^2} \frac{\mathcal{F}}{k_B T} = \frac{1}{1 - \hat{\Psi}_1^2} - \frac{1}{2} N\chi (f_1 - f_2)^2. \quad (2.20)$$

Thus, Eq. 2.18 becomes

$$1 - \frac{1}{2} N\chi_{\text{spin}} (f_1 - f_2)^2 = 0, \quad (2.21)$$

for which the solution is

$$N\chi_{\text{spin}} = \frac{2}{(f_1 - f_2)^2}. \quad (2.22)$$

The binodal can be found via the double-tangent construction, as in a homopolymer blend. Conceptually, consider two coexisting phases x and y (two volumes), containing n_x and n_y polymers, respectively. The total free energy per chain is

$$\frac{\mathcal{F}}{k_B T n} = p_x \left(\frac{\mathcal{F}_x}{k_B T n_x} - \frac{\mathcal{F}_y}{k_B T n_y} \right) + \frac{\mathcal{F}_y}{k_B T n_y}, \quad (2.23)$$

where $p_x = n_x/n$ and $p_y = 1 - p_x$. At coexistence, the symmetry implies that $\hat{\Psi}_{1y} = -\hat{\Psi}_{1x}$, and thus $\mathcal{F}_y/(k_B T n_y) = \mathcal{F}_x/(k_B T n_x)$. Setting the derivative of $\mathcal{F}/(k_B T n)$ with respect to $\hat{\Psi}_1$ to zero yields

$$0 = \ln \left(\frac{1 + \hat{\Psi}_1}{1 - \hat{\Psi}_1} \right) + N\chi_{\text{bin}} (f_1 - f_2) \left[-1 + f_1 + f_2 + (f_1 - f_2) \hat{\Psi}_1 \right]. \quad (2.24)$$

Solving for the segregation at the binodal gives

$$N\chi_{\text{bin}} = \frac{1}{(f_1 - f_2)(f_1 + f_2 - 1 + (f_1 - f_2)\hat{\Psi}_1)} \ln\left(\frac{1 + \hat{\Psi}_1}{1 - \hat{\Psi}_1}\right). \quad (2.25)$$

In the symmetric limit $f_1 = 1 - f_2$ and $n_1 = n_2$ (so $\hat{\Psi}_1 = 0$), the binodal coincides with the spinodal

$$N\chi_{\text{bin}} = N\chi_{\text{spin}} = \frac{2}{(1 - 2f)^2}. \quad (2.26)$$

The fact that the binodal and spinodal are located at the same spot tells us that the transition is second order and there is no metastable single phase region.

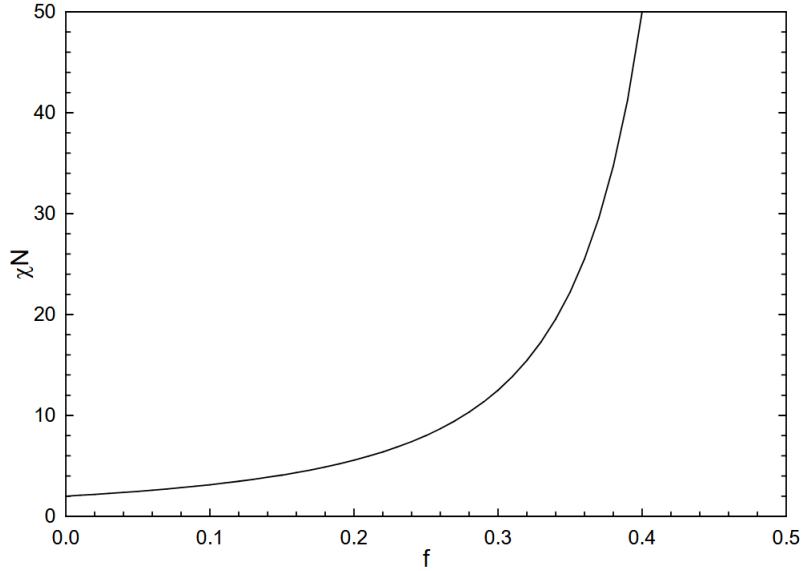


Figure 2.2: Plot of the spinodal as a function of f . At $f = 0$ we recover the expected $(\chi N)_{\text{spin}} = 2$. The divergence near $f = 0.5$ reflects the breakdown of the uniform-field approximation in the symmetric diblock limit, where the phase transition is to the lamellar (LAM) phase.

Finally, we ask over what range this constant-field approximation is valid. For $f = 0.5$ the system is a symmetric diblock melt, and the transition is to the lamellar phase.

Therefore, the uniform-field assumption must break down after some value of f when the two phase coexistence is replaced by the lamellar phase. To locate the transition between the lamellar and disordered (DIS) phases, we next compute the structure factor for weakly inhomogeneous fields, using the random-phase approximation (RPA).

2.2 Random-Phase Approximation

In the previous chapter, we analyzed the mean-field theory for homogeneous fields. We now study the transition when fluctuations about the homogeneous mean fields are weak. To do this, we will calculate the structure factor. In Appendix C, it was shown that the structure factor can be written as

$$\frac{S(\mathbf{k})}{\rho_0 N} = \frac{n}{4V^2} \langle \hat{\phi}_-(-\mathbf{k}) \hat{\phi}_-(\mathbf{k}) \rangle = \frac{n}{4V^2} \left(\frac{4}{\chi^2} \langle W_-(-\mathbf{k}) W_-(\mathbf{k}) \rangle - \frac{2V}{\chi \rho_0} \right). \quad (2.27)$$

We will evaluate this in the limit of weak fluctuations around homogeneous mean fields. To proceed, we need the second moment of the composition field W_- . The partition function is

$$\mathcal{Z} \propto \int \mathcal{D}W_+ \mathcal{D}W_- \exp \left[-\frac{\mathcal{H}}{k_B T} \right], \quad (2.28)$$

with Hamiltonian

$$\frac{\mathcal{H}}{k_B T} = -n_1 \ln \left(\frac{Q_1}{n_1} \right) - n_2 \ln \left(\frac{Q_2}{n_2} \right) + \rho_0 \int d\mathbf{r} \left(\frac{W_-^2(\mathbf{r})}{\chi} - W_+(\mathbf{r}) + \frac{\chi}{4} \right). \quad (2.29)$$

We now expand the Hamiltonian around the mean fields $w_{\pm}$. Let the fluctuating fields be $\Delta W_{\pm} \equiv W_{\pm} - w_{\pm}$. Then

$$\begin{aligned} \frac{\mathcal{H}}{k_B T} &= \frac{\mathcal{H}}{k_B T}[w_+, w_-] - n_1 \ln \left(\frac{\Delta Q_1}{n_1} \right) - n_2 \ln \left(\frac{\Delta Q_2}{n_2} \right) \\ &\quad + \rho_0 \int d\mathbf{r} \left(\frac{[\Delta W_-(\mathbf{r})]^2}{\chi} - \Delta W_+(\mathbf{r}) + \frac{\chi}{4} \right), \end{aligned} \quad (2.30)$$

where $\Delta Q_{\kappa} \equiv Q_{\kappa}[\Delta W_+, \Delta W_-]$ is the single-chain partition function evaluated with the fluctuations in the fields $\Delta W_{\pm}$. Using the weak-inhomogeneity expansion (shown in Appendix B), we have

$$\ln(\Delta Q_{\kappa}) = \frac{N^2}{2V^2} \int d\mathbf{r} d\mathbf{r}' \Delta \mathbf{W}^T(\mathbf{r}') \mathbf{G}^{(2)}(\mathbf{r}', \mathbf{r}; f_{\kappa}) \Delta \mathbf{W}(\mathbf{r}), \quad (2.31)$$

with

$$\Delta \mathbf{W} = \begin{bmatrix} \Delta W_-(\mathbf{r}) \\ \Delta W_+(\mathbf{r}) \end{bmatrix}, \quad \mathbf{G}^{(2)}(f) = \begin{bmatrix} G_{--}^{(2)}(\mathbf{r}', \mathbf{r}; f) & G_{-+}^{(2)}(\mathbf{r}', \mathbf{r}; f) \\ G_{+-}^{(2)}(\mathbf{r}', \mathbf{r}; f) & G_{++}^{(2)}(\mathbf{r}', \mathbf{r}; f) \end{bmatrix}. \quad (2.32)$$

We have used $\int d\mathbf{r} \Delta W_{\pm} = 0$ so the linear terms proportional to $\mathbf{G}^{(1)}$ vanish. Substituting this quadratic approximation into the Hamiltonian gives

$$\begin{aligned} \frac{\mathcal{H}}{k_B T} &= \frac{\mathcal{H}}{k_B T}[w_+, w_-] \\ &- \frac{nN^2}{2V^2} \int d\mathbf{r}' d\mathbf{r} \Delta \mathbf{W}^T(\mathbf{r}') \left[\frac{n_1}{n} \mathbf{G}^{(2)}(\mathbf{r}', \mathbf{r}; f_1) + \frac{n_2}{n} \mathbf{G}^{(2)}(\mathbf{r}', \mathbf{r}; f_2) \right] \Delta \mathbf{W}(\mathbf{r}) \\ &+ \frac{nN^2}{2V^2} \int d\mathbf{r}' d\mathbf{r} \Delta \mathbf{W}^T(\mathbf{r}') \left[\frac{2V}{\chi N} \begin{bmatrix} 1 & 0 \\ 0 & 0 \end{bmatrix} \delta(\mathbf{r}' - \mathbf{r}) \right] \Delta \mathbf{W}(\mathbf{r}). \end{aligned} \quad (2.33)$$

To proceed, we define the two-point function for the diblock blend

$$\mathbf{C}^{(2)}(\mathbf{r}' - \mathbf{r}) = -\frac{n_1}{n} \mathbf{G}^{(2)}(\mathbf{r}', \mathbf{r}; f_1) - \frac{n_2}{n} \mathbf{G}^{(2)}(\mathbf{r}', \mathbf{r}; f_2) + \frac{2V}{\chi N} \begin{bmatrix} 1 & 0 \\ 0 & 0 \end{bmatrix} \delta(\mathbf{r}' - \mathbf{r}). \quad (2.34)$$

Given the isotropy of the DIS phase, we can Fourier transform with wavevector $\mathbf{k}$ conjugate to $\mathbf{r}' - \mathbf{r}$. This yields

$$\mathbf{C}^{(2)}(\mathbf{k}) = -\frac{n_1}{n} \mathbf{G}^{(2)}(\mathbf{k}, f_1) - \frac{n_2}{n} \mathbf{G}^{(2)}(\mathbf{k}, f_2) + \frac{2}{\chi N} \begin{bmatrix} 1 & 0 \\ 0 & 0 \end{bmatrix}. \quad (2.35)$$

Thus,

$$\frac{\mathcal{H}}{k_B T} = \frac{\mathcal{H}}{k_B T}[w_+, w_-] + \frac{nN^2}{2V^2} \int d\mathbf{k} \Delta \mathbf{W}^T(-\mathbf{k}) \mathbf{C}^{(2)}(\mathbf{k}) \Delta \mathbf{W}(\mathbf{k}). \quad (2.36)$$

The Gaussian integral for the W_- correlations is then

$$\langle W_-(\mathbf{k}') W_-(\mathbf{k}) \rangle = \int \mathcal{D}W_+ \mathcal{D}W_- W_-(\mathbf{k}') W_-(\mathbf{k}) e^{-\frac{\mathcal{H}}{k_B T}[w_+, w_-] - \frac{nN^2}{2V^2} \int d\mathbf{k} \Delta \mathbf{W}^T(-\mathbf{k}) \mathbf{C}^{(2)} \Delta \mathbf{W}(\mathbf{k})}. \quad (2.37)$$

It is useful to introduce the generating functional

$$\Gamma_0[\Delta \phi(\mathbf{k})] = \ln \int \mathcal{D}W_+ \mathcal{D}W_- e^{-\frac{\mathcal{H}}{k_B T}[w_+, w_-] - \frac{nN^2}{2V^2} \int d\mathbf{k} \Delta \mathbf{W}^T(-\mathbf{k}) \mathbf{C}^{(2)}(\mathbf{k}) \Delta \mathbf{W}(\mathbf{k}) + \int d\mathbf{k} \Delta \phi^T(-\mathbf{k}) \Delta \mathbf{W}(\mathbf{k})}, \quad (2.38)$$

where the external field $\Delta\phi$ couples to $\Delta\mathbf{W}$. Performing the Gaussian integral and dropping $\Delta\phi$ independent constants yields,

$$\Gamma_0[\Delta\phi] = \frac{V^2}{2nN^2} \int d\mathbf{k} \Delta\phi^T(-\mathbf{k}) [\mathbf{C}^{(2)}(\mathbf{k})]^{-1} \Delta\phi(\mathbf{k}). \quad (2.39)$$

Therefore, the second moment is

$$\langle W_-(\mathbf{k}') W_-(\mathbf{k}) \rangle = \left. \frac{\delta^2 \Gamma_0}{\delta\phi_-(\mathbf{k}) \delta\phi_-(\mathbf{k}')} \right|_{\phi=0} = \frac{V^2}{nN^2} [\mathbf{C}^{(2)}(\mathbf{k})^{-1}]_{--} \delta(\mathbf{k} + \mathbf{k}'), \quad (2.40)$$

where

$$\mathbf{C}^{(2)} = \begin{bmatrix} C_{--} & C_{-+} \\ C_{+-} & C_{++} \end{bmatrix}, \quad [\mathbf{C}^{(2)}]^{-1} = \frac{1}{\det \mathbf{C}^{(2)}} \begin{bmatrix} C_{++} & -C_{-+} \\ -C_{+-} & C_{--} \end{bmatrix}. \quad (2.41)$$

Inserting the “--” component of $[\mathbf{C}^{(2)}]^{-1}$ into Eq. 2.40,

$$\langle W_-(-\mathbf{k}) W_-(\mathbf{k}) \rangle = \frac{V^2}{nN^2} \frac{C_{++}}{\det \mathbf{C}^{(2)}}. \quad (2.42)$$

Substituting this into Eq. 2.27 gives

$$\frac{S(\mathbf{k})}{\rho_0 N} = \frac{1}{-(\chi N)^2 \frac{\det \mathbf{S}^{(2)}}{S_{++}^{(2)}} + 2\chi N} - \frac{1}{2\chi N}, \quad (2.43)$$

where we have defined

$$\mathbf{S}^{(2)}(\mathbf{k}) = -\frac{n_1}{n} \mathbf{G}^{(2)}(\mathbf{k}, f_1) - \frac{n_2}{n} \mathbf{G}^{(2)}(\mathbf{k}, f_2). \quad (2.44)$$

Rearranging,

$$\frac{S(\mathbf{k})}{\rho_0 N} = \frac{1}{4 \frac{S_{++}^{(2)}}{\det \mathbf{S}^{(2)}} - 2\chi N}. \quad (2.45)$$

Switching from the $\pm$ basis to the A/B basis,

$$\det \mathbf{S}^{(2)} = 4 \det \mathbf{S}_{A/B}^{(2)} = 4(S_{AA}^{(2)} S_{BB}^{(2)} - S_{AB}^{(2)} S_{BA}^{(2)}), \quad (2.46)$$

and thus Eq. 2.43 becomes

$$\frac{S(\mathbf{k})}{\rho_0 N} = \frac{1}{\frac{S_{BB}^{(2)} + S_{AB}^{(2)} + S_{BA}^{(2)} + S_{AA}^{(2)}}{S_{AA}^{(2)} S_{BB}^{(2)} - S_{AB}^{(2)} S_{BA}^{(2)}} - 2\chi N}. \quad (2.47)$$

This matches the standard RPA form known for block copolymers [41], with

$$F(\mathbf{k}) = \frac{S_{BB}^{(2)} + S_{AB}^{(2)} + S_{BA}^{(2)} + S_{AA}^{(2)}}{S_{AA}^{(2)} S_{BB}^{(2)} - S_{AB}^{(2)} S_{BA}^{(2)}}. \quad (2.48)$$

Now that we can compute the structure factor, we ask what it implies for the phase behavior. In Fig. 2.3 the structure factor is plotted for several values of f with $\chi N = 4$. For $f = 0.2$, $S(\mathbf{k})$ peaks at $k^* = 0$, whereas for $f = 0.5$ and $f = 0.3$, the peak occurs at nonzero k^* .

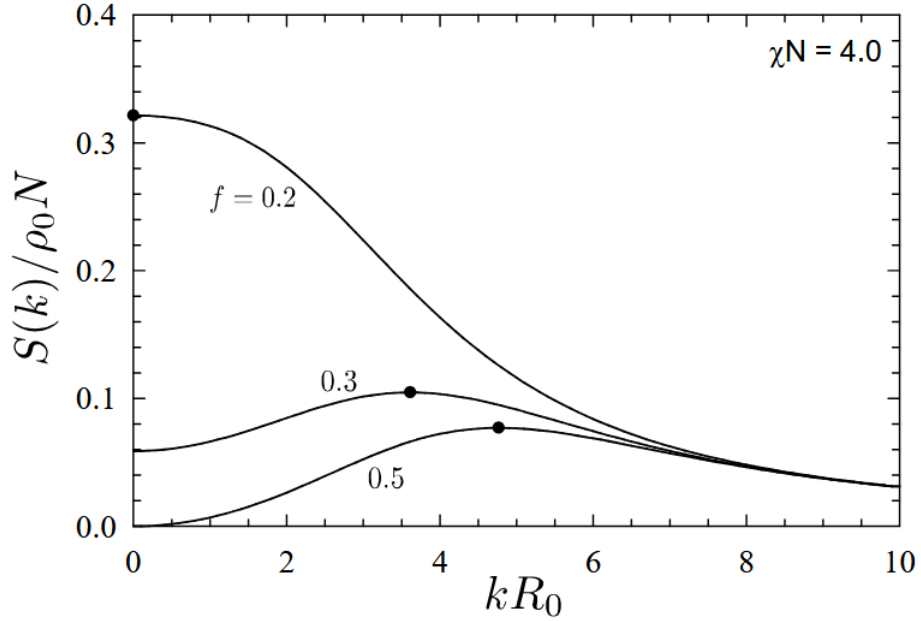


Figure 2.3: RPA structure factor for blends with different f , calculated at $\chi N = 4$. Black circles indicate the peak positions, k^* .

Because $F(k)$ is independent of χN , the peak in the structure factor occurs at the same value of f where $F(k)$ is minimized. When $\chi N = \frac{1}{2}F(k^*)$, the denominator vanishes and

$S(k)$ diverges, giving a second-order transition from the DIS phase to a periodic phase with a principal wavevector of k^* . We can determine $F(k^*)$ numerically (Fig. 2.4) and compare it with the spinodal for homogeneous fields from the previous chapter.

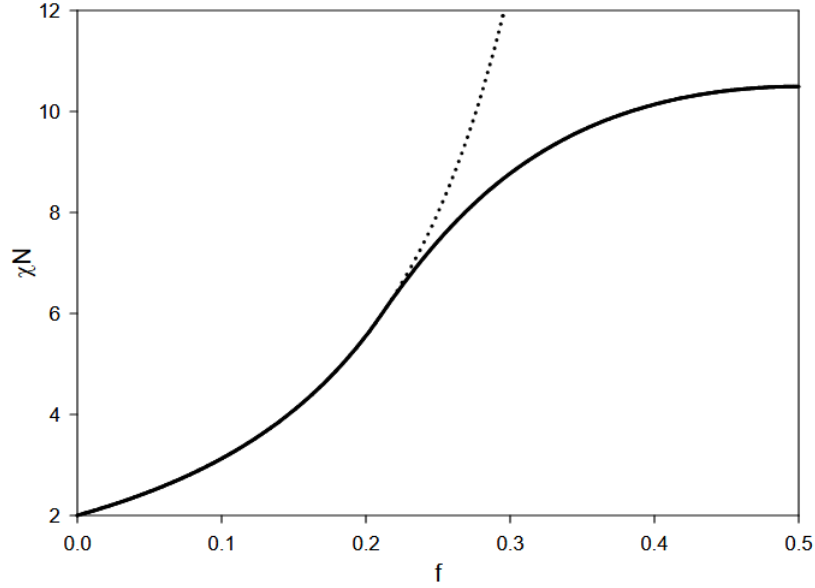


Figure 2.4: Solid curve: $(\chi N)_{\text{spin}} = 1/[2F(k^*)]$ from the RPA. Dotted curve: homogeneous-field spinodal from Section 2.1.

For small f , the two curves coincide. For larger f , they diverge; at $f = 0.5$ the RPA spinodal remains finite, $(\chi N)_{\text{spin}} \approx 10.495$, whereas the homogeneous-field spinodal diverges. The difference is explained by the peak position k^* shown in Fig. 2.5.

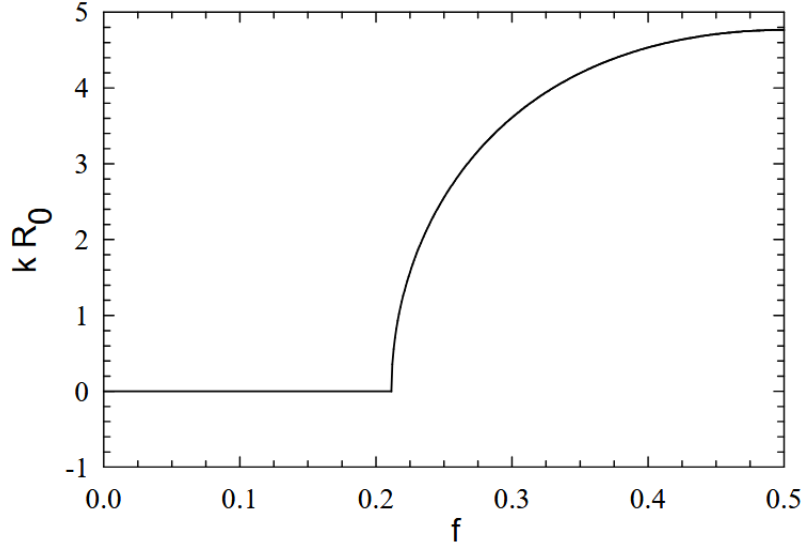


Figure 2.5: Peak position k^* as a function of f (independent of χN in the RPA). The point where k^* goes to zero near $f \simeq 0.215$ is the (isotropic) Lifshitz point, marking a change from DIS-2 ϕ to DIS-LAM transitions.

Over the range where the curves in Fig. 2.4 overlap, $k^* = 0$ as shown in Fig. 2.5. The diverging fluctuation at the spinodal is then the zero mode, and the transition is to two-phase coexistence. The difference begins once k^* becomes nonzero, signaling a transition to the lamellar phase. The point where the peak wavevector becomes nonzero is an isotropic Lifshitz point. One can analyze it by expanding $F(k)$ near $k = 0$ to obtain an analytic condition for the Lifshitz point.

2.3 Lifshitz Point

We now determine the value of f corresponding to the Lifshitz point. To do this, expand $F(k)$ about $k = 0$. The single-chain Green's functions for the diblocks are expanded as

$$\begin{aligned} G_{AA}^{(2)}(\mathbf{k}, f_i) &= f_i^2 \left(1 - \frac{x_{i,A}}{3} + \frac{x_{i,A}^2}{12} \right) + \mathcal{O}(x^3), \\ G_{BB}^{(2)}(\mathbf{k}, f_i) &= (1 - f_i)^2 \left(1 - \frac{x_{i,B}}{3} + \frac{x_{i,B}^2}{12} \right) + \mathcal{O}(x^3), \\ G_{AB}^{(2)}(\mathbf{k}, f_i) &= f_i(1 - f_i) \left(1 - \frac{x_{i,A}}{2} - \frac{x_{i,B}}{2} + \frac{x_{i,A}^2}{6} + \frac{x_{i,A}x_{i,B}}{4} + \frac{x_{i,B}^2}{6} \right) + \mathcal{O}(x^3), \end{aligned} \quad (2.49)$$

where $x_{i,A} \equiv k^2 a_{i,A}^2 f_i N/6$ and $x_{i,B} \equiv k^2 a_{i,B}^2 (1 - f_i) N/6$.

We now specialize to $a_{i,A} = a_{i,B} = 1$ and for our complementary diblocks, with $f \equiv f_1 = 1 - f_2$ and $1 - f \equiv f_2 = 1 - f_1$, the blend correlations are

$$\begin{aligned} S_{AA}(\mathbf{k}) &= \frac{1 + \hat{\Psi}_1}{2} G_{AA}^{(2)}(\mathbf{k}, f_1) + \frac{1 - \hat{\Psi}_1}{2} G_{AA}^{(2)}(\mathbf{k}, f_2), \\ S_{AB}(\mathbf{k}) &= \frac{1 + \hat{\Psi}_1}{2} G_{AB}^{(2)}(\mathbf{k}, f_1) + \frac{1 - \hat{\Psi}_1}{2} G_{AB}^{(2)}(\mathbf{k}, f_2), \\ S_{BA}(\mathbf{k}) &= \frac{1 + \hat{\Psi}_1}{2} G_{BA}^{(2)}(\mathbf{k}, f_1) + \frac{1 - \hat{\Psi}_1}{2} G_{BA}^{(2)}(\mathbf{k}, f_2), \\ S_{BB}(\mathbf{k}) &= \frac{1 + \hat{\Psi}_1}{2} G_{BB}^{(2)}(\mathbf{k}, f_1) + \frac{1 - \hat{\Psi}_1}{2} G_{BB}^{(2)}(\mathbf{k}, f_2). \end{aligned} \quad (2.50)$$

Substituting Eq. 2.49 into Eq. 2.50, the expansion simplifies to

$$\begin{aligned}
S_{AA} &= \frac{1 + \hat{\Psi}_1}{2} f^2 + \frac{1 - \hat{\Psi}_1}{2} (1 - f)^2 - \left[\frac{1 + \hat{\Psi}_1}{2} \frac{f^3}{3} + \frac{1 - \hat{\Psi}_1}{2} \frac{(1 - f)^3}{3} \right] x \\
&\quad + \left[\frac{1 + \hat{\Psi}_1}{2} \frac{f^4}{12} + \frac{1 - \hat{\Psi}_1}{2} \frac{(1 - f)^4}{12} \right] x^2 + \mathcal{O}(x^3), \\
S_{BB} &= \frac{1 + \hat{\Psi}_1}{2} (1 - f)^2 + \frac{1 - \hat{\Psi}_1}{2} f^2 - \left[\frac{1 + \hat{\Psi}_1}{2} \frac{(1 - f)^3}{3} + \frac{1 - \hat{\Psi}_1}{2} \frac{f^3}{3} \right] x \\
&\quad + \left[\frac{1 + \hat{\Psi}_1}{2} \frac{(1 - f)^4}{12} + \frac{1 - \hat{\Psi}_1}{2} \frac{f^4}{12} \right] x^2 + \mathcal{O}(x^3), \\
S_{AB} = S_{BA} &= f(1 - f) \left(1 - \frac{x}{2} + \frac{f^2 - f + 2}{12} x^2 \right) + \mathcal{O}(x^3).
\end{aligned} \tag{2.51}$$

In the symmetric-blend limit, $n_1 = n_2$ (equivalently $\hat{\Psi}_1 = 0$). Inserting these expressions into

$$F(x) \equiv \frac{S_{BB}^{(2)} + S_{AB}^{(2)} + S_{BA}^{(2)} + S_{AA}^{(2)}}{S_{AA}^{(2)} S_{BB}^{(2)} - S_{AB}^{(2)} S_{BA}^{(2)}} \tag{2.52}$$

and expanding to $\mathcal{O}(x^2)$ (i.e., to $\mathcal{O}(k^4)$) gives

$$\begin{aligned}
F(x) &= \frac{4}{(1 - 2f)^2} + 4 \frac{6f^2 - 6f + 1}{3(1 - 2f)^4} x \\
&\quad + \frac{-48f^6 + 144f^5 - 108f^4 - 24f^3 + 48f^2 - 12f + 1}{9(1 - 2f)^6} x^2 + \mathcal{O}(x^3).
\end{aligned} \tag{2.53}$$

The mean-field spinodal satisfies $2\chi N = F(k^*)$, yielding

$$(\chi N)_{\text{spin}} = \frac{2}{(1 - 2f)^2} \tag{2.54}$$

for $k^* = 0$. The point where the most unstable mode moves off $k = 0$, referred to as the Scott line [2, 42], occurs when the slope of F at $x = 0$ changes sign:

$$\left. \frac{dF}{dx} \right|_{x=0} = 6f^2 - 6f + 1 = 0. \tag{2.55}$$

Solving for f yields,

$$f = \frac{1}{2} \pm \frac{1}{2\sqrt{3}}. \quad (2.56)$$

By A/B symmetry, there are two solutions; taking the one with $f < \frac{1}{2}$ gives a Lifshitz composition of

$$f_L = \frac{1}{2} - \frac{1}{2\sqrt{3}} \approx 0.2113, \quad (2.57)$$

The corresponding χN at the Lifshitz point is obtained by evaluating the $k = 0$ spinodal in Eq. 2.54 at f_L ,

$$(\chi N)_L = \frac{2}{(1 - 2f_L)^2} = \frac{2}{\left(\frac{1}{\sqrt{3}}\right)^2} = 6. \quad (2.58)$$

For values of $f > f_L$, the peak position in $S(\mathbf{k})$ is obtained from solving $dF/dx = 0$ to leading order,

$$0 = 4 \frac{6f^2 - 6f + 1}{3(1 - 2f)^4} + \frac{2(-48f^6 + 144f^5 - 108f^4 - 24f^3 + 48f^2 - 12f + 1)}{9(1 - 2f)^6} x^*, \quad (2.59)$$

which gives

$$x^* = \frac{1}{6} R_0^2 k^2 = - \frac{6(1 - 2f)^2 (6f^2 - 6f + 1)}{-48f^6 + 144f^5 - 108f^4 - 24f^3 + 48f^2 - 12f + 1}. \quad (2.60)$$

This provides a small- k estimate of the peak wavevector beyond the Lifshitz point. Note that at $f = \frac{1}{2}$, $(1 - 2f) = 0$ and the small- k expansion fails. The approximation is nevertheless accurate in a neighborhood of f_L where k^* is small. Using $2\chi N = F(x^*)$ to the same order gives

$$\chi N = \frac{2}{(1 - 2f)^2} - \frac{13(6f^2 - 6f + 1)^2}{4(1 - 2f)^2(-48f^6 + 144f^5 - 108f^4 - 24f^3 + 48f^2 - 12f + 1)}, \quad (2.61)$$

which is the leading correction to the $k = 0$ spinodal on the $k^* > 0$ side of the Lifshitz point, and is consistent with a nonzero peak wavevector (see Fig 2.6).

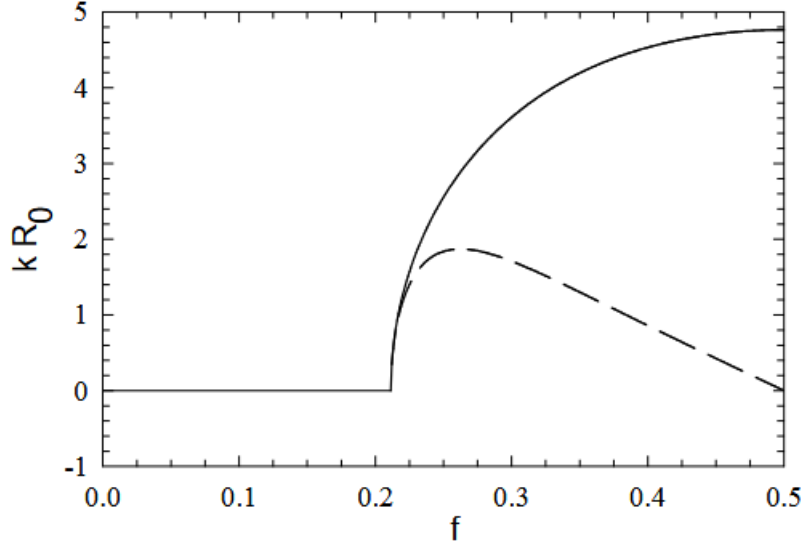


Figure 2.6: Peak position k^* as a function of f . The solid curve is a full RPA calculation and the dashed curve is an expansion for small k . The point where k^* goes to zero and the two curves converge is $f_L = \frac{1}{2} - \frac{1}{2\sqrt{3}}$, the Lifshitz point.

At $f = 0.5$, the small- k expansion fails because it is expanded around the spinodal for $k^* = 0$, which diverges. This is what causes the return to $k^* = 0$ for $f = 0.5$, as our expansion cannot create the infinite correction needed to give a finite value of $\chi_{spin}N$ at $f = 0.5$. To analyze the symmetric point, one must work with the full $F(x)$. However, we can see in Fig 2.6 that the expansion is a reasonable approximation around the Lifshitz point where k^* is small.

2.4 Mean-Field Phase Diagram

Having identified the transitions with the DIS phase, the remaining boundary is the transition between the LAM phase and the coexisting $A+B$ region. To address this, we must go beyond the perturbative expansions used previously and solve for the mean fields numerically using SCFT. In particular, we evaluate the path integral Q_κ for the single-chain partition function numerically.

We model a melt of bead-spring polymers of length N , with harmonic bonds and statistical segment length a . The melt consists of a binary blend of n_κ AB diblock copolymers

created by joining $N_{A,\kappa}$ A -type monomers to $N_{B,\kappa}$ B -type monomers, where $\kappa = 1, 2$ denotes the two molecular species. Chains are indexed by $i = 1, 2, \dots, N$ from the A end, and $\mathbf{r}_{\kappa,i,j}$ is the position of the j th monomer of the i th chain of type κ . The composition of species κ is $f_\kappa \equiv N_{A,\kappa}/N$. The contact interactions are as defined in Chapter 1.

We represent the fields on a periodic box of volume $V = L_x L_y L_z$. The box is discretized into cells of volume $v_{\text{cell}} = \Delta_x \Delta_y \Delta_z$; there are $m_i = L_i/\Delta_i$ grid points along direction $i \in \{x, y, z\}$ and $M = m_x m_y m_z$ total grid sites. Fields $w_\pm(\mathbf{r})$ are stored as $w_{\pm,i} \equiv w_\pm(\mathbf{r}_i)$ on the lattice. Using row-major ordering with zero-based indices, a site (x, y, z) maps to a linear index

$$i = x + m_x (y + m_y z), \quad 0 \leq x < m_x, \quad 0 \leq y < m_y, \quad 0 \leq z < m_z. \quad (2.62)$$

This converts the continuous-space theory for bead-spring polymers into a lattice theory amenable to computation. The melt is incompressible with monomer volume ρ_0^{-1} , such that the total number of chains is $n \equiv n_1 + n_2 = \rho_0 V/N$.

Following polymer field theory [43, 44, 37, 45], the particle model is mapped to an equivalent field model, as described in Chapter 1. From Chapter 2, the free-energy functional is the Hamiltonian evaluated at the mean fields

$$\frac{\mathcal{H}}{nk_B T} = \frac{H_{\text{can}}^Q}{nk_B T} + \frac{\chi N}{4} + \frac{N}{V} \int d\mathbf{r} \left(\frac{w_-^2(\mathbf{r})}{\chi} - w_+(\mathbf{r}) \right), \quad (2.63)$$

where H_{can}^Q is the free energy of non-interacting chains in external fields $w_\pm$. On the lattice, this becomes

$$\frac{\mathcal{H}}{nk_B T}[\{w_{+,i}\}, \{w_{-,i}\}] = \frac{H_{\text{can}}^Q}{nk_B T}[\{w_{+,i}\}, \{w_{-,i}\}] + \frac{\chi N}{4} + \frac{N}{M} \sum_{i=1}^M \left(\frac{w_{-,i}^2}{\chi} - w_{+,i} \right). \quad (2.64)$$

To evaluate H_{can}^Q , we need the single-chain partition functions Q_κ on the lattice. We define the forward partial partition function $q_{j,\kappa}(\mathbf{r})$ for the first j segments with the j th segment constrained at site $\mathbf{r}$, and the backward propagator $q_{j,\kappa}^\dagger(\mathbf{r})$ for the last $N - j + 1$ segments. Using the Gaussian recursion relationship derived in Chapter 1 in terms of the function

$$g(R) = \left(\frac{3}{2\pi a^2} \right)^{3/2} \exp\left(-\frac{3R^2}{2a^2} \right), \quad (2.65)$$

and local Boltzmann weight

$$h_{j,\kappa}(\mathbf{r}) = \exp\left[-w_+(\mathbf{r}) - \gamma_{j,\kappa} w_-(\mathbf{r}) \right], \quad (2.66)$$

the discrete recursion relations are

$$q_{j+1,\kappa}(\mathbf{r}) = h_{j+1,\kappa}(\mathbf{r}) v_{\text{cell}} \sum_{l=1}^M g(R_l) q_{j,\kappa}(\mathbf{r} - \mathbf{R}_l), \quad (2.67)$$

$$q_{j-1,\kappa}^\dagger(\mathbf{r}) = h_{j-1,\kappa}(\mathbf{r}) v_{\text{cell}} \sum_{l=1}^M g(R_l) q_{j,\kappa}^\dagger(\mathbf{r} + \mathbf{R}_l), \quad (2.68)$$

with initial conditions $q_{1,\kappa}(\mathbf{r}) = h_{1,\kappa}(\mathbf{r})$ and $q_{N,\kappa}^\dagger(\mathbf{r}) = h_{N,\kappa}(\mathbf{r})$. These can be solved efficiently using the fast Fourier transform [46, 47] as discussed in Section 1.4 to get

$$\begin{aligned} q_{j+1,\kappa}(\mathbf{r}) &= h_{j+1,\kappa}(\mathbf{r}) \mathcal{F}^{-1}[g(\mathbf{k}) q_{j,\kappa}(\mathbf{k})], \\ q_{j-1,\kappa}^\dagger(\mathbf{r}) &= h_{j-1,\kappa}(\mathbf{r}) \mathcal{F}^{-1}[g(\mathbf{k}) \mathbf{q}_{j,\kappa}^\dagger(\mathbf{k})], \end{aligned} \quad (2.69)$$

where the Fourier transform of $g(\mathbf{r})$ is $g(\mathbf{k}) = \exp\left(-\frac{a^2}{6} \|\mathbf{k}\|^2\right)$. The single-chain partition function can be evaluated at any contour index j as

$$Q_\kappa = \frac{1}{M} \sum_{i=1}^M \frac{q_{j,\kappa}(\mathbf{r}_i) q_{j,\kappa}^\dagger(\mathbf{r}_i)}{h_{j,\kappa}(\mathbf{r}_i)}. \quad (2.70)$$

Usually, one chooses $j = 1$ or $j = N$ to get a simpler relationship.

We solve the self-consistent field equations iteratively, using Anderson mixing [47, 48]. The fields at iteration k on site j are denoted w_{j+}^k and w_{j-}^k . The iteration continue until the residuals at iteration k ,

$$d_j^k = \frac{\partial}{\partial w_{j,+}^k} \left(\frac{\mathcal{H}}{nk_B T} \right), \quad d_{j+M}^k = \frac{\partial}{\partial w_{j,-}^k} \left(\frac{\mathcal{H}}{nk_B T} \right), \quad (2.71)$$

satisfy

$$\left[\frac{1}{M} \sum_{j=1}^{2M} (d_j^k)^2 \right]^{1/2} = \epsilon^k \leq \epsilon_{\text{tol}} = 10^{-4}. \quad (2.72)$$

If this condition is not satisfied, we calculate

$$U_{nm} = \sum_{j=1}^{2M} (d_j^k - d_j^{k-m}) (d_j^k - d_j^{k-n}), \quad (2.73)$$

$$V_m = \sum_{j=1}^{2M} (d_j^k - d_j^{k-m}) d_j^k, \quad (2.74)$$

where the index $m, n \in 1.2 \dots n_r$. The maximum size of these matrices, n_h , is generally set to 10 and the value $n_r = \min(k, n_h)$. From the matrices, we evaluate the coefficients

$$C_n = \sum_{m=1}^{n_r} (U^{-1})_{nm} V_m^k. \quad (2.75)$$

With mixing parameter λ , we update the fields according to,

$$w_{j,+}^{k+1} = w_{j,+}^k + \sum_{n=1}^{n_r} C_n (w_{j,+}^{k-n} - w_{j,+}^k) + \lambda \left(d_j^k + \sum_{n=1}^{n_r} C_n (d_j^{k-n} - d_j^k) \right), \quad (2.76)$$

$$w_{j,-}^{k+1} = w_{j,-}^k + \sum_{n=1}^{n_r} C_n (w_{j,-}^{k-n} - w_{j,-}^k) + \lambda \left(d_{j+M}^k + \sum_{n=1}^{n_r} C_n (d_{j+M}^{k-n} - d_{j+M}^k) \right). \quad (2.77)$$

Following [36], we use $\lambda = 1 - 0.9^k$.

Once converged, the saddle-point fields yield the free energy by evaluating $\mathcal{H}$ at those fields. For the lamellar phase, we also minimize the free energy with respect to the box size to find the equilibrium period and the corresponding free energy. We then compare the LAM free energy to that of the coexisting $A+B$ phase. The LAM- $A+B$ transition is first order and occurs when the two free energies are equal. Combining this with the RPA order-disorder transition (ODT) yields the mean-field phase diagram in Fig. 2.7.

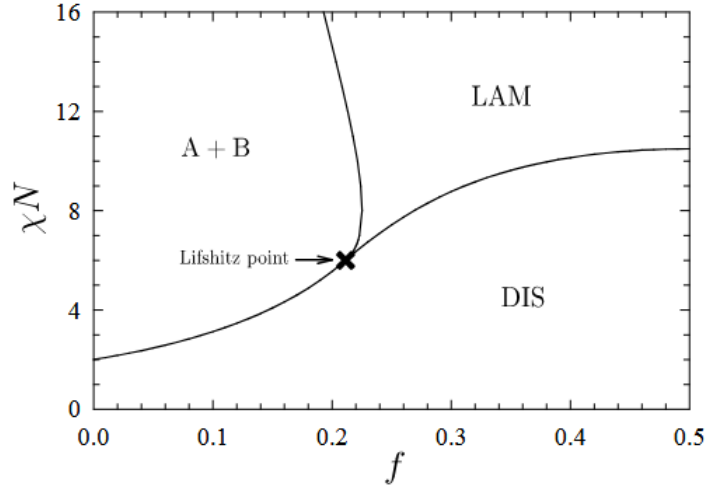


Figure 2.7: SCFT phase diagram showing the order-disorder transition (ODT) to $A+B$ coexistence for $k^* = 0$ and to the LAM phase for $k^* > 0$. The cross marks the Lifshitz point separating these behaviors. Calculations use the standard Gaussian-chain model.

This SCFT phase diagram becomes exact if the partition function of the system is completely dominated by the value of the field at the saddle point. The deviations from mean-field theory that come from fluctuations in the fields can be quantified by the invariant polymerization index $\bar{N} = \rho_o^2 a^6 N$, such that in the limit $\bar{N} \rightarrow \infty$, mean-field theory is exact. At finite $\bar{N}$, fluctuation effects not only shift critical points, they also destroy the Lifshitz critical point. This causes the highly swollen LAM phase to disorder into a bicontinuous microemulsion (B μ E), similar to the behavior of ternary systems. Unlike the three-component systems however, three-phase coexistence cannot occur in the two-component system. Hence, the fluctuation-induced B μ E will not be at risk of macrophase separation. Next, we will use field-theoretic simulation (FTSs) to confirm these expectations.

Chapter 3

Beyond Mean-Field Theory

In the limit $\bar{N} \rightarrow \infty$, the saddle-point (mean-field) approximation becomes exact and yields the free energy and phase diagram. Real polymer melts, however, have finite $\bar{N}$, typically $\bar{N} \sim 10^2$ – 10^4 . We therefore need a method to estimate fluctuation corrections to the field integral.

One approach is to expand the path integral about the saddle point. This requires carrying the weak-inhomogeneity expansion to fourth order by evaluating the quartic vertex function derived by Leibler [41]. Using this expansion, corrections to the random-phase approximation (RPA) from Chapter 2 can be computed [49, 50]. Then these vertex functions can be approximated near the spinodal in what is called weak crystallization theory [51, 52, 53]. With this weak crystallization theory, the free energy of the disordered (DIS) and lamellar (LAM) phase can be calculated and an order–disorder transition (ODT) found. Fredrickson and Helfand applied this method to a single-species diblock melt [54] and showed that, for $f = 0.5$, the ODT occurs at

$$(\chi N)_{\text{ODT}} = 10.495 + 41.0 \bar{N}^{-1/3}. \quad (3.1)$$

Furthermore, the second-order transition is replaced by a first-order one as Leibler originally predicted [41].

In this work, we instead evaluate the full field theory numerically using field-theoretic simulations (FTSs). It has been demonstrated that FTSs are considerably more efficient than conventional particle-based simulations [55]. Similar to the self-consistent field theory (SCFT) calculations, our FTSs are performed in orthorhombic boxes of size $L_x \times L_y \times L_z$ with periodic boundary conditions. The fields $W_-(\mathbf{r})$ and $W_+(\mathbf{r})$ are represented on a uniform cubic grid with spacing Δ (we use $\Delta = 0.2R_0$). The box volume is $V = L_x L_y L_z$ and

the cell volume is $v_{\text{cell}} = \Delta^3$. The convolutions required for chain statistics (to obtain Q and the concentrations $\phi_{\pm}$) are computed as in the SCFT section, using fast-Fourier transforms (FFTs). We implement the Fourier transform with the FFTW library implemented in CUDA from [46].

The discretized Hamiltonian functional is

$$\frac{\mathcal{H}[\{W_{+,i}\}, \{W_{-,i}\}]}{nk_BT} = \frac{H^Q[\{W_{+,i}\}, \{W_{-,i}\}]}{nk_BT} + \frac{\chi_b N}{4} + \frac{N}{M} \sum_{i=1}^M \left(\frac{W_{-,i}^2}{\chi_b} - W_{+,i} \right), \quad (3.2)$$

where H^Q , in either the canonical or semi-grand canonical ensemble, is the free energy of non-interacting chains in the external fields $W_{\pm}$, χ_b is the bare Flory parameter, and M is the number of grid points. Thermal averages of observables O are given by

$$\langle O[\{W_{+,i}\}, \{W_{-,i}\}] \rangle = \frac{1}{Z} \int \left(\prod_{i=1}^M dW_{+,i} dW_{-,i} \right) O[\{W_{+,i}\}, \{W_{-,i}\}] e^{-\frac{\mathcal{H}}{k_BT}}. \quad (3.3)$$

This set of $2M$ integrals could, in principle, be evaluated numerically by summing over all combinations of the real-valued $W_{-,i}$ field and the imaginary-valued $W_{+,i}$ field. However, there are three major problems with this direct approach.

If we discretize the allowed values of each field $W_{\pm,i}$ into n_s possible states at each site, the total number of terms in the sum would be n_s^{2M} . Such an enormous number of configurations makes direct numerical evaluation impossible. We therefore require a method to sample only the relevant terms in the sum. This is called an importance sampling method and it allows us to explore field configurations efficiently. In this work, we employ Langevin sampling, which evolves the fields stochastically to generate configurations distributed according to the Boltzmann weight.

The integrals over the imaginary $W_{+,i}$ field cause the Boltzmann factor to oscillate strongly, resulting in large cancellations of the integrand in Eq. 3.3 between the different configurations. As a result, unrealistic levels of accuracy are required for the integral to converge. This issue is known as the numerical sign problem. It is a serious difficulty in complex-valued path integrals of all types, and there is no general solution [56, 57]. In this work, we eliminate this problem using the partial saddle-point approximation, in which the incompressibility field W_+ is set to its real valued saddle-point value for each configuration of W_- . This approximation retains the essential composition fluctuations while removing the oscillatory phase, and yields a system that can be efficiently sampled with the Langevin sampling method.

In discretizing the theory, we represent the fields on a lattice of M sites, each of volume $v_{\text{cell}} = \Delta^3$. One would hope, the exact continuum limit would be recovered as $\Delta \rightarrow 0$. However, as the grid spacing decreases, certain observables such as the thermal average of the Hamiltonian diverge. This divergence arises because short-wavelength fluctuations contribute finite energy even below some physical cutoff length. This phenomenon is known as an ultraviolet (UV) divergence [58, 50, 59].

The remedy is renormalization, which absorbs the divergent part of the free energy into a redefined interaction parameter. Specifically, the divergent contribution is absorbed into the Flory–Huggins parameter, redefining it as

$$\chi \approx z_{\infty} \chi_b, \quad (3.4)$$

where χ_b is the bare unrenormalized value used in the simulations, and χ is the effective, renormalized, parameter that determines physical observables. In the mean-field limit, $\bar{N} \rightarrow \infty$, fluctuations vanish and renormalization is unnecessary, as the saddle-point approximation becomes exact.

3.1 Partial Saddle-Point Approximation

One major difficulty discussed previously is the numerical sign problem. It arises because the incompressibility field W_+ is imaginary, which makes the Boltzmann weight $\exp(-\mathcal{H}/k_B T)$ complex-valued. Consequently, it cannot be interpreted as a probability distribution, prohibiting the use of standard sampling techniques such as Markov chain Monte Carlo or conventional Langevin dynamics [32, 37].

A possible approach is to allow both W_+ and W_- to explore the entire complex plane. This method is known as complex Langevin sampling and has been extensively applied to polymer field theories [44, 60, 61, 62]. However, it is well known that the method can become unstable for small $\bar{N}$, where fluctuations are strong [45, 59].

Here we adopt a different approach by replacing the imaginary field W_+ with its real-valued saddle-point field w_+ . This substitution yields a real Boltzmann weight, allowing the remaining field W_- to be sampled with standard real-valued simulation techniques. To see how this approximation emerges, we can reorganize the partition function and expand the integral over W_+ semiclassically about its saddle point. Let

$$W_+ = w_+[W_-] + \xi, \quad (3.5)$$

where $w_+[W_-]$ is the saddle-point value satisfying

$$\frac{\mathcal{D}\mathcal{H}}{\mathcal{D}W_+} = 0, \quad (3.6)$$

and ξ represents fluctuations about that saddle point. The partition function can then be written as

$$Z = \int \mathcal{D}W_+ \mathcal{D}W_- e^{-\mathcal{H}[W_+, W_-]/k_B T} = \int \mathcal{D}W_- \left(\int \mathcal{D}\xi e^{-\mathcal{H}[w_+ + \xi, W_-]/k_B T} \right). \quad (3.7)$$

We can expand the Hamiltonian as a power series in ξ with a functional Taylor series [63]:

$$Z = \int \mathcal{D}W_- e^{-\mathcal{H}[w_+, W_-]/k_B T} \left(\int \mathcal{D}\xi e^{-\frac{1}{2k_B T} \int d\mathbf{r}' d\mathbf{r} \frac{\mathcal{D}^2 \mathcal{H}}{\mathcal{D}\xi(\mathbf{r}') \mathcal{D}\xi(\mathbf{r})} \Big|_{\xi=0} \xi(\mathbf{r}') \xi(\mathbf{r}) + \mathcal{O}(\xi^3)} \right). \quad (3.8)$$

In principle, this inner integral could be evaluated perturbatively for small fluctuations ξ by dropping the terms of order ξ^3 and performing the Gaussian integral. However, in the large $\bar{N}$ limit, the saddle-point approximation is accurate, implying that $\xi = W_+ - w_+$ is small and fluctuations in ξ are negligible [64]. We can therefore neglect these fluctuations entirely and approximate

$$Z \approx \int \mathcal{D}W_- e^{-\mathcal{H}[w_+, W_-]/k_B T}. \quad (3.9)$$

This is known as the partial saddle-point approximation, because we fix W_+ at its saddle-point value w_+ while allowing W_- to fluctuate fully [36]. The saddle-point condition for W_+ follows from

$$\frac{1}{k_B T} \frac{\mathcal{D}\mathcal{H}}{\mathcal{D}W_+} = \phi_+(\mathbf{r}) - 1 = 0, \quad (3.10)$$

which yields a mean-field approximation to the incompressibility constraint

$$\phi_+(\mathbf{r}) = 1. \quad (3.11)$$

We solve for w_+ satisfying this condition using Anderson mixing to accelerate convergence. The Anderson mixing algorithm terminates when it reaches an error of 10^{-4} . This was found to be sufficient for accurate results in [36].

The partial saddle-point approximation provides two key benefits. Firstly, it produces a real Boltzmann weight, allowing conventional sampling methods such as real Langevin dynamics to be applied [65]. Second, it reduces the number of fluctuating fields from two to one, lowering the dimensionality of the field configuration space that must be sampled to obtain accurate statistical averages [64].

3.2 Langevin Sampling

In the previous section, we showed that after applying the partial saddle-point approximation, the field theory can be expressed entirely in terms of the real-valued field W_- . This allows us to apply standard statistical sampling techniques to evaluate ensemble averages. In this work, we employ a conventional Langevin algorithm to sample the field configurations.

We begin by writing the field-theoretic partition function on a discrete lattice as

$$Z = \int \left(\prod_{i=1}^M dW_{-,i} \right) e^{-\mathcal{H}[\{w_{+,i}\}, \{W_{-,i}\}]/k_B T}. \quad (3.12)$$

Thermodynamic averages of observables are then given by

$$\langle O[\{w_{+,i}\}, \{W_{-,i}\}] \rangle = \frac{1}{Z} \int \left(\prod_{i=1}^M dW_{-,i} \right) O[\{w_{+,i}\}, \{W_{-,i}\}] e^{-\mathcal{H}[\{w_{+,i}\}, \{W_{-,i}\}]/k_B T}. \quad (3.13)$$

To sample configurations according to this Boltzmann weight, we define a stochastic process that evolves in a fictitious time variable t such that the stationary distribution reproduces the equilibrium measure. A Langevin process of the form

$$\frac{\partial W_-(\mathbf{r}, t)}{\partial t} = -\frac{1}{\rho_0} \frac{\mathcal{D}}{\mathcal{D}W_-(\mathbf{r})} \frac{\mathcal{H}}{k_B T} + N(t, \mathbf{r}), \quad (3.14)$$

has this property, as shown below.

On the discrete lattice, the functional derivative [60] becomes

$$\frac{\mathcal{D}}{\mathcal{D}W_-} = \lim_{v_{\text{cell}} \rightarrow 0} \frac{1}{v_{\text{cell}}} \frac{\partial}{\partial W_{-,i}}, \quad (3.15)$$

giving the Langevin evolution equation

$$\frac{\partial W_{-,i}}{\partial t} = -\frac{1}{\rho_0 v_{\text{cell}}} \frac{\partial}{\partial W_{-,i}} \frac{\mathcal{H}}{k_B T} + N(t, \mathbf{r}_i), \quad (3.16)$$

where we define $F_{-,i} \equiv \frac{\partial}{\partial W_{-,i}} \frac{\mathcal{H}}{k_B T}$ as the force on site i . The stochastic noise term, $N(t, \mathbf{r}_i)$, is Gaussian white noise with zero mean,

$$\langle N(t, \mathbf{r}) \rangle = 0, \quad \langle N(t, \mathbf{r}) N(t', \mathbf{r}') \rangle = \Gamma \delta(t - t') \delta_{\mathbf{r}, \mathbf{r}'}. \quad (3.17)$$

The corresponding Fokker–Planck equation (in Stratonovich form [31]) for the probability density $P(t, \{W_{-,i}\})$ is

$$\frac{\partial P}{\partial t} = \frac{\partial}{\partial W_{-,i}} \left[\frac{1}{\rho_0 v_{\text{cell}}} \left(F_{-,i} + \frac{\Gamma}{2} \frac{\partial}{\partial W_{-,i}} \right) P(t, \{W_{-,i}\}) \right]. \quad (3.18)$$

At equilibrium, the probability distribution is stationary ($\partial_t P = 0$), and thus

$$\left(\frac{1}{\rho_0 v_{\text{cell}}} F_{-,i} + \frac{\Gamma}{2} \frac{\partial}{\partial W_{-,i}} \right) P(\{W_{-,i}\}) = c_i, \quad (3.19)$$

where c_i is a constant. Integrating Eq. 3.19 then gives

$$P(\{W_{-,i}\}) = C \exp \left[-\frac{2}{v_{\text{cell}} \rho_0 \Gamma} \frac{\mathcal{H}}{k_B T} \right] + \frac{2}{\Gamma} \sum_{i=1}^M c_i W_{-,i}, \quad (3.20)$$

where C is another constant related to normalization. For this to be normalized, we require $c_i = 0$ and $C = 1/Z$. To reproduce the desired Boltzmann weight $e^{-\mathcal{H}/k_B T}$, we require $\Gamma = 2/(\rho_0 v_{\text{cell}})$.

Our lattice simulations must be done in discrete time. We define a timestep Δt , then the Langevin equation becomes

$$\frac{W_{-,i}(t + \Delta t) - W_{-,i}(t)}{\Delta t} = -\frac{1}{\rho_0 v_{\text{cell}}} \frac{\partial}{\partial W_{-,i}} \frac{\mathcal{H}}{k_B T} + N(t, \mathbf{r}_i). \quad (3.21)$$

Rearranging yields

$$W_{-,i}(t + \Delta t) = W_{-,i}(t) - \frac{1}{\rho_0 v_{\text{cell}}} \frac{\partial}{\partial W_{-,i}} \frac{\mathcal{H}}{k_B T} \Delta t + N(t, \mathbf{r}_i) \Delta t. \quad (3.22)$$

Absorbing Δt into the stochastic term defines $\mathcal{N}(t, \mathbf{r}_i)$ with

$$\langle \mathcal{N}(t, \mathbf{r}) \rangle = 0, \quad \langle \mathcal{N}(t, \mathbf{r}) \mathcal{N}(t', \mathbf{r}') \rangle = \frac{2\Delta t}{\rho_0 v_{\text{cell}}} \delta_{t,t'} \delta_{\mathbf{r},\mathbf{r}'}. \quad (3.23)$$

This noise is calculated with the CUDA default random number generator, which uses the algorithm XORWOW [66] that has a period of $2^{192} - 2^{32}$. As such,

$$W_{-,i}(t + \Delta t) = W_{-,i}(t) - \Lambda_f \Delta t + \mathcal{N}(t, \mathbf{r}_i), \quad (3.24)$$

where

$$\Lambda_f = \frac{1}{\rho_0 v_{\text{cell}}} \frac{\partial}{\partial W_{-,i}} \frac{\mathcal{H}}{k_B T}. \quad (3.25)$$

In the limit $\Delta t \rightarrow 0$, this process generates the equilibrium distribution

$$P(\{W_{-,i}\}) = \frac{1}{Z} e^{-\mathcal{H}/k_B T}. \quad (3.26)$$

For our field theory,

$$\Lambda_f = \frac{1}{\rho_0 v_{\text{cell}}} \frac{\partial}{\partial W_{-,i}} \frac{\mathcal{H}}{k_B T} = \phi_{-,i} + \frac{2}{\chi_b} W_{-,i}, \quad (3.27)$$

where $\phi_{-,i}$ is the local composition difference in the non-interacting system. Equation 3.24 is integrated using the Leimkuhler–Matthews stochastic integration scheme [67, 68, 69]. This method works by saving the random noise generated at the previous step and averaging it with new noise generated for this step. The advantage of this method is it is exact for harmonic potentials, letting us take large steps in t . Our simulations use $\Delta t = 8.0/N$. This large step size lets the simulations both equilibrate quickly and allows us to take independent samples more often. We take samples every 10 Langevin steps so they are separated by a time of $t = 80/N$. This is sufficient to allow the samples to be uncorrelated.

The concentration fields $\phi_{\pm}(\mathbf{r})$ are obtained from the partial chain partition functions. For polymers of type α , the composition is

$$\phi_{-, \alpha}(\mathbf{r}) = C_{\alpha} \sum_{i=1}^N \gamma_{i, \alpha} \frac{q_{i, \alpha}(\mathbf{r}) q_{i, \alpha}^{\dagger}(\mathbf{r})}{h_{i, \alpha}(\mathbf{r})}, \quad (3.28)$$

and the total monomer concentration is

$$\phi_{+, \alpha}(\mathbf{r}) = C_{\alpha} \sum_{i=1}^N \frac{q_{i, \alpha}(\mathbf{r}) q_{i, \alpha}^{\dagger}(\mathbf{r})}{h_{i, \alpha}(\mathbf{r})}. \quad (3.29)$$

In the canonical ensemble, the normalization constants are

$$C_1 = \frac{1 + \Psi_1}{2N Q_1}, \quad C_2 = \frac{1 - \Psi_1}{2N Q_2}, \quad (3.30)$$

and in the semi-grand canonical ensemble,

$$C_1 = \frac{z}{N(z Q_1 + Q_2)}, \quad C_2 = \frac{1}{N(z Q_1 + Q_2)}. \quad (3.31)$$

The overall concentrations are

$$\phi_{\pm}(\mathbf{r}) = \phi_{\pm,1}(\mathbf{r}) + \phi_{\pm,2}(\mathbf{r}). \quad (3.32)$$

Using these quantities, the force term is computed and the field $W_{-}(\mathbf{r}_i, t)$ is evolved according to Eq. 3.24, while the incompressibility field $w_{+}(\mathbf{r}_i, t)$ is updated to satisfy Eq. 3.11. This enables the evaluation of ensemble averages and phase behavior for the complementary diblock system.

3.3 Renormalization, Calibration, and Universality

We calculate the effective Flory–Huggins interaction parameter, χ , that maps our discrete Gaussian chains onto the standard model involving continuous Gaussian chains [70], while also accounting for the ultraviolet (UV) divergence [58] that appears in FTSs. For this we employ the Morse calibration, originally devised for particle-based simulations [71, 72, 73]. The first step is to match the free energy of a neat diblock melt in the weak-segregation limit to the Flory–Huggins expression $F/(nk_B T) \approx \chi N f(1-f)$ [59]. Concretely, we expand the free energy for weak fields, i.e., $\chi N \approx 0$.

The free energy follows from the partition function,

$$\frac{F}{k_B T} = -\ln \mathcal{Z} = -\ln \left[\int \mathcal{D}W_{+} \mathcal{D}W_{-} e^{-\mathcal{H}/k_B T} \right], \quad (3.33)$$

with Hamiltonian

$$\frac{\mathcal{H}}{k_B T} = -n_1 \ln \left(\frac{Q_1}{n_1} \right) - n_2 \ln \left(\frac{Q_2}{n_2} \right) + \rho_0 \int d\mathbf{r} \left(\frac{W_{-}^2(\mathbf{r})}{\chi} - W_{+}(\mathbf{r}) + \frac{\chi_b}{4} \right). \quad (3.34)$$

We expand the Hamiltonian to quadratic order about the mean fields $w_{\pm}$ (the same weak-inhomogeneity expansion used in the RPA calculations of Section 2.2). Writing the fluctuations as $\Delta W_{\pm} \equiv W_{\pm} - w_{\pm}$ gives

$$\frac{\mathcal{H}}{k_B T} = \frac{\mathcal{H}[w_{+}, w_{-}]}{k_B T} + \frac{nN^2}{2V^2} \int d\mathbf{k} \Delta \mathbf{W}^T(-\mathbf{k}) \mathbf{C}^{(2)}(\mathbf{k}) \Delta \mathbf{W}(\mathbf{k}), \quad (3.35)$$

where $\Delta \mathbf{W} = (\Delta W_{-}, \Delta W_{+})^T$ and $\mathbf{C}^{(2)}$ is the same 2×2 matrix of quadratic coefficients from Eq. 2.34.

Within the partial saddle-point approximation (PSP) we eliminate ΔW_+ by imposing the saddle-point condition

$$0 = \frac{\mathcal{D}}{\mathcal{D}(\Delta W_+)} \frac{\mathcal{H}}{k_B T} = \frac{nN^2}{V^2} \left[C_{++}^{(2)}(\mathbf{k}) \Delta W_+(\mathbf{k}) + C_{+-}^{(2)}(\mathbf{k}) \Delta W_-(\mathbf{k}) \right], \quad (3.36)$$

which yields a real valued $\Delta W_+(\mathbf{k})$ calculated from the condition

$$\Delta W_+(\mathbf{k}) = -\frac{C_{+-}^{(2)}(\mathbf{k})}{C_{++}^{(2)}(\mathbf{k})} \Delta W_-(\mathbf{k}). \quad (3.37)$$

This condition replaces the imaginary valued fluctuations in W_+ with real valued fluctuations. These real valued fluctuations are determined by the fluctuations in W_- through Eq. 3.37. Substituting Eq. 3.37 back into Eq. 3.33 gives a Gaussian integral over ΔW_- with kernel

$$F(\mathbf{k}) = \frac{4S_{++}^{(2)}(\mathbf{k})}{\det \mathbf{S}^{(2)}(\mathbf{k})}. \quad (3.38)$$

Thus,

$$\frac{F}{k_B T} = -\frac{\mathcal{H}[w_+, w_-]}{k_B T} - \ln \left[\int \mathcal{D}(\Delta W_-) \exp \left(-\frac{\rho_0}{V \chi_b} \int d\mathbf{k} \left(1 - \frac{2\chi_b N}{F(\mathbf{k}_i)} \right) |\Delta W_-(\mathbf{k})|^2 \right) \right]. \quad (3.39)$$

Our simulation lattice has M sites of volume $v_{\text{cell}} = \Delta^3$ and periodic boundary conditions, so the $\mathbf{k}$ -integral becomes a sum over the M independent wavevectors $\{\mathbf{k}_i\}$ with $-\pi/\Delta < k_i \leq \pi/\Delta$. Performing the resulting product of 1D Gaussian integrals gives

$$\frac{F}{k_B T} = -\frac{\mathcal{H}[w_+, w_-]}{k_B T} + \frac{1}{2} \sum_{i=1}^M \ln \left(1 - \frac{2\chi_b N}{F(\mathbf{k}_i)} \right) - \frac{M}{2} \ln \left(\frac{\chi_b}{2\rho_0 v_{\text{cell}}} \right). \quad (3.40)$$

For small χ , we use $\ln(1-x) \approx -x$ to obtain

$$\frac{F}{k_B T} = -\frac{\mathcal{H}[w_+, w_-]}{k_B T} - \sum_{i=1}^M \frac{\chi_b N}{F(\mathbf{k}_i)} - \frac{M}{2} \ln \left(\frac{\chi_b M}{2\rho_0 V} \right). \quad (3.41)$$

The last term diverges as $v_{\text{cell}} = V/M \rightarrow 0$, resulting in the ultraviolet (UV) divergence, which must be removed from F . Defining

$$\frac{F_{\text{UV}}}{k_B T} \equiv -\frac{M}{2} \ln \left(\frac{\chi_b M}{2\rho_0 V} \right), \quad (3.42)$$

and the homogeneously mixed compositions $\phi_{A,0} = (f_1 n_1 + f_2 n_2)/n$ and $\phi_{B,0} = 1 - \phi_{A,0}$, the free energy per chain then reads

$$\begin{aligned} \frac{F}{k_B T n} - \frac{F_{UV}}{k_B T n} &= \frac{n_1}{n} \ln\left(\frac{n_1}{n}\right) + \frac{n_2}{n} \ln\left(\frac{n_2}{n}\right) \\ &+ \left(1 - \sum_{i=1}^M \frac{2\chi_b N}{n F(\mathbf{k}_i) \phi_{A,0} \phi_{B,0} n}\right) N \chi \phi_{A,0} \phi_{B,0}. \end{aligned} \quad (3.43)$$

Rearranging gives an effective linear mapping $\chi \approx z_\infty \chi_b$ with

$$z_\infty = 1 - \sum_{i=1}^M \frac{2}{n \phi_{A,0} \phi_{B,0} F(\mathbf{k}_i)}. \quad (3.44)$$

Then the free energy is the Flory-Huggins form,

$$\begin{aligned} \frac{F}{k_B T n} - \frac{F_{UV}}{k_B T n} &= \frac{n_1}{n} \ln\left(\frac{n_1}{n}\right) + \frac{n_2}{n} \ln\left(\frac{n_2}{n}\right) \\ &+ z_\infty N \chi \phi_{A,0} \phi_{B,0}. \end{aligned} \quad (3.45)$$

In the thermodynamic limit, the sum becomes an integral,

$$z_\infty = 1 - \frac{N}{(2\pi)^3 \rho_0 \phi_{A,0} \phi_{B,0}} \int d\mathbf{k} \frac{1}{F(\mathbf{k})}. \quad (3.46)$$

To expose the large- k behavior entering the UV, we use the discrete-chain asymptotics (large $x \equiv a^2 N k^2/6$ and N)

$$G_{AA}^{(2)}(\mathbf{k}) \simeq \frac{f}{N \tanh(x/2N)}, \quad G_{BB}^{(2)}(\mathbf{k}) \simeq \frac{1-f}{N \tanh(x/2N)}, \quad G_{AB}^{(2)}(\mathbf{k}) \simeq 0. \quad (3.47)$$

This gives $F(\mathbf{k}) \simeq \frac{N \tanh(\frac{x}{2N})}{\phi_{A,0} \phi_{B,0}}$ and hence

$$z_\infty = 1 - \frac{1}{(2\pi)^3 \rho_0} \int d\mathbf{k} \frac{1}{\tanh(\frac{a^2 k^2}{12})}. \quad (3.48)$$

The same analytic expression is given in Ref [36].

There are a number of considerations in choosing the size of the grid, Δ , used to represent the fields on the computer. Naturally, a larger Δ reduces the computational

cost of the simulations. However, Δ needs to be small relative to the domain sizes of the morphology. Furthermore, it needs to be sufficiently small for the renormalization of χ to work accurately. We have found $\Delta = 0.2R_0$ to be an appropriate compromise, and therefore we use this value for all our simulations. This choice for the grid resolution combined with our choice for the monomer density, $\rho_0 = 15.81/a^3$, yields $z_\infty = 0.8782$.

A purely linear mapping is insufficient at finite $\bar{N}$. We therefore match the peak of the disordered-state structure function, $S(k^*)$, for symmetric diblocks to the renormalized one-loop (ROL) prediction [74, 75] (Fig. 3.1, solid curve). From the FTS data we compute $S(k)$ using the relation derived in Appendix C and fit the peak with a modified RPA form,

$$\frac{S(\mathbf{k})}{\rho_0 N} = \frac{A + Bk^2}{F(k) - 2\chi N + Ck^2 + Dk^4}. \quad (3.49)$$

The open symbols in Fig. 3.1 show the inverse peak heights evaluated using the linear $\chi \approx z_\infty \chi_b$, which deviates from ROL. Given our large $\bar{N}$, the nonlinearity should be weak, and we therefore assume a truncated Taylor expansion

$$\chi \approx z_\infty \chi_b + c_2 (z_\infty \chi_b)^2, \quad (3.50)$$

and adjust c_2 to match the ROL prediction. We obtain $c_2 = 0.112$ (solid symbols in Fig. 3.1). As shown previously [59], c_2 is independent of the grid spacing Δ , but depends (weakly) on ρ_0 .

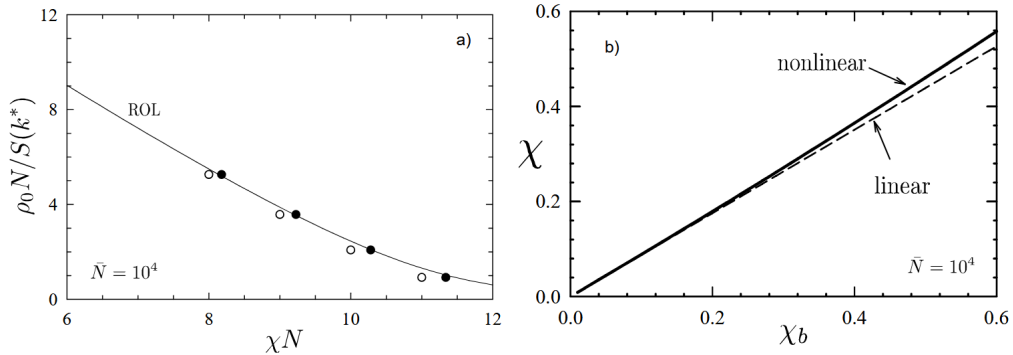


Figure 3.1: (a) Inverse peak height $S^{-1}(k^*)$ for symmetric diblocks with $\rho_0 = 15.81/a^3$ and $\bar{N} = 10^4$, plotted versus the linear $\chi \approx z_\infty \chi_b$ (open circles) and the nonlinear χ from Eq. 3.50 (solid circles). The solid curve is the ROL prediction. (b) Linear and nonlinear χ as functions of the bare χ_b .

Chapter 4

Results

In this chapter, we apply the field-theoretic simulation (FTS) method developed in the previous sections to a melt of two complementary diblock copolymers. Our goal is to correct the self-consistent field theory (SCFT) phase diagram presented in Chapter 3 by incorporating fluctuation effects that arise at finite $\bar{N}$. Specifically, we will calculate corrections to the boundaries separating the three regions of the phase diagram: the disordered (DIS) phase, the lamellar (LAM) microphase, and the macrophase-separated (A+B) coexistence region.

The first boundary we consider is the transition between the DIS state and the microphase-separated lamellar region. This transition is first order, meaning that it occurs when the free energies of the two phases become equal. To accurately locate this transition, we must compute the free-energy difference between the LAM and DIS phases as a function of system parameters.

To accomplish this, we employ a metadynamics approach, which enables efficient sampling of rare events and the estimation of free-energy barriers. By biasing the system along a suitable collective variable that distinguishes between ordered and disordered morphologies, metadynamics allows us to reconstruct the free-energy landscape. The point at which the free-energy difference between the LAM and DIS states vanishes corresponds to the order-disorder transition (ODT) that we seek to determine.

4.1 Well-Tempered Metadynamics for First-Order Phase Transitions

Having established a simulation method capable of computing ensemble averages and a calibrated χ parameter, we now turn to locating the first-order transition line between the DIS and LAM phases. To accomplish this, we employ well-tempered metadynamics (WTMD), which provides direct access to the free-energy difference between competing phases [76, 77, 78].

The first step is to define an order parameter that distinguishes between the LAM and DIS morphologies. Following previous work [79], we use

$$\hat{\Psi}_2 = \frac{1}{R_0^3} \left(\frac{V}{(2\pi)^3} \int f(k) |W_-(\mathbf{k})|^4 d\mathbf{k} \right)^{1/4}, \quad (4.1)$$

where

$$f(k) = \frac{1}{1 + \exp[12(k_c/k - 1)]}, \quad (4.2)$$

and we choose $k_c = 4.2/R_0$. This order parameter discriminates between the two phases, because the LAM phase produces a large value of $|W_-(\mathbf{k}^*)|^4$ at the characteristic wavevector $\mathbf{k}^*$ corresponding to its lamellar period, as compared to the DIS phase which exhibits only weak structure and thus a smaller $\hat{\Psi}_2$.

The key idea of WTMD is to introduce an external bias potential, $U(\Psi_2)$, that depends only on the order parameter $\hat{\Psi}_2$. This potential is added to the polymer Hamiltonian, modifying the Langevin force term to become

$$\Lambda = \Lambda_f + \frac{U'(\hat{\Psi}_2)}{nk_B T} \frac{V^2 \mathcal{F}^{-1}[f(k) |W_-(\mathbf{k})|^2 W_-(\mathbf{k})]}{N \hat{\Psi}_2^3 R_0^9}. \quad (4.3)$$

The bias potential, $U(\Psi_2)$, is constructed dynamically during the simulation. We initialize $U(\Psi_2) = 0$ and periodically add Gaussian functions of the form

$$\delta U(\Psi_2) = k_B T \exp \left[-\frac{U(\Psi_2)}{k_B \Delta T} \right] \exp \left[-\frac{(\hat{\Psi}_2 - \Psi_2)^2}{2\Delta_\Psi^2} \right], \quad (4.4)$$

where $\Delta_\Psi = 20R_0$ is the width of the Gaussian, centered at the instantaneous value of $\hat{\Psi}_2$. A new Gaussian is deposited every 10^3 Langevin steps to allow sufficient time for equilibration.

As $U(\Psi_2)$ builds up, it smooths the underlying free-energy landscape of the polymer Hamiltonian, enabling the system to cross freely between metastable and stable minima. This leads to spontaneous phase transitions that allow efficient sampling of both ordered and disordered configurations. The amplitude of the Gaussians decays as $\exp[-U(\Psi_2)/k_B\Delta T]$, ensuring convergence to a steady-state bias. For optimal performance, $k_B\Delta T$ should be comparable to the free-energy barrier separating the two phases.

Once $U(\Psi_2)$ has converged, the free-energy profile is obtained from

$$F(\Psi_2; \chi_b) = -\frac{T + \Delta T}{\Delta T} U(\Psi_2) + \text{constant}. \quad (4.5)$$

This allows direct comparison of the free energies of the LAM and DIS phases. However, because the free-energy differences near the ODT are very small, it is often more convenient to analyze the corresponding probability distribution,

$$P(\Psi_2; \chi_b) \propto \exp\left[-\frac{F(\Psi_2; \chi_b)}{k_B T}\right]. \quad (4.6)$$

Figure 4.1 shows the resulting histogram of Ψ_2 from a WTMD simulation at $f = 0.225$ and $z_\infty \chi_b^* N = 9.2$. Here, we used the asterisk to denote the χ_b that the simulation was run at, to distinguish extrapolated values of χ_b . The dashed curve corresponds to the raw simulation result, while the solid curve shows the extrapolated distribution at the ODT, $z_\infty \chi_b N = 9.215$. The two peaks at $\Psi_2 \approx 175$ and $\Psi_2 \approx 340$ correspond to the DIS and LAM phases, respectively. In this case, the DIS peak is higher, indicating that the disordered phase is stable and that the ODT occurs at slightly higher χ_b .

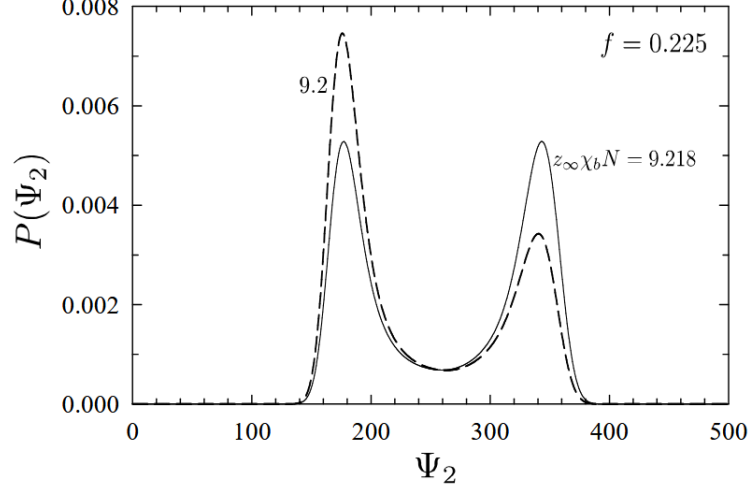


Figure 4.1: Histogram of the order parameter, Ψ_2 , from a WTMD simulation for $f = 0.225$, evaluated at $z_\infty\chi_b^*N = 9.2$ (dashed curve) and extrapolated to the ODT at $z_\infty\chi_bN = 9.218$ (solid curve).

The simulations are performed in cubic boxes roughly three lamellar periods in length to minimize finite-size effects that could shift the ODT [59]. It would be computationally costly to repeat simulations at multiple χ_b values, searching for the point of coexistence. A more efficient option is available provided the sampled values of Ψ_2 span both peaks. If this is the case, we can then extrapolate to nearby χ_b values using a linear approximation for the free energy [73, 80, 81]

$$F(\Psi_2; \chi_b) = F(\Psi_2; \chi_b^*) + \frac{\partial F}{\partial \chi_b}(\chi_b - \chi_b^*), \quad (4.7)$$

where the derivative is computed as

$$\frac{1}{k_B T} \frac{\partial F}{\partial \chi_b} = \frac{1}{k_B T} \left\langle \frac{\partial \mathcal{H}}{\partial \chi_b} \right\rangle_{\Psi_2} = \frac{\rho_0 V}{4} - \frac{\rho_0}{\chi_b^{*2}} \left\langle \int W_-^2(\mathbf{r}) d\mathbf{r} \right\rangle_{\Psi_2}. \quad (4.8)$$

The brackets $\langle \cdot \rangle_{\Psi_2}$ denote a conditional thermal average at fixed Ψ_2 , obtained by binning simulation data by instantaneous values of $\hat{\Psi}_2$ and averaging within each bin.

The ODT is determined by adjusting χ_b until the two peaks of $P(\Psi_2; \chi_b)$ are of equal height, yielding $(z_\infty\chi_bN)_{\text{ODT}} = 9.218$. Alternatively, one could use the criterion that

the areas under the two peaks are equal [79], though this requires a somewhat arbitrary division between them. The difference between the two definitions is a finite-size effect that vanishes in the thermodynamic limit. For our large simulation boxes, this difference is negligible, due to the rapid change in the peak heights with χ_b , see Fig. 4.1.

We next repeat these calculations for other integer values of $N_{1,A}$, which fixes the composition $f = N_{1,A}/N$ at discrete values. The next lower integer, $N_{1,A} = 8$ ($f = 0.200$), lies below the Lifshitz point ($f_L = 0.211$) and is therefore outside the lamellar regime. To probe smaller f values without crossing the Lifshitz point, we choose $N_{1,A} = 9$ with $N = 41$ ($f = 0.220$) and $N = 42$ ($f = 0.214$). The WTMD results for these cases are shown in Fig. 4.2.

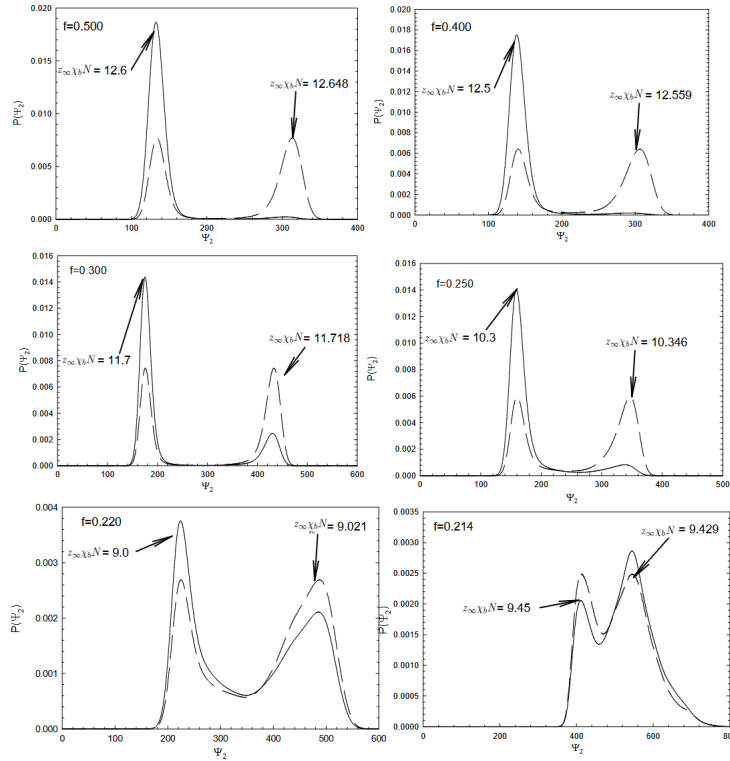


Figure 4.2: Histogram of the order parameter, Ψ_2 , from WTMD simulations for a range of f , evaluated at $z_\infty \chi_b^* N$ near the ODT (dashed curves) and extrapolated to the ODT (solid curves).

The lamellar period at the ODT, D_{ODT} , is determined directly from the ordered con-

figurations corresponding to the ordered peak of $\hat{\Psi}_2$. The finite size of the simulation box restricts the allowed periods, but the lamellar phase retains flexibility by changing its orientation [82]. In Fig. 4.3, the symbols denote the most common period, while the error bars indicate the neighboring allowed periods. The solid curve represents the SCFT prediction for the standard Gaussian chain model (GCM), evaluated using the nonlinear χ corresponding to the fluctuation-corrected ODT. Despite the inclusion of fluctuations, SCFT continues to provide accurate estimates for D_{ODT} , though deviations become apparent in the highly swollen lamellar phase near the Lifshitz regime.

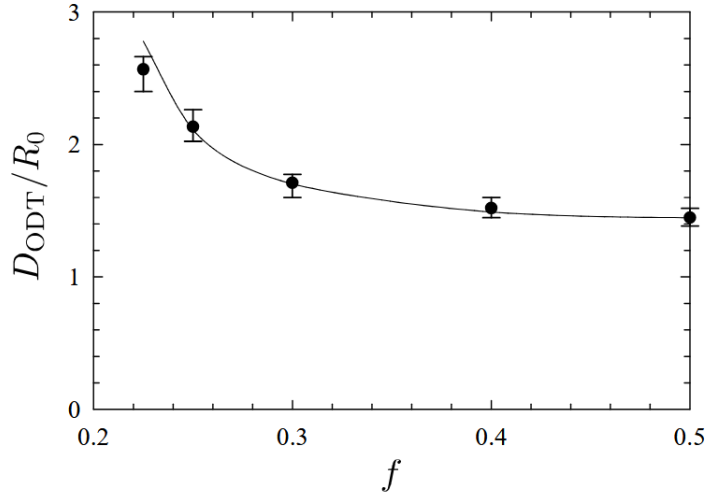


Figure 4.3: Equilibrium lamellar period, D_{ODT} , at the ODT. The solid curve shows the SCFT prediction evaluated with the nonlinear χ from Eq. 3.50. Error bars represent the distance to the next allowed LAM period in our simulation box.

Finally, Fig. 4.4 presents the fluctuation-corrected phase boundary for LAM-DIS transition. The gray dashed lines indicate SCFT phase boundaries, while the red symbols mark the ODTs obtained from WTMD. The inclusion of fluctuations shifts the phase boundaries to higher χN , consistent with the suppression of long-range order predicted by fluctuation theory.

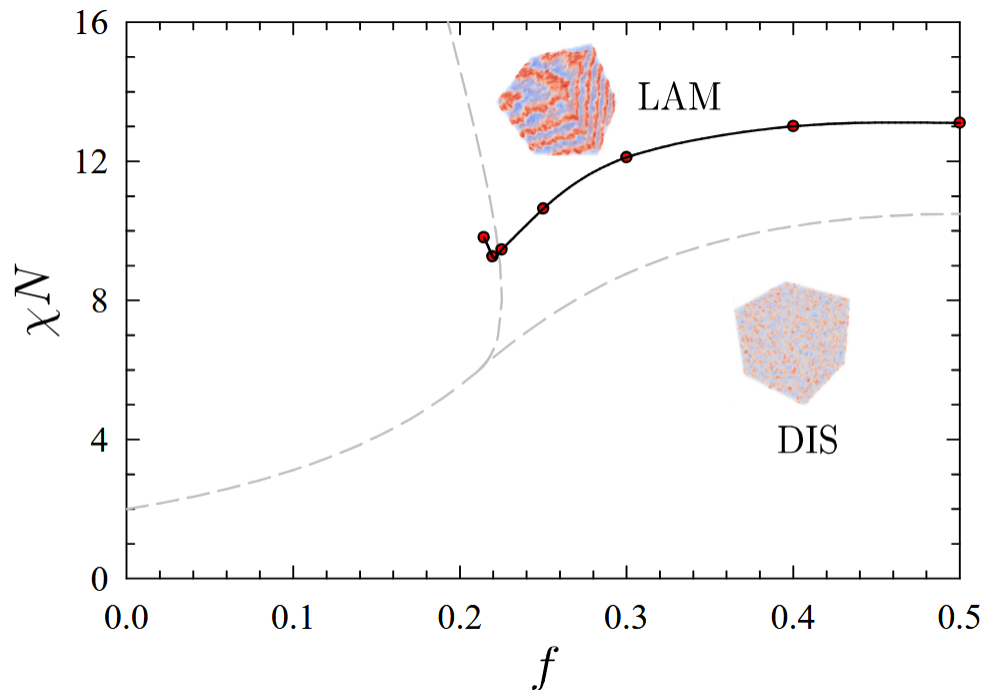


Figure 4.4: Phase diagram for the symmetric melt. Gray dashed lines show SCFT phase boundaries; red symbols denote LAM–DIS transitions obtained from WTMD. Note that the numerical inaccuracies are smaller than the symbols.

We now turn to the second-order phase transition between the macrophase-separated A+B region and the DIS phase.

4.2 Transitions Near the Lifshitz Point

In the previous chapter, we noted that the order parameter Ψ_2 begins to lose discriminatory power between LAM and DIS as we approach the mean-field Lifshitz point. As the two WTMD peaks move closer, metadynamics struggles to differentiate between the two competing phases and the ODT estimates lose accuracy. This starts to occur already at $f = 0.214$, and so we adopt an alternative strategy.

We construct initial configurations by splicing equilibrated LAM and DIS states obtained from simulations above and below the ODT, respectively, into a single rectangular

box of length $L = 19.2 R_0$. From this initial configuration of coexisting phases, we perform a series of unbiased FTS runs at nearby values of χ_b . As illustrated in Fig. 4.5, the LAM region invades the DIS region for $z_\infty \chi_b N \geq 9.6$, whereas DIS overtakes LAM for $z_\infty \chi_b N \leq 9.5$. Although this domain competition method is not as precise as WTMD, it yields a robust bracket and thus an estimate of $(z_\infty \chi_b N)_{\text{ODT}} = 9.55 \pm 0.05$ for $f = 0.214$.

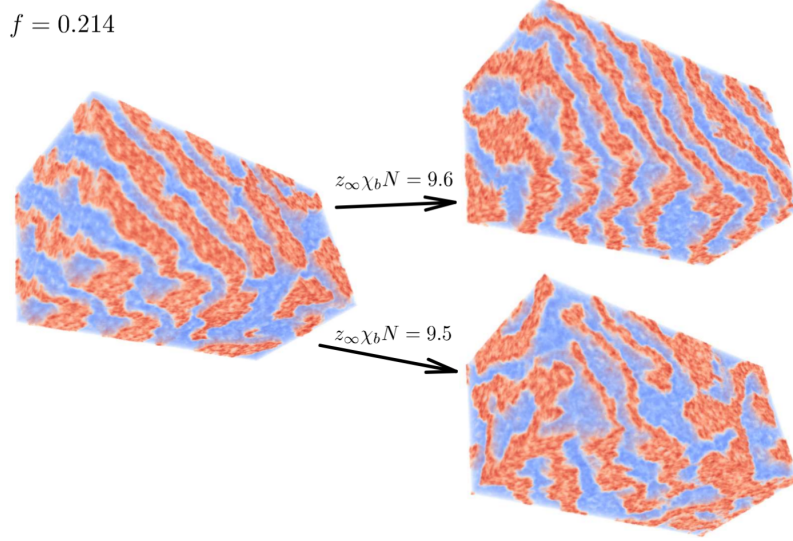


Figure 4.5: Equilibrated morphologies for $f = 0.214$ from FTSs at $z_\infty \chi_b N = 9.5$ and 9.6 (right). Both were initialized from a configuration with coexisting LAM and DIS regions (left).

Reducing the composition to $f = 0.213$ with $N = 47$, and $N_{1,A} = 10$. We find that LAM+DIS coexistence no longer evolves toward DIS. Instead, it transforms into $A+B$ coexistence. To locate the LAM-(A+B) boundary, we initialize our simulations with the configuration of coexisting A-rich, lamellar, and B-rich phase shown in Fig. 4.6 on the left. We then run FTSs at nearby χ_b values. As shown in Fig. 4.6 on the right, LAM grows when $z_\infty \chi_b N \geq 10.2$, while the $A+B$ state gradually overtakes when $z_\infty \chi_b N \leq 10.1$. The dynamics is extremely slow in the latter case, indicating proximity to the transition and suggesting the LAM/(A+B) boundary is near $z_\infty \chi_b N \approx 10.1$ for $f = 0.213$. Because relaxation further slows at higher segregation, a more efficient locator than brute-force competition will be required for finer resolution in this regime.

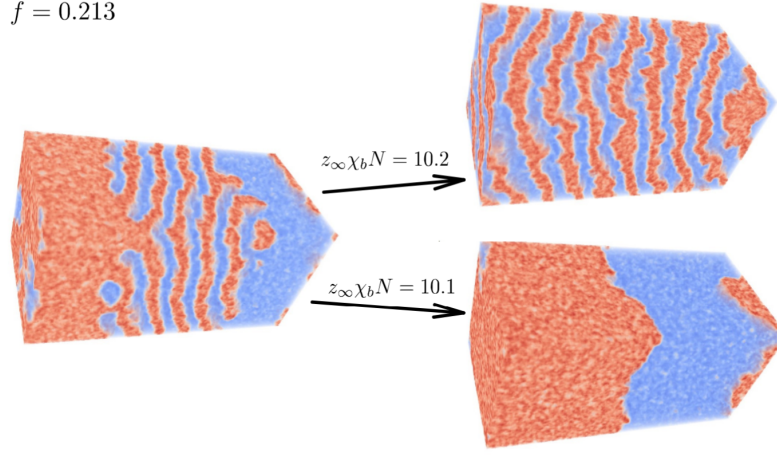


Figure 4.6: Equilibrated morphologies for $f = 0.213$ from FTSs at $z_{\infty}\chi_b N = 10.1$ and 10.2 (right). Both were initialized with coexisting A -rich, lamellar, and B -rich regions (left).

Figure 4.7 compiles the fluctuation-corrected boundaries obtained by WTMD (where reliable) and by domain-competition near the Lifshitz regime. Gray dashed lines indicate SCFT predictions. The red symbols denote new fluctuation-corrected transitions. The crossover from DIS-LAM to DIS-(A+B) competition upon decreasing f toward the Lifshitz point is clearly visible.

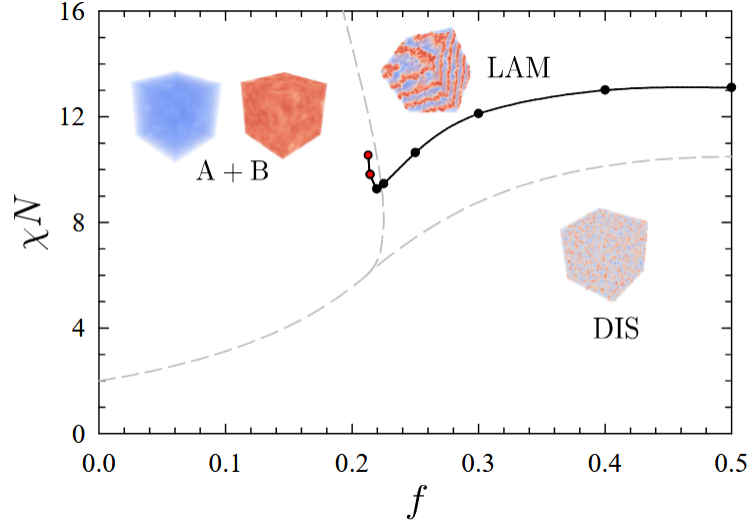


Figure 4.7: Phase diagram in the Lifshitz regime. Gray dashed lines: SCFT transitions. Red symbols: fluctuation-corrected transitions obtained via WTMD or domain-competition FTSs. Note that the numerical inaccuracies are smaller than the symbols.

The next section analyzes the transitions between the two-phase ($A+B$) state and the disordered phase, where criticality and finite-size scaling provide sharper tools than metadynamics or domain competition.

4.3 Finite-Size Scaling for Second-Order Transitions

In this section, we determine the fluctuation correction to the macrophase separation transition between the DIS phase and the $A+B$ coexistence. For this type of transition, the finite size of the simulation box L , significantly affects the apparent location of the transition. This effect is especially pronounced in the canonical ensemble, where phase coexistence requires the formation of an interface between the A - and B -rich regions. The presence of this interface introduces an excess free energy proportional to its surface area, which suppresses the two-phase state and shifts the apparent transition to higher values of $z_\infty \chi_b$.

We can mitigate this interfacial effect by working in the semi-grand canonical ensemble, which allows the exchange of f and $1-f$ diblocks. This freedom enables the system to form A - or B -rich phases without an interface, thereby removing the surface energy penalty.

The macrophase separation we are studying is continuous, exhibiting a second-order phase transition characterized by critical fluctuations. Because the length scale of these fluctuation diverges as the critical point is approached, finite-size effects remain significant regardless of system size. Thus, absolute values of observables cannot be used directly to locate the transition. Instead, we exploit finite-size scaling by analyzing thermodynamic averages from simulations with varying box sizes, L .

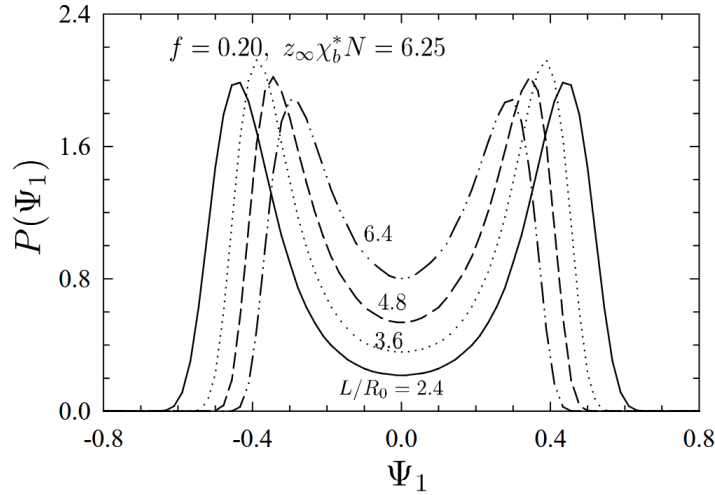


Figure 4.8: Histograms of the order parameter Ψ_1 from semi-grand canonical simulations in different box sizes for blends with $f = 0.2$ and $z_\infty \chi_b^* N = 6.25$.

Now to do finite size scaling we want to calculate a normalized histogram of the order parameter, $\hat{\Psi}_1$, shown in Fig. 4.8. This histogram is calculated at $f = 0.2$ and $z_\infty \chi_b N = 6.25$ in cubic simulation boxes of four different sizes $L = 2.4R_0, 3.6R_0, 4.8R_0, 6.4R_0$. At this value of $z_\infty \chi_b N$, we see that all of our histograms exhibit two peaks indicating that the system is in the A+B coexistence state. However, these simulations are run below the transition. This tells us that in the semi-grand ensemble the finite size effects act to stabilize the two-phase states and push the transition to lower $z_\infty \chi_b$. Now, because the system is below the transition, the peaks begin to merge into a single peak as the box size increases. If we ran in an infinite sized box, we would see a single peak characteristic of the DIS phase. To locate the true transition, we need to use finite-size scaling.

Rather than analyzing the full distribution, we can summarize its shape using the

Binder cumulant [83],

$$U_L = 1 - \frac{\langle \hat{\Psi}_1^4 \rangle}{3\langle \hat{\Psi}_1^2 \rangle^2}. \quad (4.9)$$

In the DIS phase, $U_L \rightarrow 0$ as $L \rightarrow \infty$, while in the two-phase coexistence region, $U_L \rightarrow 2/3$. The points at $z_\infty \chi_b N = 6.25$ in Fig. 4.9 show that U_L approaches zero with increasing L , confirming that the system is below the critical transition.

To avoid repeating simulations for each χ_b , we apply the histogram reweighting method of Refs. [84, 85]. This will require k^{th} moment of the order parameter evaluated at χ_b

$$\langle \hat{\Psi}_1^k \rangle_{\chi_b} = \frac{1}{Z} \int \mathcal{D}W_- \hat{\Psi}_1^k e^{-\frac{\mathcal{H}}{k_B T}|_{\chi_b}}. \quad (4.10)$$

Adding and subtracting $\mathcal{H}|_{\chi_b^*}$ in the exponent gives,

$$\langle \hat{\Psi}_1^k \rangle_{\chi_b} = \frac{1}{Z} \int \mathcal{D}W_- \hat{\Psi}_1^k e^{\frac{\mathcal{H}}{k_B T}|_{\chi_b^*} - \frac{\mathcal{H}}{k_B T}|_{\chi_b}} e^{-\frac{\mathcal{H}}{k_B T}|_{\chi_b^*}}. \quad (4.11)$$

The difference in the Hamiltonians is given by

$$\frac{\mathcal{H}}{k_B T}|_{\chi_b^*} - \frac{\mathcal{H}}{k_B T}|_{\chi_b} = \left[\frac{1}{\chi_b^*} - \frac{1}{\chi_b} \right] \hat{I}, \quad (4.12)$$

where

$$\hat{I} = \frac{1}{V} \int d\mathbf{r} W_-^2(\mathbf{r}). \quad (4.13)$$

Inserting this into Eq. (4.11) gives

$$\langle \hat{\Psi}_1^k \rangle_{\chi_b} = \langle \hat{\Psi}_1^k e^{\left(\frac{1}{\chi_b^*} - \frac{1}{\chi_b}\right) \hat{I}} \rangle_{\chi_b^*}. \quad (4.14)$$

Which is calculated from a simulation at χ_b^* . To evaluate it, we store the instantaneous values of $\hat{\Psi}_{1,i}$ and $\hat{I}_i$ at each, i , configuration. Given m sampled configurations, the k th moment of $\hat{\Psi}_1$ is estimated as[23]

$$\langle \hat{\Psi}_1^k \rangle = \frac{1}{\mathcal{N}} \sum_{i=1}^m \hat{\Psi}_{1,i}^k e^{\left(\frac{1}{\chi_b^*} - \frac{1}{\chi_b}\right) \hat{I}_i}, \quad (4.15)$$

where

$$\mathcal{N} = \sum_{i=1}^m e^{\left(\frac{1}{\chi_b^*} - \frac{1}{\chi_b}\right) \hat{I}_i}. \quad (4.16)$$

The accuracy of the reweighting decreases as $|\chi_b - \chi_b^*|$ increases, but remains reliable near critical points because the broad fluctuations generate overlapping ensembles. The curves in Fig. 4.9 were obtained by reweighting data from simulations at $z_\infty \chi_b^* N = 6.25$. The intersection of the cumulant curves identifies the critical point at $(z_\infty \chi_b N)_c = 6.28$.

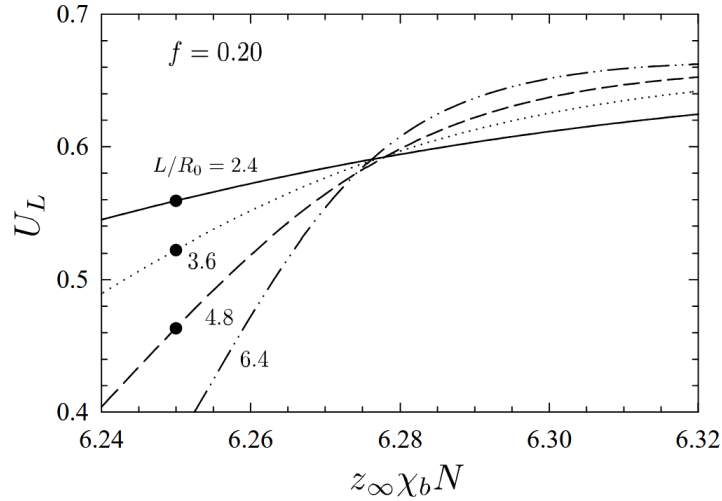


Figure 4.9: Binder cumulant U_L for each system size, plotted as a function of $z_\infty \chi_b N$. The crossing point locates the critical transition at $(z_\infty \chi_b N)_c = 6.28$.

At the critical point, the order parameter histograms become size-independent when rescaled by their standard deviation,

$$\sigma_\Psi = \sqrt{\langle \hat{\Psi}_1^2 \rangle}, \quad (4.17)$$

as demonstrated in Fig. 4.10. This collapse confirms that the system exhibits universal critical behavior.

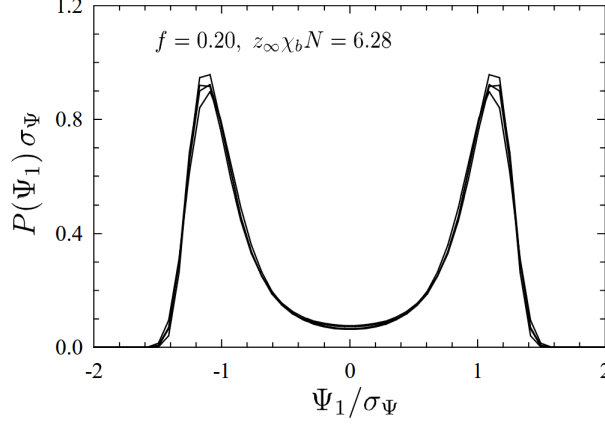


Figure 4.10: Histograms from Fig. 4.8, reweighted to the critical point and rescaled by σ_Ψ . The collapse confirms that the transition is critical.

Likewise, the Binder cumulant curves collapse when the χ_b axis is scaled by $L^{1/\nu}$, where ν is the critical exponent for the correlation length. Figure 4.11 demonstrates this behavior using $\nu = 0.630$, consistent with the 3D-Ising universality class [86].

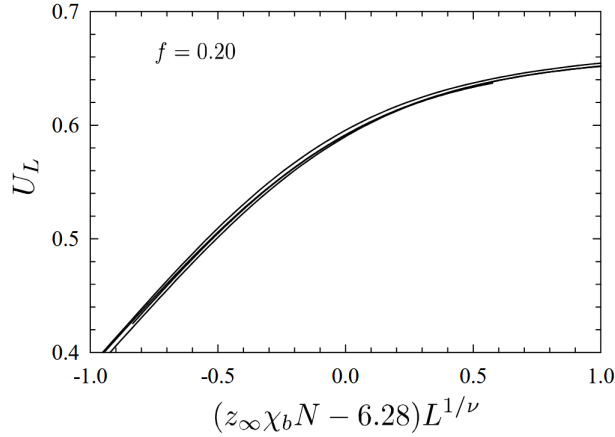


Figure 4.11: Scaling plot of the cumulants from Fig. 4.9, using the critical exponent $\nu = 0.630$. Their collapse confirms that the critical point belongs to the 3D Ising universality class.

We repeat this analysis for other values of f to identify the $z_\infty\chi_bN$ values where the

finite-size effects in U_L vanish. Figure 4.12 presents the resulting Binder cumulant plots for $f = 0.175, 0.15, 0.10$, and 0.05 , with each showing the intersection point between curves of different box sizes. The resulting transition points are $(z_\infty \chi_b N)_{\text{ODT}} = 5.098, 4.243, 3.229$, and 2.865 , respectively.

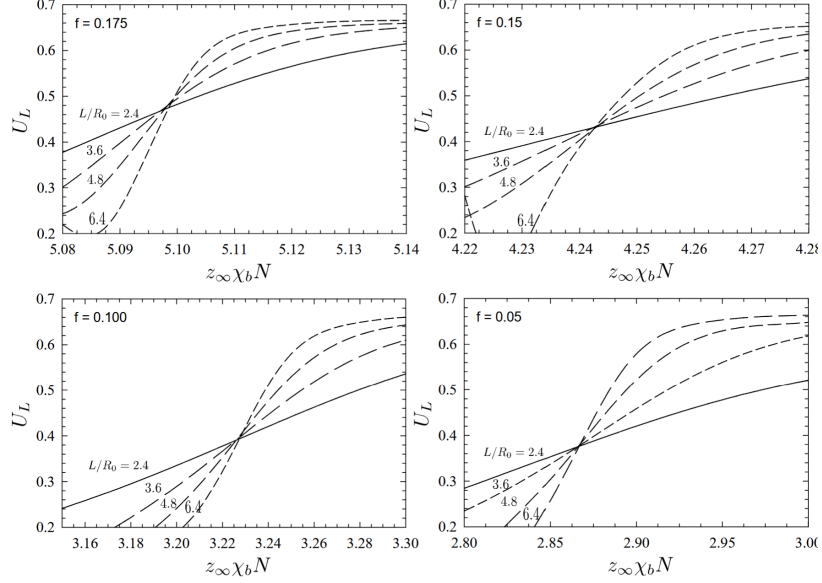


Figure 4.12: Binder cumulant plots for $f = 0.175, 0.15, 0.10$, and 0.05 . For each f , four system sizes are shown as a function of χ_b . The crossing points identify the ODTs at $(z_\infty \chi_b N)_{\text{ODT}} = 5.098, 4.243, 3.229$, and 2.865 , respectively.

Finally, Fig. 4.13 presents the updated fluctuation-corrected phase diagram, including both first-order (LAM-DIS) and second-order (A+B-DIS) transitions. The gray dashed lines denote SCFT phase boundaries, while the red symbols represent the fluctuation-corrected results obtained from FTSS. Fluctuations are seen to suppress the ordered phases, shifting both the ODT and critical points relative to their mean-field predictions.

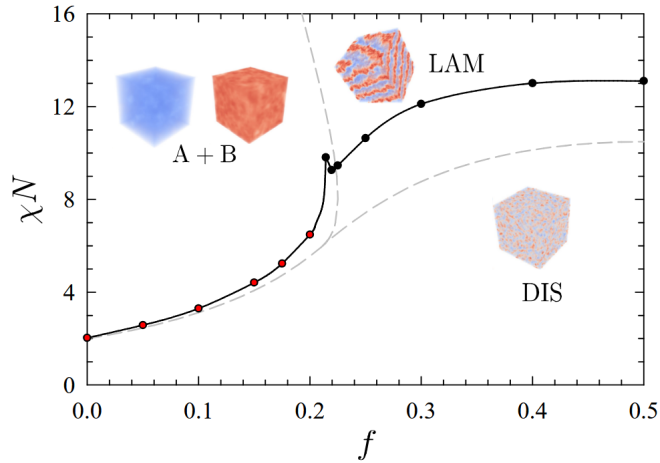


Figure 4.13: Updated phase diagram for the symmetric melt. Gray dashed lines denote SCFT phase boundaries. Red symbols mark fluctuation-corrected phase transitions obtained from WTMD (first-order) and finite-size scaling (second-order) analysis. Note that the numerical inaccuracies are smaller than the symbols.

With these results, we have determined the fluctuation-corrected phase boundaries for all $f \leq 0.2$. In the next section, we extend this analysis to compositions near the Lifshitz point, where the character of the phase behavior changes qualitatively.

4.4 Tricritical Point and First-Order Transitions

To approach the region where mean-field theory predicts a Lifshitz critical point, we require compositions f that are not simple ratios of $N_{1,A}/40$. To achieve this, we allow the total polymerization index N to deviate from 40. Specifically, we increase the chain length to $N = 44$ and set $N_{1,A} = 9$, giving $f = 0.205$. We then repeat the finite-size scaling analysis of the order parameter histograms, as described previously. The resulting distributions are shown in Fig. 4.14.

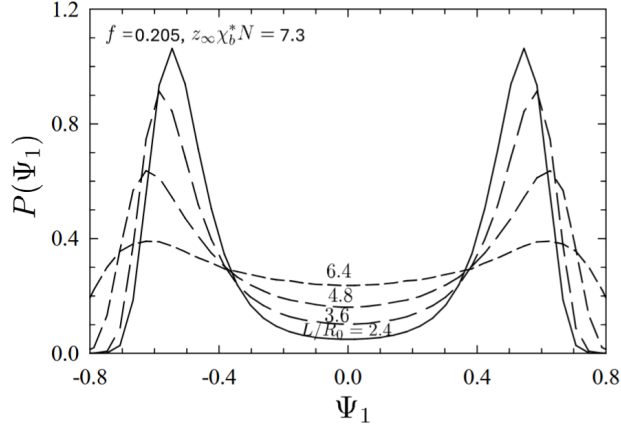


Figure 4.14: Histograms of the order parameter Ψ_1 from semi-grand canonical simulations for $f = 0.205$ and $z_\infty \chi_b^* N = 6.7$, evaluated for several system sizes.

Calculating the Binder cumulant for $f = 0.205$ using the same procedure as before yields the curves in Fig. 4.15. The intersection of these curves determines the critical point at $(z_\infty \chi_b N)_{\text{ODT}} = 6.76$.

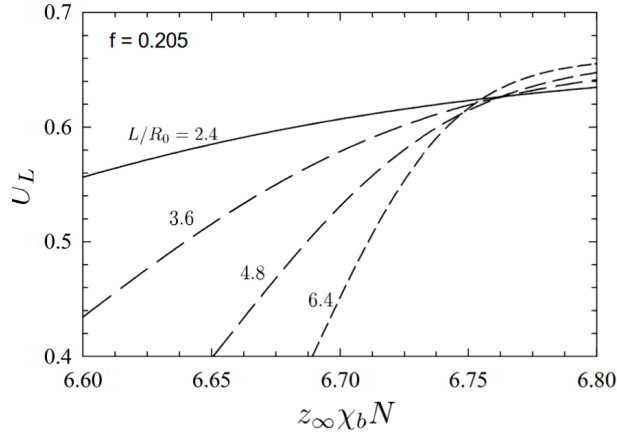


Figure 4.15: Binder cumulant U_L for $f = 0.205$. The intersection identifies the transition at $(z_\infty \chi_b N)_{\text{ODT}} = 6.76$.

Rescaling U_L according to finite-size scaling theory produces the collapse shown in

Fig. 4.16. The data collapse when using the 3D Ising exponent $\nu = 0.630$, confirming that the transition remains second order at $f = 0.205$.

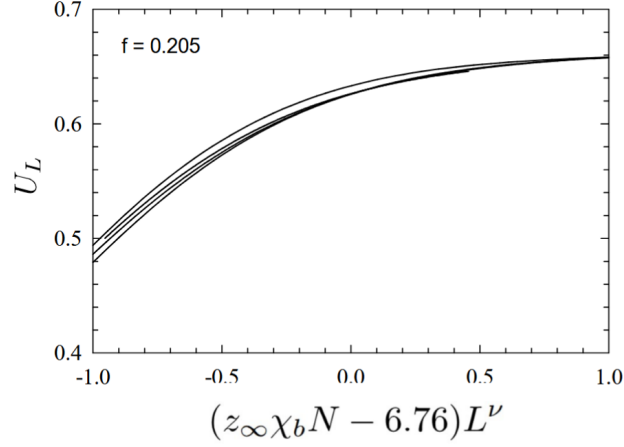


Figure 4.16: Finite-size scaling of the Binder cumulants from Fig. 4.15. The curves collapse using the 3D-Ising critical exponent $\nu = 0.630$.

As we move closer to the mean-field Lifshitz point, the nature of the transition changes rapidly. If we were to keep $N = 40$ and increase $N_{1,A}$ by one, we would bypass the region of interest. Instead, we increase the polymerization to $N = 43$ and set $N_{1,A} = 9$, yielding $f = 0.209$.

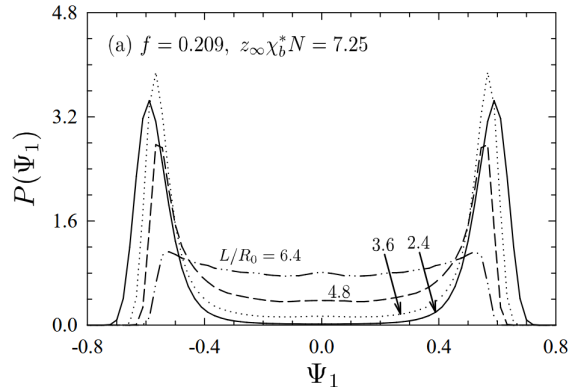


Figure 4.17: Normalized histograms of Ψ_1 for $f = 0.209$ and $z_\infty \chi_b^* N = 7.25$, evaluated for several system sizes.

Figure 4.17 shows the histograms for this composition. The corresponding Binder cumulants, plotted in Fig. 4.18, indicate that these simulations remain within the disordered phase. Applying histogram reweighting yields the fixed point at $(z_\infty \chi_b N)_c = 7.35$.

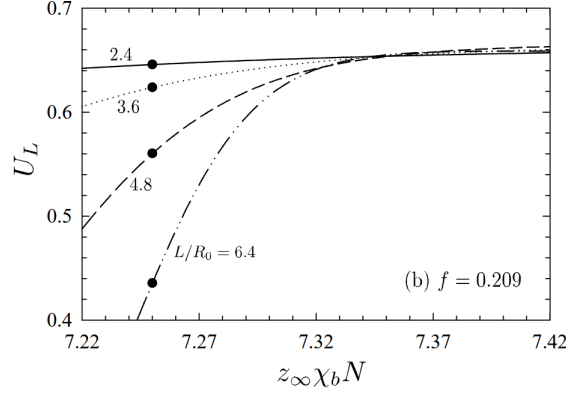


Figure 4.18: Binder cumulant U_L for $f = 0.209$ across a range of χ_b . The crossing point at $(z_\infty \chi_b N)_c = 7.35$ marks the critical transition.

Rescaling the histograms by their standard deviation, $\sigma_\Psi = \sqrt{\langle \Psi_1^2 \rangle}$, yields a collapse (Fig. 4.19), indicating that the transition is still critical.

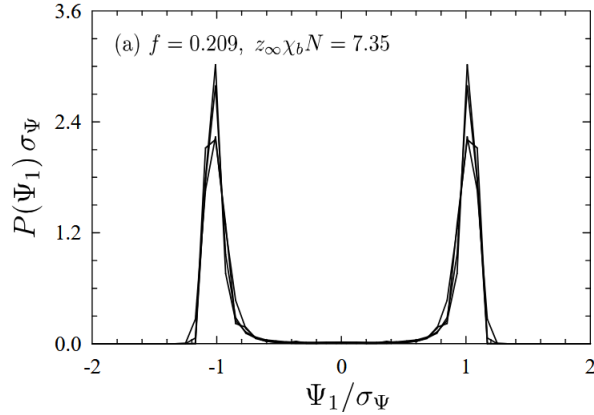


Figure 4.19: Rescaled histograms for $f = 0.209$ and $z_\infty \chi_b N = 7.35$. Their collapse confirms universal scaling behavior at criticality.

However, as shown in Fig. 4.20, the Binder cumulants no longer collapse when scaled with the Ising exponent $\nu = 0.630$ (dashed curves). When instead we use the tricritical

exponent $\nu = 0.5$ (solid curves), the cumulants collapse once more, implying that we have reached a tricritical point [87].

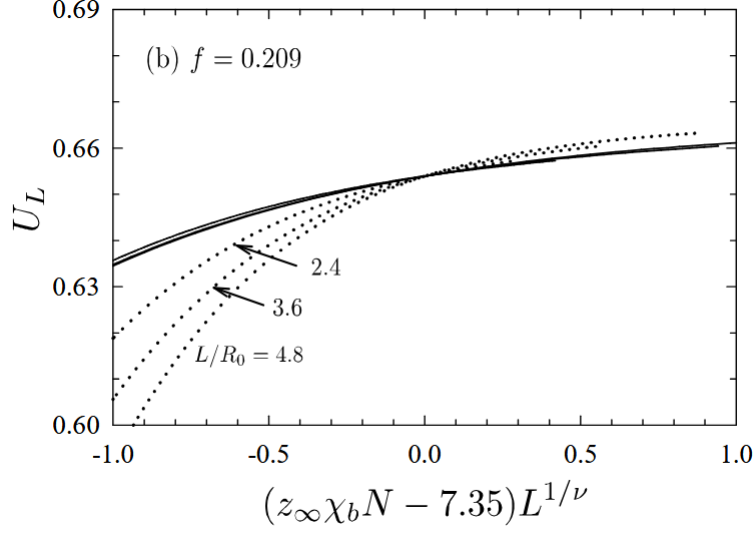


Figure 4.20: Finite-size scaling of U_L for $f = 0.209$. The dashed curves (Ising exponent $\nu = 0.630$) fail to collapse, while the solid curves (tricritical exponent $\nu = 0.5$) do.

Beyond the tricritical point, the $(A+B)/\text{DIS}$ transition becomes discontinuous [87]. To confirm this, we set $f = 0.213$ by choosing $N = 47$ and $N_{1,A} = 10$. Figure 4.21 shows the normalized histogram (dashed curve) at $z_\infty \chi_b N = 7.9$. Unlike a continuous transition, the distribution now exhibits three distinct peaks, corresponding to coexisting disordered, A -rich, and B -rich states. Adjusting χ_b via reweighting to equalize the peak heights (solid curve) gives $(z_\infty \chi_b N)_{\text{ODT}} = 7.84$.

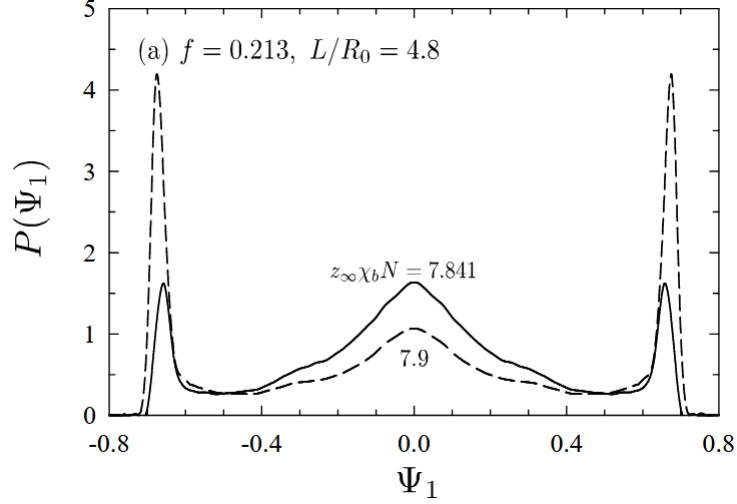


Figure 4.21: Normalized histogram for $f = 0.213$ and $z_\infty\chi_b N = 7.9$. The three peaks indicate phase coexistence characteristic of a first-order transition.

This estimate is influenced by finite-size effects (here $L = 4.8R_0$). To obtain the thermodynamic limit ($L \rightarrow \infty$), we repeat the analysis for several box sizes. Figure 4.22 shows the extrapolation of $(z_\infty\chi_b N)_{\text{ODT}}$ to infinite system size, using the fit

$$z_\infty\chi_b N = a_1 + a_2 L^{-a_3}. \quad (4.18)$$

The fitted intercept yields $(z_\infty\chi_b N)_{\text{ODT}} = 8.04$.

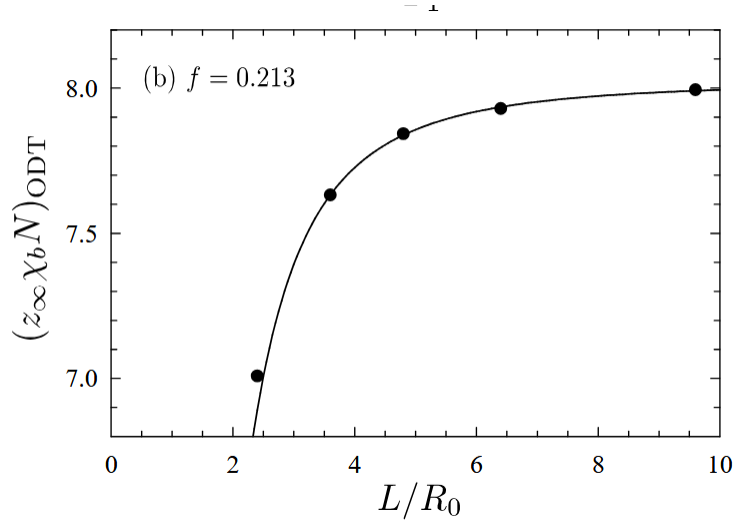


Figure 4.22: Finite-size extrapolation of the ODT for $f = 0.213$. The fit $z_\infty \chi_b N = a_1 + a_2 L^{-a_3}$ yields $(z_\infty \chi_b N)_{\text{ODT}} = 8.04$ in the thermodynamic limit. Note that the numerical inaccuracies are smaller than the symbols.

We can identify three new points along the $(A+B)/\text{DIS}$ phase boundary. The updated phase diagram in Fig. 4.23 shows the full set of fluctuation-corrected transitions between order and disordered phases. The gray dashed lines represent the mean-field SCFT predictions, while the red symbols denote transitions determined from FTSs in this section. The results clearly show the emergence of a tricritical point separating second-order and first-order behavior near the Lifshitz regime.

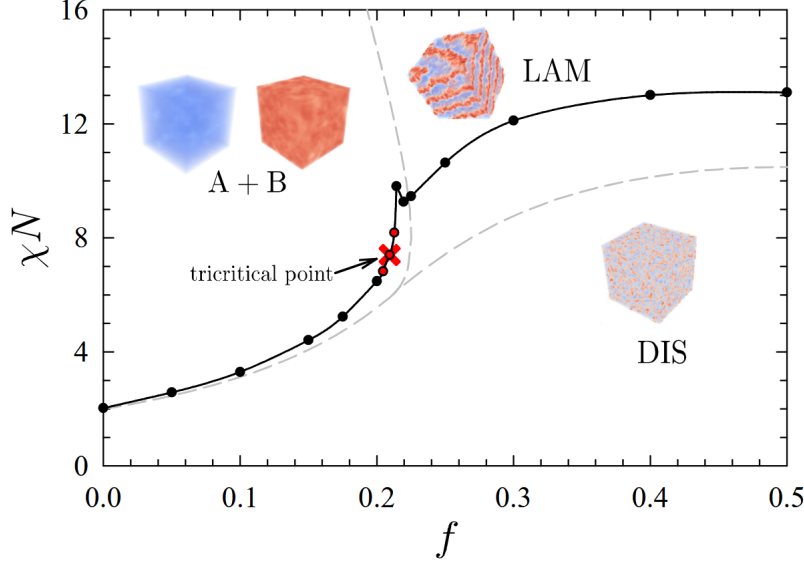


Figure 4.23: Phase diagram for the symmetric melt. Gray dashed lines denote SCFT phase boundaries. Red symbols indicate newly added fluctuation-corrected transitions between two-phase and disordered states. Note that the numerical inaccuracies are smaller than the symbols.

4.5 Tension Calculation for Order-Order Transitions

We now turn to locating the transition between the macrophase-separated $A+B$ coexistence and the microphase-separated LAM phase. Within SCFT, this transition occurs extremely close to the point where the interfacial tension, γ_{AB} , between the A - and B -rich phases approaches zero. This behavior arises because the interfacial tension represents the excess free energy per unit interfacial area. When $\gamma_{AB} < 0$, the system can lower its total free energy by creating additional interfaces. This leads naturally to the formation of a lamellar morphology with many stacked interfaces to lower energy. Conversely, when $\gamma_{AB} > 0$, the creation of interfaces is energetically costly, and the system minimizes its interfacial area by phase separating into two macroscopic domains.

To compute the interfacial tension within our FTS framework, we simulate $A+B$ coexistence in the canonical ensemble. By choosing an elongated simulation box with $L_x > L_y = L_z$, the resulting A/B interfaces preferentially orient perpendicular to the x -axis, as illustrated in Fig. 4.24. Under these conditions, the free energy of the coexistence

system is

$$F = f_{\text{bulk}}V + \gamma_{AB}\mathcal{A}, \quad (4.19)$$

where $\mathcal{A} = 2L_yL_z$ is the total interfacial area, the factor of two arising from the two interfaces created by periodic boundary conditions. The interfacial tension is thus obtained from the derivative of the free energy with respect to the box shape as

$$\gamma_{AB} = -\frac{1}{\mathcal{A}}\hat{\mathcal{D}}F, \quad (4.20)$$

where the differential operator is defined by

$$\hat{\mathcal{D}} = L_x \frac{\partial}{\partial L_x} - \frac{L_y}{2} \frac{\partial}{\partial L_y} - \frac{L_z}{2} \frac{\partial}{\partial L_z}. \quad (4.21)$$

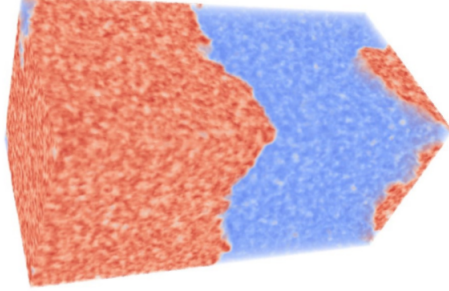


Figure 4.24: Configuration of the monomer density field ϕ_- from a canonical FTS simulation with $f = 0.2$ and $z_\infty\chi_b N = 13.0$. The snapshot shows A -rich (red) and B -rich (blue) regions separated by two planar interfaces.

The derivatives of the free energy can be expressed as ensemble averages of derivatives of the Hamiltonian, giving

$$\gamma_{AB} = -\frac{1}{\mathcal{A}}\left\langle\hat{\mathcal{D}}\mathcal{H}\right\rangle. \quad (4.22)$$

These derivatives are evaluated at constant effective χ , which is equivalent to constant bare χ_b when the grid spacing is isotropic in all three dimensions. Since only non-volume-proportional terms in $\mathcal{H}$ contribute, the interfacial tension simplifies to

$$\frac{\gamma_{AB}N^{1/2}}{a\rho_0^2k_BT} = \frac{L_z}{4R_0}\left\langle\frac{\hat{\mathcal{D}}Q_1}{Q_1} + \frac{\hat{\mathcal{D}}Q_2}{Q_2}\right\rangle, \quad (4.23)$$

where analytical forms for the derivatives $\hat{\mathcal{D}}Q_\alpha$ are provided in Ref [88]. This interfacial tension can be approximated with strong stretching theory [89, 90].

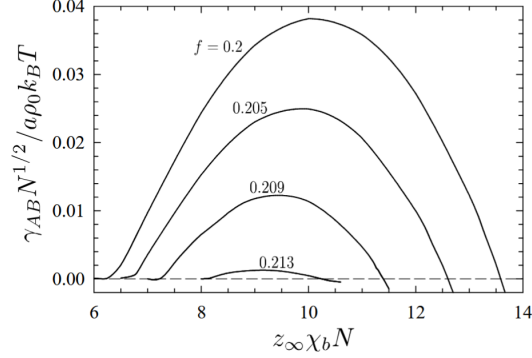


Figure 4.25: Interfacial tension γ_{AB} as a function of χ_b for several values of f in the $A+B$ coexistence region. The vanishing of γ_{AB} identifies the LAM/(A+B) transition.

Figure 4.25 plots the interfacial tension γ_{AB} versus χ_b for $f = 0.213$ and several smaller f values. As expected, γ_{AB} vanishes at the continuous DIS/(A+B) transition and becomes undefined beyond it. However, near the discontinuous LAM/(A+B) transition, γ_{AB} overshoots below zero due to the metastability of the $A+B$ coexistence. This overshoot allows us to locate the precise condition where $\gamma_{AB} = 0$. For $f = 0.213$, this occurs at $z_\infty \chi_b N = 10.12$, in close agreement with our previous estimate from domain-competition simulations. The agreement should improve at higher segregations, and therefore, to an excellent approximation, we can equate the LAM/(A+B) transition with the $\gamma_{AB} = 0$ points in Fig. 4.25.

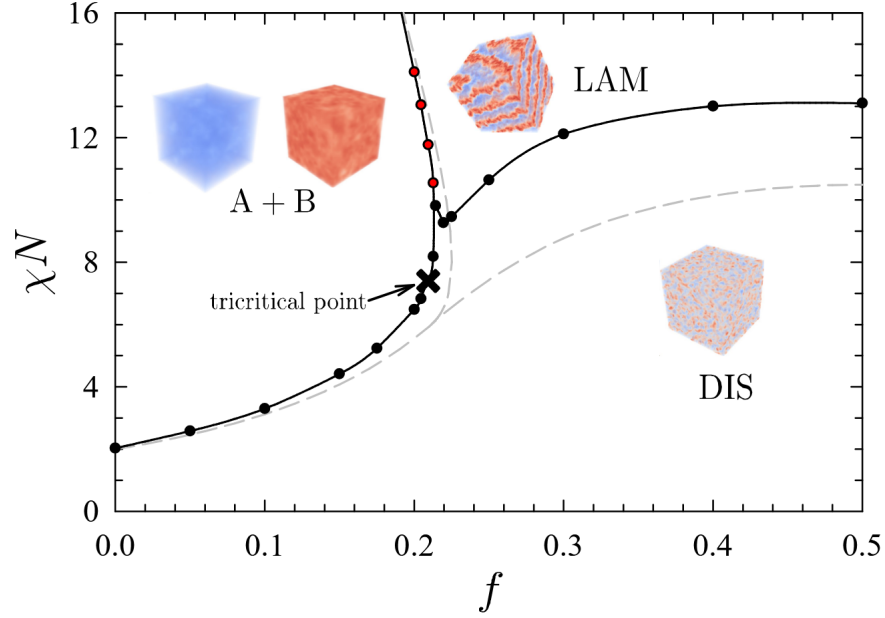


Figure 4.26: Updated phase diagram for the symmetric melt. Gray dashed lines represent SCFT phase boundaries, while red symbols denote newly determined LAM/(A+B) transition points identified from $\gamma_{AB} = 0$. Note that the numerical inaccuracies are smaller than the symbols.

In the limit of large χN , our fluctuation-corrected transition lines asymptotically approach the mean-field SCFT boundaries, confirming that the FTSs correctly recover the SCFT predictions in the strong-segregation limit.

4.6 Microemulsion-Disordered Fluid Crossover

The highly swollen LAM phase is expected to disorder into a bicontinuous microemulsion ($B\mu E$). Indeed, the morphology shown in Fig. 4.27 for $f = 0.225$ and $z_\infty \chi_b N = 9$ exhibits the characteristic features of a $B\mu E$ —namely, large, interconnected, and well-segregated domains. However, this structure gradually fades as we move away from the Lifshitz region. At lower segregation, such as $z_\infty \chi_b N = 7$, the system loses its compositional contrast, while at more symmetric compositions (e.g., $f = 0.375$), the characteristic domain size becomes significantly smaller. Because this change occurs continuously rather than

through a sharp phase transition, there is no well-defined thermodynamic point at which the B μ E becomes an ordinary disordered melt. Nevertheless, it is useful to delineate the approximate crossover between the two regimes, even if the boundary is somewhat arbitrary.

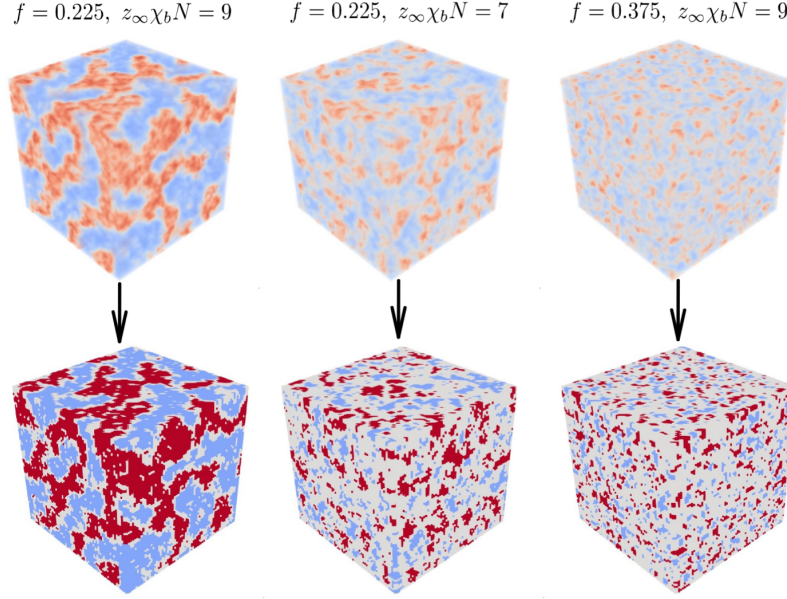


Figure 4.27: Equilibrated morphologies from FTSs in cubic boxes of size $L = 12.8R_0$ for several points within the DIS region. Top panels: continuous color scale of $\phi_-(\mathbf{r})$. Bottom panels: binary representation highlighting well-segregated regions defined by $|\phi_-(\mathbf{r})| > 0.33$.

To define a quantitative criterion for this crossover, we appeal to the physical picture of a microemulsion as a disordered but locally well-segregated fluid. During simulations, we monitor the composition field $\phi_-(\mathbf{r})$ and identify well-segregated A - and B -rich domains by the conditions $\phi_-(\mathbf{r}) > 1/3$ and $\phi_-(\mathbf{r}) < -1/3$, respectively, as illustrated in the lower panels of Fig. 4.27. Within each configuration, we determine the largest sphere that can fit entirely inside one of these domains, and we compute its ensemble-averaged diameter, $2R_{\text{sphere}}$. If this diameter exceeds the polymer end-to-end distance, R_0 , we classify the morphology as bicontinuous microemulsion. By this criterion, the configuration at $f = 0.225$ and $z_{\infty}\chi_b N = 9$ in Fig. 4.27 qualifies as a B μ E, whereas the others do not.

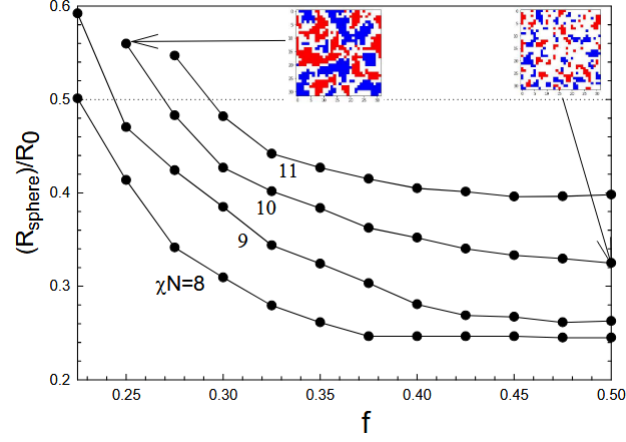


Figure 4.28: Ratio of the radius of the largest sphere that fits within a well-segregated domain, R_{sphere} , to the polymer end-to-end distance, R_0 , for several $z_{\infty}\chi_b N$ values ($z_{\infty}\chi_b N = 8, 9, 10$, and 11 , respectively).

This structural measure provides a practical way to map the continuous crossover between disordered and microemulsion-like morphologies. Figure 4.28 shows how R_{sphere}/R_0 varies with composition and segregation strength. For sufficiently asymmetric blends ($f \lesssim 0.25$) and moderate segregation ($z_{\infty}\chi_b N \approx 9\text{--}10$), $R_{\text{sphere}} > R_0/2$. This measure indicates a well-developed microemulsion structure. In contrast, for more symmetric or weakly segregated systems, R_{sphere} drops below this threshold, marking the transition to a homogeneous disordered melt.

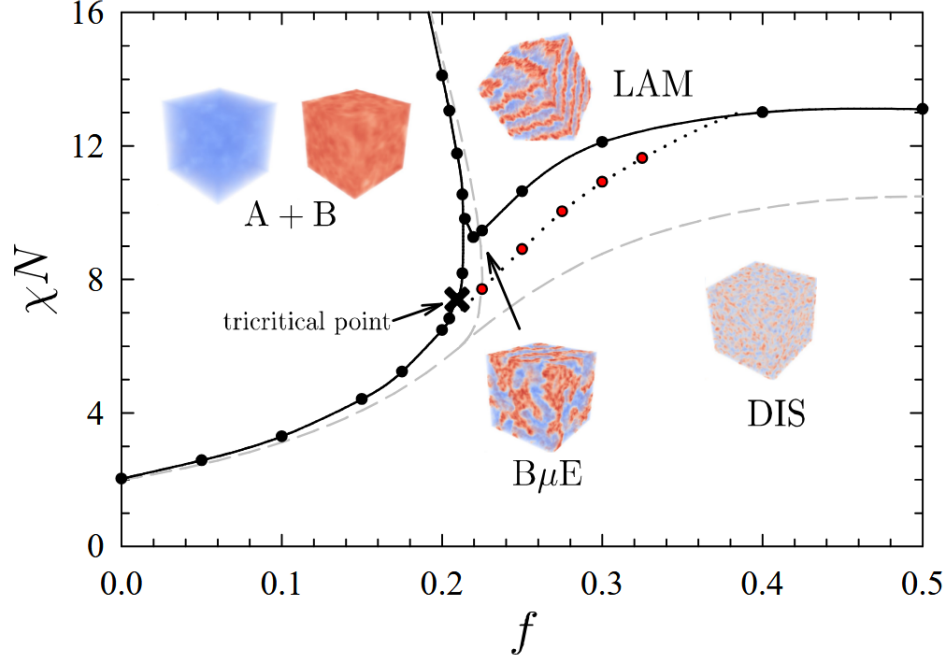


Figure 4.29: Updated phase diagram for the symmetric melt. Gray dashed lines denote the mean-field SCFT phase boundaries. Red symbols mark the approximate crossover between the disordered and microemulsion regimes. Note that the numerical inaccuracies are smaller than the symbols.

In the large- f limit, the microemulsion regime gradually disappears, as the characteristic domain size is comparable to the lamellar period. Consequently, even well-formed domains have size smaller than the polymer end-to-end distance, R_0 , and so are classified as a homogeneous disordered state by our criterion.

Chapter 5

Discussion

5.1 Phase Diagram

The phase diagram in Fig. 5.1 compares the phase transitions obtained from our field-theoretic simulation (FTS) calculations for $\bar{N} = 10^4$ with the self-consistent field theory (SCFT) phase diagram in Fig. 2.7 for $\bar{N} = \infty$. It also includes our estimated boundary separating the structured bicontinuous microemulsion (B μ E) from the relatively unstructured disordered DIS phase (dotted curve). To enable a direct comparison between SCFT and FTSs, the results are plotted in terms of an effective nonlinear χ , defined by Eq. 3.50. This calibration accounts for both the mapping from the discrete Gaussian chain model to the continuous SGCM chains and the removal of the unphysical grid-spacing dependence known as the ultraviolet divergence [58]. The coefficient c_2 used in this calibration depends on the dimensionless monomer concentration, $\rho_0 a^3 = (\bar{N}/N)^{1/2}$, where $\bar{N} = 10^4$ in our study. Ideally, this calibration should be repeated for each concentration used in the Lifshitz regime ($0.20 < f < 0.225$) because our choice of different N values causes small changes in ρ_0 . However, based on prior experience [59], c_2 depends only weakly on ρ_0 , so we adopt a constant value $c_2 = 0.112$ for all data points in Fig. 5.1.

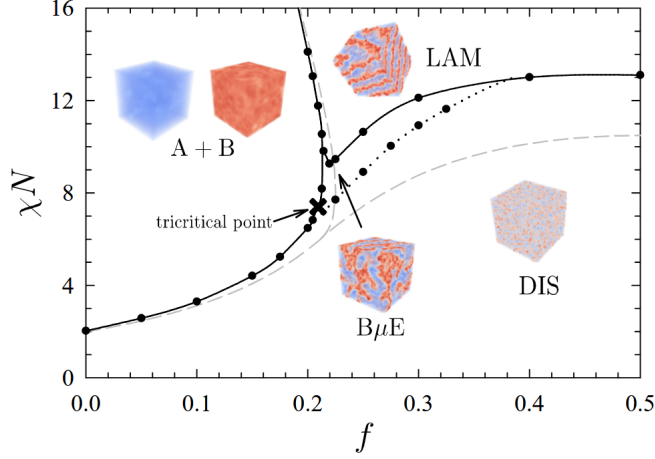


Figure 5.1: FTS phase diagram for $\bar{N} = 10^4$ plotted in terms of the nonlinear χ (solid curves), compared to the SCFT phase diagram for $\bar{N} = \infty$ (dashed curves). Fluctuations transform the mean-field Lifshitz point into a tricritical point (cross) and generate a $B\mu E$ region (dotted curve) separating the LAM and DIS phases.

A pair of complementary diblocks with compositions $f < 0.5$ and $1 - f > 0.5$ effectively behave as a single long diblock copolymer, since their longer blocks preferentially anchor to the same interface. This coupling allows a blend of two diblocks that would individually disorder at a given χN to collectively form a lamellar (LAM) morphology. As a result, complementary diblocks mimic a symmetric diblock of polymerization $2(1 - f)N$, which forms an ordered LAM phase with a larger periodicity than either component would exhibit on its own. This behavior ceases when the shorter block becomes too small to remain at the interface, at which point macrophase separation occurs. The transition from microphase to macrophase separation corresponds to the region where the $B\mu E$ phase emerges.

When $f = 0.5$, the system reduces to a simple melt of symmetric diblock copolymers. The effects of fluctuations in this case are well established: the second-order transition predicted by mean-field SCFT is replaced by a weakly first-order transition [41, 54, 79]. Moreover, fluctuations stabilize the DIS phase, shifting the order-disorder transition (ODT) to higher χN . The same behavior is observed on the right-hand side of our phase diagram ($f > 0.225$), where all transitions are first order and occur at χN values larger than the SCFT predictions. Block copolymer phase behavior becomes universal [91, 72, 73] once the molecular length scale, $R_0 = aN^{1/2}$, is sufficiently larger than the non-universal length scale (i.e. the monomer length scale, a). Our choice of $N = 40$ for this work appears to meet

this requirement. We can see this by comparing with the universal ODT for symmetric diblocks ($f = 0.5$) [73],

$$(\chi N)_{\text{ODT}} = 10.495 + 41.0\bar{N}^{-1/3} + 123.0\bar{N}^{-0.56}. \quad (5.1)$$

For $\bar{N} = 10^4$, Eq. 5.1 gives $(\chi N)_{\text{ODT}} = 13.11$, which closely matches our FTS prediction of $(\chi N)_{\text{ODT}} = 13.10$.

On the left-hand side of Fig. 5.1, SCFT predicts a continuous macrophase separation. When $f = 0$, the system reduces to a binary homopolymer blend, whose fluctuation effects are also well understood [92, 93]. Here, fluctuations are comparatively weak; the transition remains second order and shifts only slightly upward in χN relative to the mean-field prediction. We can also compare to a universal prediction for symmetric homopolymer blends ($f = 0$) [94],

$$(\chi N)_{\text{ODT}} = 2 + 1.62\bar{N}^{-1/2}. \quad (5.2)$$

Again for $\bar{N} = 10^4$, Eq. 5.2 predicts $(\chi N)_{\text{ODT}} = 2.02$, which similarly matches our FTS prediction of $(\chi N)_{\text{ODT}} = 2.03$.

At strong-segregation (large χN), the fluctuation-corrected phase boundary (solid line) between LAM and two-phase asymptotically approaches its SCFT counterpart (dashed line), confirming that our FTSs recover the mean-field predictions at large χN , as expected.

It is noteworthy that the lamellar period along the ODT, shown in Fig. 4.3, closely matches the SCFT prediction for the standard Gaussian chain model (GCM) when evaluated using the nonlinear χ obtained from the Morse calibration. This same level of agreement is observed in other FTSs [88, 59] and in particle-based simulations [80, 81] of neat diblock copolymer melts. These results imply that SCFT remains reasonably accurate for ordered phases and that fluctuations have only a modest effect on the (A+B)/LAM transition in Fig. 5.1 at large χN .

The agreement of our FTSs with the universal predictions in Eqs. 5.1 and 5.2 implies that the partial saddle-point approximation is reasonably accurate at $\bar{N} = 10^4$. It also implies that our grid resolution, $\Delta = 0.2R_0$, is adequate. Previous phase diagram calculations for neat diblock copolymer melts required a finer grid [95], but this was because the complex phases (i.e., gyroid and Fddd) are very similar in structure. Here, all the phases are reasonably distinct, and thus the same level of precision is not required.

Overall, the influence of fluctuations on binary diblock blends is remarkably similar to that observed in ternary homopolymer–diblock blends [24, 25]. In both systems, fluctuations stabilize the DIS phase, shifting both the (A+B)/DIS and LAM/DIS transitions

to higher χN . Additionally, in both cases, the mean-field Lifshitz point is destroyed and replaced by a tricritical point, with a $B\mu E$ region emerging in the Lifshitz regime.

The key difference between the binary and ternary systems lies in the nature of the order–order transitions. In ternary blends, SCFT predicts a three-phase coexistence region (A+B+LAM), where fluctuations transform the lower- χN portion into A+B+ $B\mu E$ coexistence. By contrast, in binary diblock blends, the three-phase coexistence is reduced to a one-dimensional transition line, making these systems far more robust for forming stable, single-phase $B\mu E$ without the risk of macrophase separation.

5.2 Instability of the Lifshitz Point and Microemulsion

We now have two distinct systems in which fluctuations transform a mean-field Lifshitz point into a tricritical point. The first system involving ternary blends [23, 24, 25] demonstrated this transition through the change in the (A+B)/DIS boundary from continuous to discontinuous, as evidenced by the emergence of A+B+ $B\mu E$ coexistence. We observe analogous behavior in Fig. 4.8, which shows a continuous transition at $f = 0.20$, while Fig. 4.21 reveals a discontinuous transition at $f = 0.213$. Moreover, we find direct evidence of a tricritical point at $f \approx 0.209$ in Fig. 4.20, indicated by the change in the correlation-length critical exponent to $\nu = 0.5$ [87]. Interestingly, this tricritical point remains remarkably close to the mean-field Lifshitz point at $f = 0.211$. The same proximity was observed in the ternary blends, where the tricritical and Lifshitz points occurred at copolymer volume fractions of $\bar{\phi}_c \approx 0.073$ and 0.074 respectively [25].

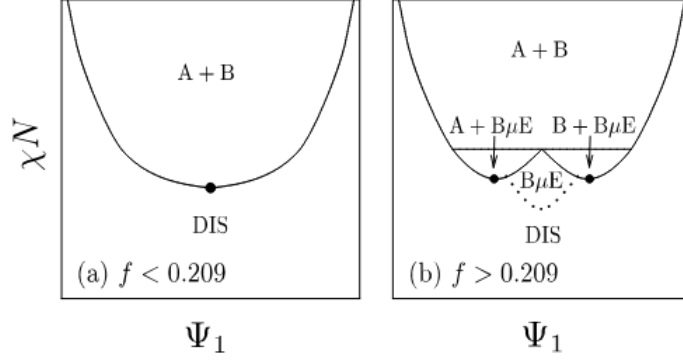


Figure 5.2: Schematic phase diagrams in the $\hat{\Psi}_1$ -plane corresponding to the (a) continuous and (b) discontinuous (A+B)/DIS transitions in Fig. 5.1. Critical points are denoted by dots. The point at $\hat{\Psi}_1 = 0$ in (a) forms the critical line visible in Fig. 5.1, while the points in (b) form two additional critical lines. All three critical lines converge to the tricritical point at $f \approx 0.209$.

The schematic phase diagrams in Fig. 5.2 illustrate the phase behavior in the vicinity of the tricritical point. At smaller f , symmetric DIS blends with $n_1 = n_2$ (i.e., $\Psi_1 = 0$) undergo continuous macrophase separation at the critical point denoted by the dot in Fig. 5.2(a). At larger f , they instead evolve into $B\mu E$ structures, which then discontinuously split into A+B coexistence above the horizontal tie line in Fig. 5.2(b). Slightly asymmetric DIS blends, such as those with $n_1 > n_2$ (i.e., $\Psi_1 > 0$), become unstable at lower χN , at which point they shed excess diblocks to form a more balanced $B\mu E$ coexisting with a B-rich phase. Conversely, for $n_1 < n_2$ (i.e., $\Psi_1 < 0$), an A+B μE coexistence occurs. Both coexistence regions terminate at lower critical points, denoted by dots in Fig. 5.2(b), which belong to two additional critical lines. All three critical lines converge to the tricritical point (cross) in Fig. 5.1, as expected.

Chapter 6

Conclusion

It is worth emphasizing the remarkable efficiency of our field-theoretic simulations (FTSs) compared to conventional particle-based methods such as molecular dynamics. For example, the simulation boxes shown in Figs. 4.5 and 4.6 each contain 1.4×10^6 polymers with a polymerization degree of $N \approx 40$. The FTSs also successfully overcame the slow dynamics that arise near phase transitions, where competing phases have nearly identical free energies. Conventional simulations of this scale would typically require thousands of graphics processing units (GPUs)[96], whereas each of our FTSs were performed on a single GPU. For our largest systems, we employed a new machine-learning algorithm to solve $w_+(\mathbf{r})$ [97], which increased computational speed by more than a factor of two. As a relatively new approach compared to mature techniques such as molecular dynamics, FTS is still rapidly evolving, and continued methodological advances are expected to further enhance its computational advantage.

In this work, FTSs were used to determine fluctuation corrections to the self-consistent field theory (SCFT) phase diagram of binary blends containing equal amounts of two AB diblock copolymers. The blends have invariant polymerizations of $\bar{N} = 10^4$ and complementary compositions of f and $1 - f$. The system was modeled as an incompressible melt of discrete Gaussian chains with contact interactions of strength χ_b between A and B monomers. Each polymer contained approximately $N \approx 40$ segments, providing sufficient separation between the monomer and molecular length scales (i.e., a and $R_0 = aN^{1/2}$, respectively) to exhibit universal behavior characteristic of the large- N limit. This universality was confirmed by the order-disorder transitions (ODTs) computed for $f = 0.5$ and $f = 0.0$, which matched the universal results in Eqs. 5.1 and 5.2, respectively, when expressed in terms of the effective Flory-Huggins interaction parameter χ determined from the Morse calibration [59, 98], as given by Eq. 3.50.

We located the second-order (A+B)/DIS transition using finite-size scaling of the Binder cumulant. For $f < 0.209$, its dependence on system size followed the critical exponent $\nu = 0.630$ characteristic of the three-dimensional Ising universality class. However, at $f \approx 0.209$, the scaling exponent switched to $\nu = 0.50$, the value expected at a tricritical point, which is where a line of second-order transitions changes into a line of first-order ones. This interpretation is consistent with the histograms of the order parameter, Ψ_1 , which exhibited three distinct peaks for $f > 0.209$, indicating coexistence of the (A+B) and disordered (DIS) phases at a discontinuous transition. Together, these observations provide conclusive evidence that fluctuations transform the mean-field Lifshitz critical point into a tricritical point.

The discontinuous LAM/DIS transition was identified using well-tempered metadynamics (WTMD). The lamellar period along the order-disorder transition (ODT) closely matched SCFT predictions, deviating only slightly for $f \approx 0.225$. This result agrees with previous FTS studies [88, 59] and particle-based simulations [80, 81] of diblock copolymer melts, all of which show that fluctuations have a relatively minor effect on ordered phases. Just above the tricritical point we further found that the (A+B)/LAM transition coincides with the condition where the interfacial tension, γ_{AB} , between A- and B-rich phases approaches zero. This relationship was then used to accurately estimate the transition at stronger segregations.

In the DIS region of the phase diagram near the mean-field Lifshitz critical point, the disordered morphology takes the form of a bicontinuous microemulsion (B μ E), characterized by large, well-segregated, and interpenetrating A- and B-rich domains. We proposed a criterion to distinguish the B μ E from the ordinary DIS phase. Our criterion is that a morphology is classified as B μ E if spheres of diameter R_0 can fit entirely within the well-segregated domains. This criterion was then applied to identify the region of the phase diagram corresponding to the B μ E phase.

The fluctuation effects observed in the binary diblock blends are remarkably similar to those found in previously studied ternary homopolymer-diblock blends [24, 25], where the bicontinuous microemulsion (B μ E) phase was first identified experimentally [1]. The key distinction is that three-phase coexistence regions are absent in the binary system, which makes it more favorable for forming a stable single-phase B μ E. Overall, the similarity in behavior indicates that B μ E formation is a general feature of systems for which SCFT predicts a Lifshitz critical point.

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APPENDICES

Appendix A

Hubbard-Stratonovich Transformation

To recover the Hubbard-Stratonovich transformation [32, 36, 39, 40] we begin with a general Gaussian functional integral of the form

$$\mathcal{I} = \int \mathcal{D}W \exp \left[-\frac{1}{2} \int d\mathbf{r} d\mathbf{r}' W(\mathbf{r}') A(\mathbf{r}', \mathbf{r}) W(\mathbf{r}) - \int d\mathbf{r} \phi(\mathbf{r}) W(\mathbf{r}) \right]. \quad (\text{A.1})$$

To evaluate this path integral, we discretize space onto a lattice of M sites, each with volume v_{cell} . The value of a field at the center of the i^{th} lattice cell is denoted $W(\mathbf{r}_i)$. The integrals are then replaced by Riemann sums,

$$\mathcal{I} = \int (\mathcal{N}^M \prod_{i=1}^M dW(\mathbf{r}_i)) \exp \left[-\frac{1}{2} \sum_{i=1}^M \sum_{j=1}^M v_{\text{cell}}^2 W(\mathbf{r}_j) A(\mathbf{r}_j, \mathbf{r}_i) W(\mathbf{r}_i) - v_{\text{cell}} \sum_{i=1}^M \phi(\mathbf{r}_i) W(\mathbf{r}_i) \right], \quad (\text{A.2})$$

where the factor $\mathcal{N}$ ensures that $\mathcal{I}$ remains finite in the continuum limit ($v_{\text{cell}} \rightarrow 0$, $M \rightarrow \infty$). We now introduce vector notation,

$$\mathbf{W}_i = W(\mathbf{r}_i), \quad \phi_i = \phi(\mathbf{r}_i), \quad (\text{A.3})$$

and define the matrix

$$A_{ji} = A(\mathbf{r}_j, \mathbf{r}_i). \quad (\text{A.4})$$

With these definitions, the integral becomes

$$\mathcal{I} = \mathcal{N}^M \int d^M \mathbf{W} \exp \left[-\frac{v_{\text{cell}}^2}{2} \mathbf{W}^T A \mathbf{W} - v_{\text{cell}} \boldsymbol{\phi}^T \mathbf{W} \right]. \quad (\text{A.5})$$

We diagonalize the symmetric matrix A by introducing an orthonormal eigenbasis $\{\mathbf{a}_i\}$ with eigenvalues $\{\lambda_i/v_{\text{cell}}\}$ satisfying

$$v_{\text{cell}} \sum_{j=1}^M A_{ij} (\mathbf{a}_k)_j = \lambda_k (\mathbf{a}_k)_i. \quad (\text{A.6})$$

Let T_a be the transformation matrix that converts to this eigenbasis, such that $\mathbf{W} = T_a \mathbf{W}_a$. Then,

$$\mathcal{I} = \mathcal{N}^M \int d^M \mathbf{W}_a |T_a| \exp \left[-\frac{v_{\text{cell}}}{2} \sum_{i=1}^M \lambda_i W_{a,i}^2 - v_{\text{cell}} \sum_{i=1}^M \phi_{a,i} W_{a,i} \right]. \quad (\text{A.7})$$

Choosing the eigenbasis to be orthonormal gives $|T_a| = 1$. The multidimensional integral thus factorizes into a product of M one-dimensional Gaussian integrals:

$$\mathcal{I} = \mathcal{N}^M \prod_{i=1}^M \int_{-\infty}^{\infty} dW_{a,i} \exp \left[-\frac{v_{\text{cell}}}{2} \lambda_i W_{a,i}^2 - v_{\text{cell}} \phi_{a,i} W_{a,i} \right]. \quad (\text{A.8})$$

Using the standard identity

$$\int_{-\infty}^{\infty} dx e^{-\frac{a}{2}x^2 - yx} = e^{\frac{y^2}{2a}} \sqrt{\frac{2\pi}{a}}, \quad (\text{A.9})$$

we can directly evaluate the product to obtain

$$\begin{aligned} \mathcal{I} &= \mathcal{N}^M \prod_{i=1}^M \sqrt{\frac{2\pi}{\lambda_i}} \exp \left(\frac{v_{\text{cell}}}{2\lambda_i} \phi_{a,i}^2 \right) \\ &= \mathcal{N}^M \sqrt{\frac{(2\pi)^M}{\det A}} \exp \left(\frac{v_{\text{cell}}^2}{2} \boldsymbol{\phi}^T A^{-1} \boldsymbol{\phi} \right). \end{aligned} \quad (\text{A.10})$$

In the last step we used $\det A = \prod_i \lambda_i$ and $\sum_i (v_{\text{cell}}/\lambda_i) \phi_{a,i}^2 = v_{\text{cell}}^2 \boldsymbol{\phi}^T A^{-1} \boldsymbol{\phi}$. Taking the continuum limit ($v_{\text{cell}} \rightarrow 0$, $M \rightarrow \infty$) gives

$$\mathcal{I} = \left[\det \left(\frac{A}{2\pi \mathcal{N}^2} \right) \right]^{-1/2} \exp \left[\frac{1}{2} \int d\mathbf{r} d\mathbf{r}' \phi(\mathbf{r}') A^{-1}(\mathbf{r}', \mathbf{r}) \phi(\mathbf{r}) \right]. \quad (\text{A.11})$$

Finally, equating this expression with the original definition of $\mathcal{I}$ yields the Hubbard-Stratonovich transformation:

$$e^{\frac{1}{2} \int d\mathbf{r} d\mathbf{r}' \phi(\mathbf{r}') A^{-1}(\mathbf{r}', \mathbf{r}) \phi(\mathbf{r})} = \sqrt{\det\left(\frac{A}{2\pi\mathcal{N}^2}\right)} \int \mathcal{D}W e^{-\frac{1}{2} \int d\mathbf{r} d\mathbf{r}' W(\mathbf{r}') A(\mathbf{r}', \mathbf{r}) W(\mathbf{r}) - \int d\mathbf{r} \phi(\mathbf{r}) W(\mathbf{r})}. \quad (\text{A.12})$$

Appendix B

Weak Inhomogeneity Approximation

We aim to expand $\ln Q_\kappa[W_+, W_-]$ for weak, slowly varying fields as is done in [104, 30, 34]. Starting from the single-chain partition function of a Gaussian chain of length N ,

$$\ln Q_\kappa[W_+, W_-] = \ln \left(\frac{1}{V} \int \prod_{i=1}^N d\mathbf{r}_i \exp \left[-\frac{3}{2d^2} \sum_{i=1}^{N-1} \|\mathbf{r}_{i+1} - \mathbf{r}_i\|^2 - \sum_{s=1}^N (W_+(\mathbf{r}_s) + \gamma_{\kappa,s} W_-(\mathbf{r}_s)) \right] \right), \quad (\text{B.1})$$

we introduce the microscopic monomer densities for a single chain

$$\hat{\phi}_+^{(1)}(\mathbf{r}) = \frac{V}{N} \sum_{s=1}^N \delta(\mathbf{r} - \mathbf{r}_s), \quad \hat{\phi}_-^{(1)}(\mathbf{r}) = \frac{V}{N} \sum_{s=1}^N \gamma_{\kappa,s} \delta(\mathbf{r} - \mathbf{r}_s). \quad (\text{B.2})$$

We know that interactions with the fields can be expressed as an integral over these two densities, as seen in Section 1.4

$$\sum_{s=1}^N (W_+(\mathbf{r}_s) + \gamma_{\kappa,s} W_-(\mathbf{r}_s)) = \frac{N}{V} \int d\mathbf{r} [W_+(\mathbf{r}) \hat{\phi}_+^{(1)}(\mathbf{r}) + W_-(\mathbf{r}) \hat{\phi}_-^{(1)}(\mathbf{r})]. \quad (\text{B.3})$$

Substituting Eq. B.3 into Eq. B.1 lets us express the single-chain partition function as

$$Q_\kappa[W_+, W_-] = \frac{1}{V} \left\langle \exp \left[-\frac{N}{V} \int d\mathbf{r} (W_+ \hat{\phi}_+^{(1)} + W_- \hat{\phi}_-^{(1)}) \right] \right\rangle_0, \quad (\text{B.4})$$

where $\langle \cdots \rangle_0 = \int \prod_{i=1}^N d\mathbf{r}_i \cdots e^{-\frac{3}{2d^2} \sum_{i=1}^{N-1} \|\mathbf{r}_{i+1} - \mathbf{r}_i\|^2}$ denotes an average over non-interacting Gaussian chains. We can see the single chain partition function is an average of the

Boltzmann weight of the field energy. Next we expand this Boltzmann weight as $e^x = \sum_{j=0}^{\infty} \frac{1}{j!} x^j$ to get

$$Q_{\kappa}[W_+, W_-] = \sum_{j=0}^{\infty} \frac{(-1)^j N^j}{j! V^{j+1}} \langle \left(\int d\mathbf{r} (W_+ \hat{\phi}_+^{(1)} + W_- \hat{\phi}_-^{(1)}) \right)^j \rangle_0. \quad (\text{B.5})$$

Doing the binomial expansion $(A + B)^j = \sum_{l=0}^j \binom{j}{l} A^{j-l} B^l$ we find,

$$Q_{\kappa}[W_+, W_-] = \sum_{j=0}^{\infty} \sum_{l=0}^j \frac{(-1)^j \binom{j}{l} N^j}{j! V^{j+1}} \int d\{\mathbf{r}_b\} d\{\mathbf{r}_a\} \langle \prod_{a=1}^{j-l} \prod_{b=1}^l \hat{\phi}_+^{(1)}(\mathbf{r}_a) \hat{\phi}_-^{(1)}(\mathbf{r}_b) \rangle_0 \prod_{a=1}^{j-l} \prod_{b=1}^l W_+(\mathbf{r}_a) W_-(\mathbf{r}_b), \quad (\text{B.6})$$

where we defined the $\mathcal{M}^{th}$ Green's function as

$$G_{i,...,j}^{(\mathcal{M})}(\mathbf{r}_1, ..., \mathbf{r}_{\mathcal{M}}) = \langle \hat{\phi}_i^{(1)}(\mathbf{r}_1) \dots \hat{\phi}_j^{(1)}(\mathbf{r}_{\mathcal{M}}) \rangle_0. \quad (\text{B.7})$$

Expanding $\ln Q_{\kappa}$ to quadratic order in $W_{\pm}$ with $\ln(1 + X) = x + \frac{x^2}{2}$ gives

$$\begin{aligned} \ln Q_{\kappa}[W_+, W_-] &= -\frac{N}{V} \int d\mathbf{r} \left(\mathbf{G}^{(1)\text{T}}(\mathbf{r}) \mathbf{W}(\mathbf{r}) \right) - \ln V \\ &\quad + \frac{N^2}{2V^2} \int d\mathbf{r} d\mathbf{r}' \mathbf{W}^{\text{T}}(\mathbf{r}') \left(\mathbf{G}^{(2)}(\mathbf{r}', \mathbf{r}) - \mathbf{G}^{(1)\text{T}}(\mathbf{r}') \mathbf{G}^{(1)}(\mathbf{r}) \right) \mathbf{W}(\mathbf{r}) + O(W_{\pm}^3), \end{aligned} \quad (\text{B.8})$$

with

$$\mathbf{W} = \begin{bmatrix} W_- \\ W_+ \end{bmatrix}, \quad \mathbf{G}^{(1)} = \begin{bmatrix} G_{-}^{(1)} \\ G_{+}^{(1)} \end{bmatrix}, \quad \mathbf{G}^{(2)} = \begin{bmatrix} G_{--}^{(2)} & G_{-+}^{(2)} \\ G_{+-}^{(2)} & G_{++}^{(2)} \end{bmatrix}. \quad (\text{B.9})$$

The first moments of the concentration of the non-interacting chain are

$$G_{+}^{(1)}(\mathbf{r}) = \langle \hat{\phi}_{+}^{(1)}(\mathbf{r}) \rangle_0 = 1, \quad G_{-}^{(1)}(\mathbf{r}) = \langle \hat{\phi}_{-}^{(1)}(\mathbf{r}) \rangle_0 = 2f_{\kappa} - 1, \quad (\text{B.10})$$

using $\langle \delta(\mathbf{r} - \mathbf{r}_s) \rangle_0 = 1/V$ and $f_{\kappa} = N_{A,\kappa}/N$. The second moments can be expressed via A/B block Green's functions by writing $\hat{\phi}_{\pm}^{(1)} = \hat{\phi}_A^{(1)} \pm \hat{\phi}_B^{(1)}$:

$$G_{++}^{(2)} = G_{AA}^{(2)} + G_{AB}^{(2)} + G_{BA}^{(2)} + G_{BB}^{(2)}, \quad (\text{B.11})$$

$$G_{+-}^{(2)} = G_{AA}^{(2)} - G_{AB}^{(2)} + G_{BA}^{(2)} - G_{BB}^{(2)}, \quad (\text{B.12})$$

$$G_{-+}^{(2)} = G_{AA}^{(2)} + G_{AB}^{(2)} - G_{BA}^{(2)} - G_{BB}^{(2)}, \quad (\text{B.13})$$

$$G_{--}^{(2)} = G_{AA}^{(2)} - G_{AB}^{(2)} - G_{BA}^{(2)} + G_{BB}^{(2)}. \quad (\text{B.14})$$

Now we can solve the sums in terms of A and B starting with $G_{AA}^{(2)}(\mathbf{r}_2, \mathbf{r}_1)$. We know that

$$\mathcal{F}[\langle \delta(\mathbf{r}_j - \mathbf{r}) \delta(\mathbf{r}_i) \rangle_0] = \langle e^{i\mathbf{k} \cdot \mathbf{r}_j} e^{-i\mathbf{k} \cdot \mathbf{r}_i} \rangle_0 = \exp\left(-\frac{a^2 N k^2}{6} |i - j|\right) \quad (\text{B.15})$$

from Chapter 1, so we can do the sum in Fourier space. Fourier transforming $G_{AA}^{(2)}(\mathbf{r})$ gives

$$G_{AA}^{(2)}(\mathbf{k}) = \langle \hat{\phi}_A^{(1)}(\mathbf{k}) \hat{\phi}_A^{(1)}(-\mathbf{k}) \rangle_0 = \frac{1}{N^2} \sum_{i=1}^{fN} \sum_{j=1}^{fN} e^{-\frac{a^2}{6} |\mathbf{k}|^2 |i-j|} = \frac{1}{N^2} \sum_{i=1}^{fN} \sum_{j=1}^{fN} e^{-\frac{x}{N} |i-j|}, \quad (\text{B.16})$$

where $x = \frac{a^2}{6} N |\mathbf{k}|^2$. As the sum is geometric, the analytical solution is found as

$$G_{AA}^{(2)}(\mathbf{k}) = \frac{f}{N} + \frac{2}{N^2} \sum_{j=2}^{fN} \sum_{i=1}^{j-1} e^{-\frac{x}{N} (j-i)} = \frac{1}{N} + \frac{2}{N^2} \sum_{j=2}^{fN} \frac{e^{\frac{x}{N} j} - e^{\frac{x}{N}}}{e^{\frac{x}{N}} - 1}, \quad (\text{B.17})$$

$$G_{AA}^{(2)}(\mathbf{k}) = \frac{f}{N} - \frac{2e^{-\frac{x}{N}} (1 - e^{-fx} + fN(e^{-x/N} - 1))}{N^2 (e^{-\frac{x}{N}} - 1)^2} \quad (\text{B.18})$$

Now in the limit $N \rightarrow \infty$ we get the continuous chain. We call this the Debye function, which has the form

$$\lim_{N \rightarrow \infty} G_{AA}^{(2)}(\mathbf{k}) = \frac{2}{x^2} (e^{-fx} + fx - 1). \quad (\text{B.19})$$

Similarly, we can get the B to B Green's function as

$$\begin{aligned} G_{BB}^{(2)}(\mathbf{k}) &= \langle \hat{\phi}_B^{(1)}(\mathbf{k}) \hat{\phi}_B^{(1)}(-\mathbf{k}) \rangle_0 = \frac{1}{N^2} \sum_{i=fN+1}^N \sum_{j=fN+1}^N e^{-\frac{a^2}{6} |i-j| |\mathbf{k}|^2} \\ &= \frac{1-f}{N} - \frac{2e^{-\frac{x}{N}} (1 - e^{-(1-f)x} + (1-f)N(e^{-x/N} - 1))}{N^2 (e^{-\frac{x}{N}} - 1)^2}. \end{aligned} \quad (\text{B.20})$$

We can take the limit $N \rightarrow \infty$ to get

$$\lim_{N \rightarrow \infty} G_{BB}^{(2)}(\mathbf{k}) = \frac{2}{x^2} (e^{-(1-f)x} + (1-f)x - 1). \quad (\text{B.21})$$

The next step is to find the other terms. They have a symmetric form, so then,

$$\begin{aligned}
G_{AB}^{(2)}(\mathbf{k}) &= G_{BA}^{(2)}(\mathbf{k}) = \langle \hat{\phi}_A^{(1)}(\mathbf{k}) \hat{\phi}_B^{(1)}(-\mathbf{k}) \rangle_0 = \frac{1}{N^2} \sum_{i=1}^{fN} \sum_{j=fN+1}^N e^{-\frac{x}{N}|i-j|} \\
&= \frac{1}{N^2} \sum_{i=1}^{fN} e^{\frac{x}{N}i} \sum_{j=fN+1}^N e^{-\frac{x}{N}j} = \frac{1}{N^2} \left(\frac{1 - e^{-fx}}{1 - e^{-x/N}} \right) \left(\frac{1 - e^{-(1-f)x}}{e^{x/N} - 1} \right).
\end{aligned} \tag{B.22}$$

Taking the limit $N \rightarrow \infty$ gives,

$$G_{AB}^{(2)}(\mathbf{k}) = G_{BA}^{(2)}(\mathbf{k}) = \frac{1}{x^2} (1 - e^{-fx})(1 - e^{-(1-f)x}). \tag{B.23}$$

With that we have everything we need to calculate $\ln Q_\kappa$ to second order for a continuous chain, using Eq. B.8. This lets us make calculates for the SGCM. We use this approximation in both Section 2.2 on the random-phase approximation (RPA), and Section 3.3 on the renormalization of χ .

Appendix C

Calculation of the Structure Function

From our field-theoretic simulations (FTSs) we have direct access to the moments of the field W_- . However, the quantity of particular relevance to experiments is the structure function, which is proportional to the scattering intensity observed in neutron or x-ray scattering. To compare with experiments we need

$$S(\mathbf{k}) \equiv \frac{\rho_0^2}{V} \langle \delta \hat{\phi}_A(-\mathbf{k}) \delta \hat{\phi}_A(\mathbf{k}) \rangle. \quad (\text{C.1})$$

We derive $S(\mathbf{k})$ starting from a particle-based model from Section 1.5 of the form

$$\mathcal{Z} = \frac{1}{n_1! n_2!} \int \tilde{\mathcal{D}}\Xi \exp \left[\frac{\rho_0}{4} \int d\mathbf{r} (\chi \hat{\phi}_-^2(\mathbf{r}) + 1) \right] \delta[1 - \hat{\phi}_+(\mathbf{r})]. \quad (\text{C.2})$$

To generate moments of $\hat{\phi}_-$ we follow [99, 43], introducing a source field $U(\mathbf{r})$ coupled to $\hat{\phi}_-$, defining the moment-generating functional $\mathcal{Z}[U]$, and then using $\ln \mathcal{Z}[U]$ as the cumulant generating functional of the form

$$\ln \mathcal{Z}[U] = \ln \left(\frac{1}{n_1! n_2!} \int \tilde{\mathcal{D}}\Xi e^{\frac{\rho_0}{4} \int d\mathbf{r} (\chi \hat{\phi}_-^2(\mathbf{r}) + 4U(\mathbf{r})\hat{\phi}_-(\mathbf{r}) + 1)} \delta[1 - \hat{\phi}_+(\mathbf{r})] \right). \quad (\text{C.3})$$

The first two functional derivatives give

$$\left. \frac{\mathcal{D} \ln \mathcal{Z}[U]}{\mathcal{D}U(\mathbf{r})} \right|_{U=0} = \rho_0 \langle \hat{\phi}_-(\mathbf{r}) \rangle, \quad (\text{C.4})$$

and

$$\left. \frac{\mathcal{D}^2 \ln \mathcal{Z}[U]}{\mathcal{D}U(\mathbf{r}') \mathcal{D}U(\mathbf{r})} \right|_{U=0} = \rho_0^2 \left(\langle \hat{\phi}_-(\mathbf{r}') \hat{\phi}_-(\mathbf{r}) \rangle - \langle \hat{\phi}_-(\mathbf{r}') \rangle \langle \hat{\phi}_-(\mathbf{r}) \rangle \right), \quad (\text{C.5})$$

which are the desired cumulants. Completing the square in the source term gives,

$$\mathcal{Z}[U] = \frac{1}{n_1! n_2!} \int \tilde{\mathcal{D}}\Xi \, e^{\frac{\rho_0 \chi}{4} \int d\mathbf{r} \left(\hat{\phi}_-(\mathbf{r}) + \frac{2}{\chi} U(\mathbf{r}) \right)^2 + \frac{\rho_0}{4} \int d\mathbf{r} \left(1 - \frac{4}{\chi} U^2(\mathbf{r}) \right)} \delta[1 - \hat{\phi}_+(\mathbf{r})]. \quad (\text{C.6})$$

Next we apply a Hubbard–Stratonovich transformation to linearize the quadratic term, yielding

$$\exp \left[\frac{\chi \rho_0}{4} \int \left(\hat{\phi}_- + \frac{2}{\chi} U \right)^2 d\mathbf{r} \right] \propto \int \mathcal{D}W_- \exp \left[- \int d\mathbf{r} \frac{W_-^2}{\chi \rho_0} + \int d\mathbf{r} \left(\hat{\phi}_- + \frac{2}{\chi} U \right) W_- \right]. \quad (\text{C.7})$$

Representing the incompressibility constraint by its functional Fourier transform, we obtain

$$\delta[1 - \hat{\phi}_+] \propto \int \mathcal{D}W_+ \exp \left[-i \int d\mathbf{r} (1 - \hat{\phi}_+(\mathbf{r})) W_+(\mathbf{r}) \right]. \quad (\text{C.8})$$

Substituting these into $\mathcal{Z}[U]$, absorbing constants, applying Stirling’s approximation, and finally rescaling the fields $W_+ \rightarrow i\rho_0 W_+$ and $W_- \rightarrow \rho_0 W_-$, we obtain an analogous result to Section 1.5

$$\begin{aligned} \mathcal{Z}[U] \propto \int \mathcal{D}W_+ \mathcal{D}W_- \exp \left\{ n_1 \ln \left(\frac{Q_1[W_+, W_-]}{n_1} \right) + n_2 \ln \left(\frac{Q_2[W_+, W_-]}{n_2} \right) \right. \\ \left. - \rho_0 \int d\mathbf{r} \left(\frac{W_-^2}{\chi} - W_+ + \frac{\chi}{4} - \frac{2}{\chi} U W_- + \frac{1}{\chi} U^2 \right) \right\}. \end{aligned} \quad (\text{C.9})$$

We can now express the cumulants of $\hat{\phi}_-$ in terms of the field W_- :

$$\langle \hat{\phi}_-(\mathbf{r}) \rangle = \frac{1}{\rho_0} \frac{\mathcal{D} \ln \mathcal{Z}[U]}{\mathcal{D}U(\mathbf{r})} \Big|_{U=0} = -\frac{2}{\chi} \langle W_-(\mathbf{r}) \rangle, \quad (\text{C.10})$$

and

$$\begin{aligned} \langle \hat{\phi}_-(\mathbf{r}') \hat{\phi}_-(\mathbf{r}) \rangle_c &\equiv \langle \hat{\phi}_-(\mathbf{r}') \hat{\phi}_-(\mathbf{r}) \rangle - \langle \hat{\phi}_-(\mathbf{r}') \rangle \langle \hat{\phi}_-(\mathbf{r}) \rangle \\ &= \frac{1}{\rho_0^2} \frac{\mathcal{D}^2 \ln \mathcal{Z}[U]}{\mathcal{D}U(\mathbf{r}') \mathcal{D}U(\mathbf{r})} \Big|_{U=0} \\ &= \frac{4}{\chi^2} \langle W_-(\mathbf{r}') W_-(\mathbf{r}) \rangle - \frac{2}{\chi \rho_0} \delta(\mathbf{r}' - \mathbf{r}) - \frac{4}{\chi^2} \langle W_-(\mathbf{r}') \rangle \langle W_-(\mathbf{r}) \rangle. \end{aligned} \quad (\text{C.11})$$

Equivalently,

$$\langle \hat{\phi}_-(\mathbf{r}') \hat{\phi}_-(\mathbf{r}) \rangle = \frac{4}{\chi^2} \langle W_-(\mathbf{r}') W_-(\mathbf{r}) \rangle - \frac{2}{\chi \rho_0} \delta(\mathbf{r}' - \mathbf{r}). \quad (\text{C.12})$$

To relate this to $S(\mathbf{k})$, note that $\hat{\phi}_A = \frac{1}{2}(\hat{\phi}_+ + \hat{\phi}_-)$ and $\delta\hat{\phi}_A(\mathbf{r}) = \hat{\phi}_A(\mathbf{r}) - \frac{1}{V} \int d\mathbf{r} \hat{\phi}_A(\mathbf{r})$. In an incompressible melt, $\hat{\phi}_+ = 1$, and for a symmetric blend $\int d\mathbf{r} \hat{\phi}_-(\mathbf{r}) = 0$. Hence,

$$\delta\hat{\phi}_A(\mathbf{r}) = \frac{1}{2} \hat{\phi}_-(\mathbf{r}). \quad (\text{C.13})$$

Therefore, we can represent the structure function in terms of $\hat{\phi}_-(\mathbf{k})$ as

$$S(\mathbf{k}) = \frac{\rho_0^2}{V} \langle \delta\hat{\phi}_A(-\mathbf{k}) \delta\hat{\phi}_A(\mathbf{k}) \rangle = \frac{\rho_0^2}{4V} \langle \hat{\phi}_-(-\mathbf{k}) \hat{\phi}_-(\mathbf{k}) \rangle. \quad (\text{C.14})$$

Dividing by $\rho_0 N$ and writing $n = \rho_0 V / N$ gives

$$\frac{S(\mathbf{k})}{\rho_0 N} = \frac{n}{4V^2} \left(\frac{4}{\chi^2} \langle W_-(-\mathbf{k}) W_-(\mathbf{k}) \rangle - \frac{2V}{\chi \rho_0} \right). \quad (\text{C.15})$$

This is a working expression used to compute the structure function in terms of W_- . We can use this result to calculate the structure function in our FTSs.