Studies of Block Copolymer Melts by Field Theory and Molecular Simulation

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Contents

List of Tables viii

List of Figures ix

1 Introduction 1
   1.1 Objectives and Outline .............................................. 4

2 Numerical Implementation of Self-Consistent Field Theory 6
   2.1 SCFT Formalism ..................................................... 8
   2.2 Modified Diffusion Equations ..................................... 10
      2.2.1 Pseudo-Spectral Method .................................... 12
      2.2.2 Extrapolation and Integration ................................. 15
      2.2.3 Stress ............................................................ 16
   2.3 Symmetry Adapted Basis Functions ................................. 18
   2.4 Iteration ............................................................. 24
      2.4.1 Newton-Raphson and Broyden’s Method ......................... 25

3 $F^0$ Triblock Copolymer Phase Behavior 28
   3.1 Introduction ...................................................... 28

iii
CONTENTS

3.2 Weak Segregation Theory .................................................. 31
  3.2.1 The Free Energy and Spinodal ...................................... 31
  3.2.2 Spinodal in AC Isopleth ............................................ 34
3.3 Phase Diagrams along AC-isopleth ...................................... 36
3.4 N-dependence of Phase Triangle ......................................... 41
3.5 Conclusions ............................................................... 45

4 Auxiliary Field Theory ....................................................... 47
  4.1 Model and Notation ...................................................... 47
  4.2 Mean Field Theory ...................................................... 50
  4.3 Loop Expansions ......................................................... 52

5 Renormalized One-loop Theory of Correlations in Polymer Blends .... 55
  5.1 Introduction ............................................................. 56
    5.1.1 Coarse-Graining and Renormalization .......................... 56
    5.1.2 Related Prior Work ............................................... 59
    5.1.3 Outline ............................................................ 60
  5.2 Theoretical Formulation ............................................... 60
    5.2.1 Model and Notation ............................................... 60
    5.2.2 One-loop Free Energy ............................................ 62
    5.2.3 Divergence and Renormalization ............................... 63
    5.2.4 Structure Function ............................................... 66
  5.3 Collective Fluctuations ................................................ 69
    5.3.1 Symmetric Blends, Critical Composition ....................... 69
    5.3.2 Vicinity of the Spinodal ........................................ 72
    5.3.3 Off-Critical Blends .............................................. 75
  5.4 Coexistence Curve ..................................................... 76
  5.5 Single Chain Properties ............................................... 78
    5.5.1 Monodisperse Melt ............................................... 79
    5.5.2 Bidisperse Melt .................................................. 80
    5.5.3 Binary Blends .................................................... 82
  5.6 Comparison to Simulation ............................................... 82
CONTENTS

5.6.1 Determining $\chi_e$ ........................................ 83
5.6.2 Composition Fluctuations in! Blends ....................... 85
5.6.3 Single-Chain Correlations ............................. 87
5.7 Thermodynamic Integration of the RPA ...................... 89
5.7.1 Variation of the Pair Potential ............................ 90
5.7.2 Variation of $\chi_0$ .................................... 91
5.8 Correlation Hole Effects .................................... 92
5.8.1 UV divergence (Unrenormalized Theory) ............... 93
5.8.2 $N$-dependence (Renormalized Theory) ................. 94
5.9 Conclusions .............................................. 96

6 Renormalized One-loop Theory of Correlations in Diblock Copolymers 98
6.1 Introduction ............................................. 99
6.2 Notation ................................................. 103
6.3 Renormalized One-Loop Theory .......................... 105
   6.3.1 Intramolecular Correlations .......................... 106
   6.3.2 Direct Correlation Function .......................... 109
   6.3.3 Self-Consistent Approximation ....................... 111
6.4 Results ................................................ 112
   6.4.1 Correlations at $\chi = 0$ ................................ 113
   6.4.2 Shift in the Peak Wavenumber ....................... 115
   6.4.3 Peak Intensity ..................................... 116
   6.4.4 Asymmetric Diblocks .................................. 117
   6.4.5 Size of Molecule and Blocks .......................... 120
6.5 Relationship of ROL and FH Theory ......................... 123
6.6 Conclusions ............................................ 126

7 Monte Carlo Simulation of Diblock Copolymer 128
7.1 Introduction ............................................. 128
7.2 Simulation Details ...................................... 129
   7.2.1 Monte Carlo Moves .................................. 130
CONTENTS

F  Review of Previous Simulation Work 205
   F.1  Lattice Models .................................................. 205
   F.2  Continuum Models .............................................. 211

G  Configuration Biased Trimer Rebridge MC Move 215
   G.1  Effective Elastic Constant for Orientation ............. 218

H  Long Distance Behavior of Correlations in Diblock Copolymer 220

I  Statistics of Intramolecular Contacts in Diblock Copolymer 223

J  Epitaxial Relation Between $F_{ddd}$ And Hex 227
List of Tables

7.1 Ratio of box size and mean field domain spacing. . . . . . . . . . 134

F.1 Collected diblock ODT data from simulation studies. . . . . . . . . 212
List of Figures

1.1 Classical morphologies found in block copolymers. ............................ 2

2.1 The waves in FFT grid and the first Brillouin zone. ............................. 13

2.2 The 5 long wavelength stars on a square lattice (including $|G| = 0$). ....... 19

2.3 Approximation to the Jacobian matrix. ............................................ 26

3.1 AC and B modulated spinodal in symmetric triblocks. ......................... 36

3.2 Phase diagram of symmetric triblocks in AC-isopleth, with $k = \chi_{AC}/\chi_{AB} = 4$. .......................................................... 38

3.3 Phase diagram of symmetric triblocks in AC-isopleth, with $k = \chi_{AC}/\chi_{AB} = 2$. .......................................................... 39

3.4 Phase diagram of symmetric triblocks in AC-isopleth, with $k = \chi_{AC}/\chi_{AB} = 1$. .......................................................... 40

3.5 Phase diagram in composition triangle of symmetric triblocks with $k = 2.7$. .......................................................... 43

3.6 Phase diagram in composition triangle of ISO triblocks. ....................... 44

5.1 One-loop prediction for $\chi_a(0)N$ versus $\chi_eN$. ................................. 70

5.2 One-loop prediction for $\sqrt{N}N\chi_*$ versus $\chi_eN$. .......................... 71
<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.3</td>
<td>Self-consistently computed $\chi_a$ versus $\chi_e$ for various compositions.</td>
<td>76</td>
</tr>
<tr>
<td>5.4</td>
<td>Coexisting curve.</td>
<td>77</td>
</tr>
<tr>
<td>5.5</td>
<td>One-loop correction to the single chain correlation function.</td>
<td>80</td>
</tr>
<tr>
<td>5.6</td>
<td>Crossover of the single chain size from contraction to swelling.</td>
<td>81</td>
</tr>
<tr>
<td>5.7</td>
<td>One-loop correction to $R_g$.</td>
<td>83</td>
</tr>
<tr>
<td>5.8</td>
<td>Comparison to Müller’s lattice data at $\bar{N} = 290$.</td>
<td>85</td>
</tr>
<tr>
<td>5.9</td>
<td>Chain length dependence of the shift in the critical temperature.</td>
<td>87</td>
</tr>
<tr>
<td>5.10</td>
<td>One-loop correction to the single chain correlation function.</td>
<td>88</td>
</tr>
<tr>
<td>5.11</td>
<td>Shrinkage of the mean squared end-to-end distance of chains in blends.</td>
<td>89</td>
</tr>
<tr>
<td>6.1</td>
<td>Illustrative diagrams for intra- and intermolecular correlations.</td>
<td>107</td>
</tr>
<tr>
<td>6.2</td>
<td>Wavevector dependence of correlation function for diblocks at $\chi_e = 0$ for $\bar{N} = 500$.</td>
<td>113</td>
</tr>
<tr>
<td>6.3</td>
<td>One-loop theory predictions of the shifts in $q^*$.</td>
<td>114</td>
</tr>
<tr>
<td>6.4</td>
<td>Wavevector dependence of inter- and intra- molecular components to the total correlation functions in diblocks.</td>
<td>115</td>
</tr>
<tr>
<td>6.5</td>
<td>Self-consistently calculated peak intensity.</td>
<td>117</td>
</tr>
<tr>
<td>6.6</td>
<td>$\bar{\chi}_a N$ dependence of the inter- and intramolecular contributions to the inverse of the peak intensity.</td>
<td>118</td>
</tr>
<tr>
<td>6.7</td>
<td>$\delta S^{-1}(q_0)$ versus $\bar{\chi}_a$ for symmetric diblocks.</td>
<td>119</td>
</tr>
<tr>
<td>6.8</td>
<td>Size of molecule and blocks for diblocks of varying $f_A$.</td>
<td>121</td>
</tr>
<tr>
<td>6.9</td>
<td>Composition and $\chi$ dependence of diblock dimensions.</td>
<td>122</td>
</tr>
<tr>
<td>6.10</td>
<td>Asymptotic comparison between Fredrickson-Helfand theory and ROL theory.</td>
<td>124</td>
</tr>
<tr>
<td>7.1</td>
<td>Typical molecular moves in Monte Carlo simulation.</td>
<td>131</td>
</tr>
<tr>
<td>7.2</td>
<td>Acceptance rate for molecule based moves.</td>
<td>132</td>
</tr>
<tr>
<td>7.3</td>
<td>Acceptance rate for replica exchange moves.</td>
<td>133</td>
</tr>
<tr>
<td>7.4</td>
<td>Wavevector dependence of diblock collective correlation function at $\alpha = 0$.</td>
<td>137</td>
</tr>
<tr>
<td>7.5</td>
<td>$q$ dependence of intramolecular correlation functions at $\alpha = 0$.</td>
<td>139</td>
</tr>
<tr>
<td>7.6</td>
<td>Fitting quality for the $q$ dependence of $S(q)$.</td>
<td>141</td>
</tr>
</tbody>
</table>
LIST OF FIGURES

7.7 $\chi$ dependence of the inverse peak intensity of diblock correlation functions. ........................................ 142
7.8 $N$ dependence of inverse peak intensity of diblock correlation functions. 143
7.9 $\chi$ dependence of peak position of diblock correlation functions. ........ 144
7.10 $\chi$ dependence of intramolecular correlation functions. .................. 146
7.11 $\chi$ dependence of Radius of gyration of diblock copolymers. .......... 147
7.12 $\chi$ dependence of mean squared block center of mass distance. ....... 148
7.13 $\chi$ dependence of radius of gyration of one block. ....................... 149

8.1 Statistical segment length and effective coordination number in Vas-siliev and Matsen’s data. ................................. 153
8.2 Matsen’s correlation functions compared to one-loop results. ............. 154
8.3 Diblock dimensions of Matsen’s FCC lattice simulation results. ......... 155
8.4 $q$ dependence of correlation function in BFM model. ...................... 157
8.5 Müller’s correlation functions compared to one-loop results. ............... 157
8.6 Map Matsen’s FCC lattice results to BSM model. ......................... 159
8.7 Map Müller’s BFM lattice results to BSM model. ........................... 160
8.8 Direct comparison of $q^*$ between FCC and BSM models. ................. 161
8.9 Direct comparison of $q^*$ between BFM and BSM models. ............... 162

A.1 Maps of spinodals in symmetric ABC triblocks along AC-isopleth. . . 187
A.2 All possible critical lines. .................................................... 188

D.1 IR asymptotics of the Brazovskii propagator. ............................ 196

E.1 Analysis of Bates-Rosedale-Fredrickson’s experimental data. ............ 200
E.2 Analysis of Bates-Rosedale-Fredrickson’s data using the independen-tially measured statistical segment length ......................... 204

G.1 Regrowth of the bridging monomer in trimer rebridge move. ............ 216

I.1 The amount of intramolecular contacts for each monomer in diblocks. 224
I.2 Chain length dependence of the average intramolecular contacts for AB diblocks. .............................................. 226
# LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>J.1</td>
<td>Unperturbed $Fddd$ morphology.</td>
<td>228</td>
</tr>
<tr>
<td>J.2</td>
<td>First Brillouin zone for the $Fddd$ unit cell.</td>
<td>229</td>
</tr>
<tr>
<td>J.3</td>
<td>Density profile of perturbed $Fddd$ morphology.</td>
<td>230</td>
</tr>
<tr>
<td>J.4</td>
<td>Instability limit of diblock $Fddd$ phase.</td>
<td>231</td>
</tr>
</tbody>
</table>
Polymers are large molecules composed of sequences of many repeating chemical units, or monomers. A molecule formed with many monomers of a single type is called a homopolymer. A block copolymer is a polymer that contains two or more blocks of identical monomers, in which only the monomers within a block are of the same type (e.g., A-A-A-B-B-B-B).

When blended, most pairs of different homopolymers tend to macroscopically phase separate, like oil and vinegar. The same tendency also exists between blocks in block copolymers, but macroscopic phase separation cannot occur, because the blocks are chemically bonded. The compromise is a phenomenon known as microphase separation: instead of separating into macroscopic domains, copolymers form periodic structures in which the blocks segregate into different micro-domains, with typical dimensions of order 10 nm. Cartoons of some of the structures that have been observed in block copolymer materials are shown in Figure 1.1: spheres on a body-centered cubic lattice, hexagonally packed cylinders, a 3-dimensional network known as the gyroid phase, and a layered (or lamellar) structure.

An enormous experimental and theoretical effort has been put, over several decades,
into characterizing the phase behavior of diblock copolymers, which contain two chemically distinct blocks. The primary theoretical approach has been Self-Consistent Field Theory (SCFT). In SCFT, the effects of interactions between polymer chains are approximated by the effects of a spatially inhomogeneous environment (represented mathematically by a field) in which polymers are assumed to move independently. The theory provides a way of predicting and comparing the thermodynamic costs (i.e., free energies) of a variety of different possible structures, and to thereby construct a “phase diagram” that indicates what structure (or phase) will be preferred for each possible set of molecular parameter values. The phase diagram predicted by SCFT for diblock copolymers agrees well with experimental data, and is well understood.

Much less is known about the behavior of the so-called ABC triblock copolymers, which contain three chemically distinct blocks. Both theoretical and (particularly) experimental study of this class of systems has been hindered by the enormously enlarged space of possible choices of values for the molecular parameters. Several experimental studies on the phase behavior of specific triblock copolymer systems have been reported, but a unified interpretation is yet to come. A systematic SCFT study of selected regions of the relevant parameter space is needed as a guide to further experimental study.

SCFT is a successful theory, but not a perfect one. Since the polymer chains are treated in SCFT as if they move independently in an average environment, phe-
nomena involving collective motions of many molecules are not accurately described. Collective composition fluctuations become very important near the order-disorder transition (ODT), the transition from a spatially homogeneous disordered phase to a periodic ordered phase with decreasing temperature. It has long been believed that these collective fluctuations can be properly accounted for within the context of a more general theory in which the “field” of SCFT is allowed to fluctuate. Until recently, however, attempts to implement this fluctuating field theory have stumbled on a severe conceptual problem: predictions of the theory for many quantities are found to be sensitive to the value chosen for a parameter (the cutoff length) whose numerical value appears to be completely arbitrary. Recently, Grzywacz, Qin, and Morse\(^2\), extending earlier work by Wang,\(^3\) have shown how the resulting ambiguity can be removed from predictions of some quantities by a procedure known as “renormalization”\(^4\). Renormalization of a field theory involves a re-interpretation of the relationship between the parameters of the model and experimentally measurable quantities. Renormalization is a standard part of the formalism of quantum field theory, where it was introduced to solve a similar conceptual problem. Grzywacz et al. showed how to construct a logically consistent renormalized theory of composition fluctuations within the spatially homogeneous phase of both a binary polymer mixture and a diblock copolymer melt. As part of my thesis research, I have examined the predictions of this theory for both homopolymer blends and diblock copolymers. To test the theory, I have conducted Monte Carlo simulations of diblock copolymer melts, and compared the results to the predictions of the renormalized one-loop theory.

More detailed understanding of both micro-phase separation in block copolymers and macro-phase separation in homopolymer blends will deepen our understanding of phase transitions more generally. The ability to predict more accurately how morphology depends upon molecular structure in block copolymer liquids will also facilitate the tailoring of physical properties and optimization of the performance of such materials for new applications.
1.1 Objectives and Outline

This thesis addresses several questions related to phase separations in polymer liquids, using three primary tools: mean field theory, fluctuating field theory, and Monte Carlo simulation.

Chapter 2 is devoted to a discussion of the numerical implementation of SCFT. I discuss the improvements I made to the code used in Prof. Morse’s group. These involved the implementation of improved algorithms for solving the modified diffusion equation (which is the central equation in the SCFT; see Chapter 2) and for iteratively solving the self-consistency conditions. I also discuss the algorithm used to generate symmetry adapted basis functions.

The phase behavior of a class of so-called non-frustrated ABC triblock copolymers is addressed in Chapter 3. A nonfrustrated ABC triblock is one in which the interaction parameters $\chi_{AB}$ and $\chi_{BC}$ that represent interactions between the end and middle-blocks are comparable and much smaller than the parameter $\chi_{AC}$ associated with the interaction between the end-blocks ($\chi_{AC} \gg \chi_{AB} \simeq \chi_{BC}$). Both numerical SCFT and the weak segregation theory are used to investigate the phase behavior of systems with symmetric interaction parameters (with $\chi_{AB} = \chi_{BC}$), and one system with slightly asymmetric interaction parameters and statistical segment lengths. The parameters of this asymmetric system were chosen to mimic those of poly(isoprene-styrene-ethylene oxide) (ISO) triblocks that have been extensively studied in experiments by students of Prof. Bates. The work on non-frustrated ABC triblocks reported here builds on earlier work that was begun by graduate student Chris Tyler, and clarifies the relationship between this earlier work by our group and several other theoretical studies of related systems.

Chapters 5 and 6 report predictions of the renormalized one-loop theory of correlations in binary blends and diblock copolymer melts, respectively. These two chapters are preceded by a very short review of the some of the theoretical background in Chapter 4. A more thorough discussion of the ideas underlying the renormalization procedure, and details of the derivation, is given in the publication by Gryzwacz, Qin and Morse, but is not reproduced in this thesis. The work on diblock copolymer
Section 1.1. Objectives and Outline

melts reported in Chapter 6 was carried out in collaboration with Piotr Grzywacz. In both of these chapters, I discuss predictions of the one-loop theory for deviations of the collective correlation function from the predictions of the earlier random-phase approximation (RPA) theory,\textsuperscript{5–7} and for deviations of the statistics of individual chains from random walk statistics.

Chapters 7 and 8 discuss the results of Monte Carlo simulations of symmetric diblock copolymer melts. My own off-lattice simulation of a bead-spring model are presented in Chapter 7. Both the collective structure function and various single chain properties are measured and compared to the predictions given in Chapter 6. In Chapter 8, I analyze analogous results from published lattice Monte-Carlo simulation results by Vassiliev, Matsen and coworkers\textsuperscript{8,9} and unpublished results of Prof. Marcus Müller, using two different lattice models. There, I compare the results of both sets of lattice simulations to each other, to my off-lattice simulations, and to our theoretical predictions. I also test the extent to which the results obtained using these three different simulation models are consistent with the assumption of universality – the assumption that their exists a universal description of long-wavelength correlations in this class of polymer liquids in which all effects of the differences between different microscopic models can be parameterized by a few phenomenological parameters.

Because the research topics covered in this thesis are diverse, discussion of the relevant scientific literature and of conclusions are given within each chapter. Possible extensions of each line of research are discussed in Chapter 9.

A variety of calculation details and peripheral topics are presented in appendices. Among these is a discussion of an epitaxial relationship between the $F_{dddd}$ and hexagonal phases of diblock copolymer melts and of the associated limit of stability of the $F_{dddd}$ phase.
CHAPTER 2

Numerical Implementation of Self-Consistent Field Theory

The statistical mechanics of polymer melts is intrinsically an interacting many-body problem. This chapter describes a numerical implementation of the self-consistent field theory (SCFT) approximation for this problem. SCFT is a coarse-grained mean field theory in which the interactions between polymers are approximated by interactions of each polymer with a self-consistently determined set of chemical potential fields.

A self-consistent field (SCF) approximation for polymer statistics was first introduced in polymer science by Edwards, in the context of a study of the size of a homopolymer with excluded volume interactions in solution. Edwards suggested that the distribution of polymer configurations may be approximated by that of a random walk in a potential field that is determined a posteriori from the monomer concentration. SCFT was later adapted by Helfand and coworkers to describe inhomogeneous structures in dense multi-component polymer liquids, such as interfaces between immiscible polymer liquids and to block copolymer melts.

Early work that used SCFT to describe ordered phases of block copolymer melts relied on approximations to the full theory that are valid only particular limits. Dif-
ferent approximations were developed to describe the strong segregation limit (SLL), in which the interfaces between microdomains are comparatively narrow and the chains are strongly stretched, and the weak segregation limit (WSL), in which the composition profile is only weakly modulated and chain conformations are almost unperturbed random walks.

To describe the SSL, Helfand and coworkers introduced the a so-called Narrow Interface Approximation (NIA),\textsuperscript{16} which they used to study the stability of the classical L (lamellae), H (hexagonal), and S (sphere) phases of diblock copolymer melts.\textsuperscript{18,19} A more sophisticated theory of the structure of polymer brushes in the SSL was later developed by Semenov\textsuperscript{20} and by Milner and coworkers.\textsuperscript{21} The SSL theory of brushes was based on a calculation of the most probable conformation of a chain in a self-consistent field, which dominates the chain’s partition function in this limit. The resulting strong-segregation theory was also used by Semenov to re-analyze the stabilities of the classical L, H and S phases of diblock copolymer melts.\textsuperscript{20}

A theory of the WSL was worked out for diblock copolymer melts by Leibler.\textsuperscript{7} Leibler’s theory is based on a Landau expansion of free energy in powers of the Fourier amplitudes of the composition with a preferred wavenumber. As an integral part of the theory, Leibler also developed the random-phase approximation (RPA) theory of composition fluctuations in diblock copolymer melts, building on work by de Gennes\textsuperscript{5,6} that used the RPA to describe correlations in polymer melts and homopolymer blends.

Numerical implementations of SCFT attempt to solve the set of equations originally proposed by Helfand and coworkers,\textsuperscript{11} without further approximations. Block copolymer mesophases correspond to spatially periodic solutions to these equations. Numerical SCFT reproduces the results of earlier theories of the SSL and WSL in the appropriate limits, and fills the gap between these approximations. The full SCFT equations were first solved for all of the known and proposed phases of diblock copolymer melts by Matsen and Schick,\textsuperscript{1} using a spectral method that we describe below. Their calculation yielded an essentially correct phase diagram for diblock copolymers over a wide range of segregation strengths.

The mathematical formulation of SCFT for an incompressible block copolymer
Section 2.1. SCFT Formalism

melt is summarized in section 2.1. The remainder of this chapter is then devoted to a discussion of numerical algorithms used in the code developed in our group to solve these equations, focusing on my own contributions.

2.1 SCFT Formalism

Because SCFT has become a standard theoretical method for studying block copolymer phase behavior, only a brief summary is given here. The theory provides a statistical description of the spatial distribution of interacting chain segments. It has two basic ingredients: chain configurations are described as random walks; monomer-monomer interactions are replaced by interactions between monomers and self-consistently determined molecular fields.

We consider an incompressible melt of monodisperse linear multiblock copolymers, in which each chain has \( N \) monomers, each of which occupies a volume \( v \). Let \( s \) denote a distance along the chain contour, defined such that \( 0 < s < 1 \). Let \( r \) represents a position in a system of total volume \( V \). Let \( \phi_\alpha(r) \) represent the average volume fraction of monomers of type \( \alpha \) at position \( r \), defined as the product of the average number such of monomers per unit volume times the monomer volume \( v \). In an incompressible liquid, we require that

\[
\sum_\alpha \phi_\alpha(r) = 1. \tag{2.1.1}
\]

where \( \sum_\alpha \) represents a sum over all types of monomer that are present in the system.

In SCFT, we imagine that each chain is a random walk that is subject to a potential energy in which each monomer of type \( \alpha \) is subjected to a chemical potential field \( \omega_\alpha(r) \). These fields are normally approximated by

\[
\omega_\alpha(r) = \sum_{\beta \neq \alpha} \chi_{\alpha\beta} \phi_\beta(r) + \xi(r). \tag{2.1.2}
\]

Here \( \chi_{\alpha\beta} \) is a Flory-Huggins interaction parameter for interactions between monomers of types \( \alpha \) and \( \beta \), and \( \xi(r) \) is a Lagrangian multiplier pressure field that must adjusted
so that the equilibrium distribution of monomers satisfies condition (2.1.1).

The main numerical problem in the evaluation of SCFT is describe the statistical weights of a Gaussian chain in a field. This is done using a mathematical trick that was introduced by Edwards,\textsuperscript{10} which allows the partition function for a single chain to be related to a partial differential equation (PDE) similar to the diffusion equation. We define a function \( q(r, s) \) that is proportional to the partition function of a segment of a block copolymer containing monomers 0 to \( sN \), when the chain is subjected to chemical potential fields \( \omega_\alpha \), and when monomer \( sN \) is constrained at position \( r \). Let \( q^\dagger(r, s) \) be the corresponding constrained partition function for a segment of chain containing monomers \( sN \) to \( N \), with monomer \( sN \) constrained at \( r \). Both of these functions are normalized such that \( q(r, 0) = q^\dagger(r, 1) = 1 \).

\begin{align}
\frac{\partial q}{\partial s}(r, s) &= N \left[ \frac{b^2_{\alpha(s)}}{6} \nabla^2 - \omega_{\alpha(s)}(r) \right] q(r, s), \\
-\frac{\partial q^\dagger}{\partial s}(r, s) &= N \left[ \frac{b^2_{\alpha(s)}}{6} \nabla^2 - \omega_{\alpha(s)}(r) \right] q^\dagger(r, s),
\end{align}

subject to the initial conditions

\begin{align}
q(r, 0) = q^\dagger(r, 1) = 1.
\end{align}

Here \( b_{\alpha(s)} \) is the statistical segment length for a monomer of the type \( \alpha(s) \) found at position \( s \), which is the same for all monomers within a block. Similarly, \( \omega_{\alpha(s)}(r) \) denotes the chemical potential for the monomer type \( \alpha \) at position \( s \). The modified diffusion equation is a recursion relation for the partition function of a chain segment, which shows how \( q(r, s) \) changes in a process in which the chain is grown by adding monomers to one end.

The composition fields \( \phi_\alpha(r) \) for an ensemble of random-walk polymers in the
Section 2.2. Modified Diffusion Equations

specified set of fields may calculated from the solutions to Eq.(2.1.3):

\[ \phi_\alpha(r) = \frac{1}{Q} \int _\alpha ds \, q(r, s) q^\dagger(r, s). \]  
\[ (2.1.5) \]

Here, \( \int _\alpha \) denotes an integral of \( s \) over all blocks that contain segments of type \( \alpha \). The normalization constant \( Q \) is a normalized partition function for an unconstrained chain:

\[ Q \equiv \frac{1}{V} \int dr \, q(r, 1). \]  
\[ (2.1.6) \]

After a self-consistent solution is found, the free energy per chain of the resulting structure is given by

\[ f = -\ln (Qe) + \frac{N}{2V} \sum _{\alpha, \beta} \chi_{\alpha \beta} \int dr \, \phi_\alpha(r) \phi_\beta(r) - \frac{N}{V} \sum _\alpha \int dr \, \omega_\alpha(r) \phi_\alpha(r). \]  
\[ (2.1.7) \]

This result will be seen later in Chapter 4 as a mean field approximation to a more general field theory (Eq. (4.2.5)).

The major task of numeric SCFT is to solve Eq. (2.1.3), (2.1.2) and (2.1.1) with some prescribed set of boundary conditions. Different mesophases of block copolymer melts correspond to spatially periodic solutions. The spatially homogeneous solution corresponds to the disordered phase, whose free energy is given Flory-Huggins theory.

The thermodynamically stable phase is identified by comparing free energies. The algorithms for solving the modified diffusion equations and iterating the \( \omega(r) \) fields are discussed in following sections.

2.2 Modified Diffusion Equations

The modified diffusion equation for the \( s \)-dependence of \( q(r, s) \) within a block containing monomers of type \( \alpha \) be expressed more compactly as an operator equation

\[ \frac{\partial q}{\partial s} = -H_\alpha q \]  
\[ (2.2.1) \]
Section 2.2. Modified Diffusion Equations

in which

\[
H_\alpha \equiv N \left[ -\frac{b_0^2}{6} \nabla^2 + \omega_\alpha(r) \right]
\]

(2.2.2)

is a linear operator with a structure similar to that of the quantum mechanical Hamiltonian operator. This problem has a formal solution

\[
q(r, s + \Delta s) = e^{-H\Delta s} q(r, s)
\]

(2.2.3)

for any \( s \) and \( s + \Delta s \) that lie within the same block of a block copolymer. A similar set of equations applies to \( q^\dagger \).

The implementation of SCFT by Matsen and Schick’s\textsuperscript{1} used a spectral method to solve Eq. (2.2.3). In this method, the functions \( q(r, s) \) and \( \omega(r) \) are expanded in terms of a finite set of \( M \) spatially extended basis functions. The basis functions used for each phase are taken to be eigenfunctions of the Laplacian with the space group symmetry of that phase. The matrix representation of \( H \) in this basis is diagonalized, and Eq. (2.2.3) is then solved using a basis of the eigenvectors of \( H \), in which both \( H \) and \( e^{-H\Delta s} \) are diagonal. One advantage of this method is that the use of symmetry-adapted basis functions substantially reduces the number of basis function needed to resolve some structures, particularly the three dimensional gyroid and BCC sphere phases. With this spectral method, the time required to solve the MDE using a set of \( M \) basis functions is proportional to \( M^3 \). This is the time required either to diagonalize an \( M \times M \) matrix, or to carry out one of several required matrix-matrix multiplications. This spectral method is extremely useful for describing ordered phases that are not too strongly segregated, particularly for highly symmetric structures, but its cost rises quickly with \( M \).

Several more recent implementations of SCFT have used either real-space or pseudo-spectral algorithms in which \( q(r, s) \) is discretized on a regular grid containing points, and in which the MDE is solved by also discretizing the contour variable \( s \) into small steps of size \( ds \) and numerically integrating a discrete approximation to Eq. (2.2.1), rather than by diagonalizing \( H \). In such methods, the cost required to solve the MDE for \( q \) scales as \( M_s N \) or (for pseudo-spectral methods) \( M_s N \ln(N) \), where \( N \) is the number of grid points used in the spatial discretization and \( M_s \) is the
number of steps used to discretize the contour variable $s$. The favorable scaling with $N$ guarantees that these methods will become more efficient than the spectral method for problems the require the use of a sufficiently large number of spatial degrees of freedom (i.e., grid points or basis functions) to resolve the equilibrium structure.

An earlier version of the SCFT code developed in Prof. Morse’s group used a spectral method similar to that of Matsen and Schick. The current version of the code uses a variant of the pseudo-spectral method that was introduced into the polymer literature Rasmussen and Kalosakas.\textsuperscript{23} Our implementation of this algorithm is described in the next two subsections.

### 2.2.1 Pseudo-Spectral Method

The pseudo-spectral method is built on the Strang splitting of propagators.\textsuperscript{24} We first discretize the chain contour into $M_s$ segments, each of length $ds$. In our implementation, the step size $ds$ can vary from block to block, but is constant within each block. The relationship between $q(r, s + ds)$ and $q(r, s)$ is given formally by Eq. (2.2.3) with $\Delta s = ds$. The product $e^{-\mathcal{H}ds}q$ is not straightforward to evaluate using either a real space discretization or a basis of plane waves (reciprocal space), because $\nabla^2$ is diagonal in reciprocal space and $\omega$ is diagonal in real space, but the two operators do not commute. The pseudo-spectral method uses the approximation

\[ q(r, s + ds) \approx \exp \left( -\frac{N\omega(r, s)}{2}ds \right) \exp \left( \frac{Nb^2\nabla^2}{6}ds \right) \exp \left( -\frac{N\omega(r, s)}{2}ds \right) q(r, s) + \mathcal{O}(ds^3). \]  

(2.2.4)

in which the factors involving $\omega$ are diagonal in real space and the factor involving the Laplacian is diagonalized in reciprocal space. The local truncation error introduced by each step of this algorithm is of $\mathcal{O}(ds^3)$, while the global error introduced by integrating over any fixed range of values of $s$ is $\mathcal{O}(ds^2)$. By using the Fast Fourier Transform (FFT) to change between these representations, the above propagator can be evaluated stepwise:
Section 2.2.1. Pseudo-Spectral Method

1. \( q^{(1)}(\mathbf{r}, s + ds) = \exp \left( -ds N\omega(\mathbf{r}, s)/2 \right) q(\mathbf{r}, s); \)

2. \( q^{(1)}(\mathbf{k}, s + ds) = \mathcal{F}\mathcal{F}\mathcal{T} \left[ q^{(1)}(\mathbf{r}, s + ds) \right]; \)

3. \( q^{(2)}(\mathbf{k}, s + ds) = \exp \left( -ds N\beta(s)^2|G_k|^2/6 \right) q^{(1)}(\mathbf{k}, s + ds); \)

4. \( q^{(2)}(\mathbf{k}, s + ds) = \mathcal{F}\mathcal{F}\mathcal{T}^{-1} \left[ q^{(2)}(\mathbf{r}, s + ds) \right]; \)

5. \( q(\mathbf{k}, s + ds) = \exp \left( -ds N\omega(\mathbf{r}, s)/2 \right) q^{(2)}(\mathbf{r}, s + ds); \)

This algorithm yields an approximate solution to Eq. (2.1.3) by propagating the initial condition \( q(\mathbf{r}, 0) = 1 \) for any periodic input \( \omega(\mathbf{r}, s) \). No knowledge of the space group symmetry of the ordered phase is needed. An analogous scheme can be designed for \( q^*(\mathbf{r}, s) \).

To use the FFT, we discretize the unit cell of the ordered phase into a grid of, say, \( N_1 \times N_2 \times N_3 \) points. For two dimensional phase, \( N_3 = 1 \); for one dimensional phase, \( N_2 = N_3 = 1 \). All spatially varying functions are defined on these grid points. This is completely equivalent to an expansion in terms of \( N = N_1 N_2 N_3 \) plane waves. The finer the grid, or the more waves available, the higher resolution of our solution.

Figure 2.1: The relation of waves defined in the first Brillouin zone (FBZ) and on FFT grid. The waves in regions labeled with A, B, C or shaded with distinct colors on the FFT grid should be shifted into the corresponding regions in the FBZ.
Section 2.2.1. Pseudo-Spectral Method

The wavevectors are not uniquely defined on lattice of finite grid points. Assume we have a two dimensional unit cell, the basis vectors being \( \mathbf{a}_1 \) and \( \mathbf{a}_2 \). The reciprocal basis vectors are

\[
\mathbf{b}_1 = 2\pi \frac{\mathbf{a}_2 \times (\mathbf{a}_1 \times \mathbf{a}_2)}{|\mathbf{a}_1 \times \mathbf{a}_2|^2}, \quad \mathbf{b}_2 = 2\pi \frac{(\mathbf{a}_1 \times \mathbf{a}_2) \times \mathbf{a}_1}{|\mathbf{a}_1 \times \mathbf{a}_2|^2}.
\]

(2.2.5)

For convenience of discussion, if the cell has been discretized to \( N = N_1 \times N_2 \) grid points, we restrict the waves on FFT grid to be:

\[
\mathbf{G}_{i,j} = i\mathbf{b}_1 + j\mathbf{b}_2, \quad i \in [0, N_1 - 1], \quad j \in [0, N_2 - 1].
\]

(2.2.6)

All waves that can be written as \( \mathbf{G}_{i,j} + mN_1\mathbf{b}_1 + nN_2\mathbf{b}_2, \) \( m \) and \( n \) being arbitrary integers, are equivalent. When evaluating \( |\mathbf{G}_k|^2 \) in the third step of the pseudo-spectral algorithm, one should use the wave having the longest wavelength, among all equivalent ones. This means we need to shift all waves on FFT grid to the first Brillouin zone (FBZ) of the discretized small cell, as shown in Figure 2.1. This choice also conserves the symmetry of the solution (more details will be discussed in Section 2.4). The plane waves in the FBZ having the same magnitudes may be imposed certain phase relationship by the space group symmetry; to maintain this relationship, their amplitudes have to be damped by the same amount.

The ratios \( N_1 : N_2 : N_3 \) should be chosen to be as close as possible to \( a_1 : a_2 : a_3 \). In case they can be made equal, the FBZ is inscribed to a sphere (circle in 2D case). For the cubic phases, this occurs when \( N_1 = N_2 = N_3 \). For some choices of \( N_i \), special waves on FFT grid can be shifted to multiple equivalent waves on the boundary of the FBZ. For instance, if \( N_1 \) is even for a 1-D cell. The wave labeled by \( N_1/2 \) sits on one side of FBZ boundary, but it is also equivalent to the \( -N_1/2 \) wave sitting on the opposite boundary. To be definite, if this happens, we keep the wave \( \mathbf{G}_{i,j,k} \) having greater values of \( k, j \) or \( i \) indices in our code.

To update \( q(\mathbf{r}, s) \) by one step of length \( ds \), two FFT are needed, which costs

\[
\mathcal{O}(2N \log_2(N))
\]

(2.2.7)
Section 2.2.2. Extrapolation and Integration

To decrease the error introduced by discretizing $s$, we apply a simple form of Richardson extrapolation. Given $q(r, s)$, we estimate $q(r, s + ds)$ by applying one step of length $ds$, and by also applying two steps of length $ds/2$. Let the two resulting approximations for $q(r, s + ds)$ be denoted by $q_{ds}$ and $q_{ds/2}$ respectively. Because the error associated with integration over a fixed contour length scales as $O(ds^2)$, the dominant errors of these two estimates differ by a factor of 4, and can be removed by the extrapolation:

$$q(r, s + ds) = \left(4q_{ds/2} - q_{ds}\right)/3. \quad (2.2.8)$$

The reasoning given above suggests that this should yield a solution with a local error of $O(ds^4)$, or a global error of $O(ds^3)$. In fact, this extrapolation yields an approximation with a local errors of $O(ds^5)$ or a global error of $O(ds^4)$. The reason is that the Strang splitting is reversible in $s$: a forward propagation of the solution followed by a backward propagation with the same step size exactly recovers the starting point.

It is known that the even order terms in the Taylor series expansion of the reversible algorithm vanishes.\(^{25}\) As a result, the global error of using (2.2.8) repeatedly to prop-
agate the solution from $q(r,0)$ to $q(r,1)$ is actually order $O(ds^4)$. The extrapolation could be continued with the cost of extra functional evaluations, but this does not appear to be necessary. With the application of a single extrapolation, we found that $ds = 0.01$ is sufficient to produce a level of accuracy comparable to that obtained in the spectral method, as compared to 0.00001 needed prior to the extrapolation, for $\chi N \approx 20$ in diblock copolymers.

The density fields are evaluated using Eq. (2.1.5) from $q(r,s)$ and $q^\dagger(r,s)$. The integration over $s$ is done using the Simpson’s rule, which also has a truncation error $O(ds^4)$. This requires that the chain contour be discretized into an even number of segments. To avoid the ambiguity of having a block junction in the middle of a step of length $ds$, we allow $ds$ to vary from block to block but require that the number of segments within each block be an even integer. The value of $ds$ for each block is chosen to be value that satisfies this constraint that is closest to a desired value that is input by the user.

### 2.2.3 Stress

The method described above works for fixed trial unit cell parameters, $\theta_i$. Depending on the crystal system, $\theta_i$ may be either the length of unit cells or the angles between two basis vectors. The free energy obtained needs to be minimized with respect to $\theta_i$: the true thermodynamic equilibrium needs to meet the additional condition:

$$\frac{df}{d\theta_i} = 0. \tag{2.2.9}$$

Since these derivatives are linearly related to the stress tensor, we call them stresses, somewhat loosely.

Consider the self-consistent condition (Eq. (2.1.2)) to be the definition of $\omega_\alpha(r)$ as functionals of $\phi_\alpha(r)$ or $q(r,s)$ and $q^\dagger(r,s)$. Eq. (2.1.3) may be thought as non-linear equations for $q$ and $q^\dagger$. By varying $\theta_i$, Tyler and Morse have derived an explicit expression for the stress:

$$\frac{df}{d\theta_i} = -\frac{1}{Q} \frac{\partial Q}{\partial \theta_i}. \tag{2.2.10}$$
Section 2.2.3. Stress

The partial derivatives refer to variations under fixed values of $\omega$ fields. To be more precise, we use the dimensionless coordinates $\tilde{r} = (\tilde{r}_1, \tilde{r}_2, \tilde{r}_3)$ defined by $r = \sum_{\mu=1}^{3} \tilde{r}_\mu a_\mu$. Fixing $\omega$ means fixing $\omega(\tilde{r})$ and varying $\theta_i$ is identical to varying $a_\mu$.

Tyler and Morse developed a first order perturbation theory and used the spectral method to evaluate $\delta Q$ for given $\delta \theta_i$, whose cost is comparable to solving the modified diffusion equations. In this section, we give the implementation using the pseudo-spectral method. Because we can use FFT to change the representation of fields freely, the cost is negligible as compared to solving for $q$ and $q^\dagger$.

For convenience, we define the Hamiltonian $H_0 \equiv Nb(s)^2 \nabla^2/6 - N\omega(r, s)$, and mimicking the Dirac notation, use $|\rangle$ and $\langle.|$ to represent column and row vectors, the argument being $r$. $|0\rangle$ represent a vector with all elements equal to 1. Vectors representing unperturbed singly constrained partition function $q_0(r, s)$ and $q^\dagger_0(r, s)$ are written as

$$|q_0(s)\rangle = e^{\int_0^s dr H_0(\tau)}|0\rangle, \quad \langle q^\dagger_0(s)| = \langle 0|e^{-\int_s^1 dr H_0(\tau)} \tag{2.2.11}$$

Under the perturbation $\delta H(s) \equiv Nb(s)^2 \delta \nabla^2/6$, the change $|\delta q(s)\rangle$ satisfies, to linear order,

$$\left(\frac{\partial}{\partial s} - H_0\right)|\delta q(s)\rangle = \delta H(s)|q_0(s)\rangle, \quad |\delta q(0)\rangle = 0. \tag{2.2.12}$$

It has a formal solution

$$|\delta q(s)\rangle = \int_0^s ds' e^{-\int_s^{s'} dr H_0(\tau)} \delta H(s')|q_0(s')\rangle. \tag{2.2.13}$$

Using Eq. (2.1.6) to express $\delta Q$ in terms of $|\delta q(1)\rangle$, we obtain:

$$\delta Q = \frac{1}{V} \langle 0|\delta q(1)\rangle = \frac{1}{V} \int_0^1 ds' \left\langle 0| e^{-\int_s^{s'} H_0(\tau) dr} \delta H(s') \right| q_0(s')\rangle$$

$$= \frac{1}{6V} \int_0^1 ds \ b(s)^2 \left\langle q^\dagger_0(s)| \delta \nabla^2| q_0(s)\rangle \right.$$  

$$= -\frac{N}{6 V} \sum_j \delta |G_j|^2 \int_0^1 ds \ b(s)^2 \langle q^\dagger_0(s)|j\rangle \langle j|q_0(s)\rangle. \tag{2.2.14}$$

17
Section 2.3. Symmetry Adapted Basis Functions

Where \( j \) runs over all waves defined on the FFT grid (shifted into FBZ) and \( G_j \) is the corresponding wave vector. \( |j\rangle \) represents the corresponding plane wave. Since \( \delta \nabla^2 \) is diagonalized in Fourier space, we changed the basis in the last step. Substituting this expression into Eq. (2.2.10), we find:

\[
\frac{df}{d\theta_i} = \frac{N}{6QV} \sum_j \frac{\partial|G_j|^2}{\partial \theta_i} \int_0^1 ds \ b(s)^2 \langle q_0^\dagger(s)|j\rangle \langle j|q_0(s)\rangle.
\]

(2.2.15)

Here, \( \langle j|q_0(s)\rangle \) and \( \langle q_0^\dagger(s)|j\rangle \) are Fourier coefficients of unperturbed \( q(r, s) \) and \( q^\dagger(r, s) \), which can be evaluated using FFT.

The derivatives \( \partial|G_j|^2/\partial \theta_i \) are calculated by noting that \( |G_j|^2 = \sum_{\mu,\nu} j_{\mu} j_{\nu} b_\mu \cdot b_\nu \), \( b_\mu \) and \( b_\nu \) being reciprocal basis vectors. Only \( b_\mu \) and \( b_\nu \) are affected by \( \delta \theta_i \); thus we have \( \delta|G_j|^2 = 2 \sum_{\mu,\nu} j_{\mu} j_{\nu} \delta b_\mu \cdot b_\nu \). \( \delta b_\mu \) is calculated using the reciprocal relation \( a_\mu \cdot b_\nu = 2\pi \delta_{\mu\nu} \), which yields \( \delta b_\mu = -\sum_\nu b_\nu \delta a_\nu \cdot b_\mu / 2\pi \).

The integration in \( s \) can be done with Simpson’s quadrature. The same Richardson extrapolation discussed in the previous section allows us to get sufficiently accurate stress using large \( ds \) values.

2.3 Symmetry Adapted Basis Functions

To solve the SCFT equations, we start from some guessed potential fields, solve the modified diffusion equation (Eq. (2.1.3)), and check if the self-consistent conditions (Eq. (2.1.2), (2.1.1) and (2.2.9)) are satisfied – if not, we update the potential fields and repeat these steps until those constraints are met.

In this section, we discuss how the groups of plane waves are related by space group operations and use them to construct basis functions. The basis functions are used in the iteration discussed in Section 2.4.

The periodic functions invariant under a space group symmetry can be expanded by a set of symmetry adapted basis functions (SABF), each being created from a group of waves of equal wavelengths, the waves forming an irreducible representation of the space group.\(^{27}\) This fact was used by Tyler and Morse to design the spectral
Section 2.3. Symmetry Adapted Basis Functions

solution to SCF equations. We will show next, the same principle applies to the pseudo-spectral method, with modifications taking care of the artifacts of discretization.

A general periodic function defined on the discretized lattice can be expanded by the plane waves having wave vectors $\mathbf{G}_j = \sum_{\mu=1}^{3} j_\mu \mathbf{b}_\mu$, where $j_\mu$ are integers and $\mathbf{b}_\mu$ are reciprocal basis vectors of the unit cell. We introduce $\tilde{\mathbf{b}}_\mu = N_\mu \mathbf{b}_\mu$ and denote their multiples by $\tilde{\mathbf{G}}_k = \sum_{\mu=1}^{3} k_\mu \tilde{\mathbf{b}}_\mu$, $k_\mu$ being arbitrary integers. All waves differing by $\tilde{\mathbf{G}}_k$ are indistinguishable on the grid. We thus restrict the range of $j_\mu$ such that $\mathbf{G}_j$ falls inside the FBZ of the discretized cells (See Figure 2.1).

Figure 2.2: The 5 long wavelength stars on a square lattice (including $|G| = 0$).

For a given space group, we denote its order by $N_g$ and its elements by $(\mathbf{R}_\alpha, \mathbf{t}_\alpha)$ ($1 \leq \alpha \leq N_g$) which represents a rotation $\mathbf{R}_\alpha$ followed by a translation $\mathbf{t}_\alpha$. The inverse of $(\mathbf{R}_\alpha, \mathbf{t}_\alpha)$ is $(\mathbf{R}_\alpha^{-1}, -\mathbf{R}_\alpha^{-1} \cdot \mathbf{t}_\alpha)$. An invariant function $f(\mathbf{r})$ upon the operation of $(\mathbf{R}_\alpha, \mathbf{t}_\alpha)$ becomes $f(\mathbf{R}_\alpha^{-1} \cdot \mathbf{r} - \mathbf{R}_\alpha^{-1} \cdot \mathbf{t}_\alpha)$. If $c_j e^{i \mathbf{G}_j \cdot \mathbf{r}}$ is part of $f(\mathbf{r})$, $c_j$ being the Fourier coefficient, it transformed into a new plane wave under the rotation:

$$c_j e^{i \mathbf{G}_j \cdot \mathbf{r}} \rightarrow c_j e^{-i \mathbf{G}_j \cdot \mathbf{R}_\alpha^{-1} \cdot \mathbf{t}_\alpha} e^{i \mathbf{G}_j \cdot \mathbf{R}_\alpha^{-1} \cdot \mathbf{r}}. \tag{2.3.1}$$

$\mathbf{G}_j \cdot \mathbf{R}_\alpha^{-1}$ is just another wave vector of the same wavelength, which we denote by $\mathbf{G}_k$. 
Section 2.3. Symmetry Adapted Basis Functions

The invariance of \( f(\mathbf{r}) \) and the orthogonality of plane waves imply that:

\[
  c_k = c_j e^{-i\mathbf{G}_j \cdot \mathbf{R}_\alpha^{-1} \cdot \mathbf{t}_\alpha},
\]

(2.3.2)

here \( c_k \) is the coefficient to \( e^{i\mathbf{G}_k \cdot \mathbf{r}} \). Since \((\mathbf{R}_\beta, \mathbf{t}_\beta) = (\mathbf{R}_\alpha^{-1}, -\mathbf{R}_\alpha^{-1} \cdot \mathbf{t}_\alpha)\) is also a group member, we conclude that if two waves are connected such that \( \mathbf{G}_k = \mathbf{G}_j \cdot \mathbf{R}_\beta \) for some \( \beta \), their coefficients satisfy \( c_k = c_j e^{i\mathbf{R}_\beta \cdot \mathbf{t}_\beta} \). If multiple rotations connects \( \mathbf{G}_k \) to \( \mathbf{G}_j \), e.g., \( (\mathbf{R}_\beta, \mathbf{t}_\beta) \) and \( (\mathbf{R}_\gamma, \mathbf{t}_\gamma) \), we need to check the consistency. If \( e^{i\mathbf{R}_\beta \cdot \mathbf{t}_\beta} \) and \( e^{i\mathbf{R}_\gamma \cdot \mathbf{t}_\gamma} \) are equal, we learn nothing new; if not, the only possibility is that \( c_j = c_k = 0 \): an invariant function should not contain these waves. Applying all symmetry operations, we can exhaust all waves that are related to \( \mathbf{G}_j \), which is called a star. Any pair of waves within the star must have a fixed relative phase as required by the symmetry operations. This phase relation is mutual and associative, for symmetry operations form a group. If any two operations impose incompatible phase relations upon any two waves, coefficients to each wave must vanish, and we say the star cancels. This type of cancellation being absent, we can create an invariant function by starting from an arbitrary wave \( e^{i\mathbf{G}_j \cdot \mathbf{r}} \):

\[
  f_j(\mathbf{r}) = \frac{1}{\sqrt{N_j}} \sum_{(\mathbf{R}_\alpha, \mathbf{t}_\alpha)} e^{i\mathbf{G}_j \cdot \mathbf{t}_\alpha} e^{i(\mathbf{G}_j \cdot \mathbf{R}_\alpha) \cdot \mathbf{r}},
\]

(2.3.3)

where \( N_j \) is the number of distinct waves in the star and the summation is taken over any \( N_j \) symmetry operations such that they generate distinct \( \mathbf{G}_j \cdot \mathbf{R}_\alpha \)'s. It is straightforward to verify that applying any symmetry operation recovers exactly the same function. Calling \( \mathbf{G}_j \) a generator, this way of constructing \( f(\mathbf{r}) \) implies that \( c_j \) is \( 1/\sqrt{N_j} \). Using a different generator at most modifies \( f(\mathbf{r}) \) by a phase factor, so one star generates one unique invariant function.

For the centrosymmetric phase, the two waves \( \mathbf{G}_k \) and \( -\mathbf{G}_k \) related by the inversion operation must coexist in the same star and their coefficients \( c_k \) and \( c_{-k} \) must be equal. \( \mathbf{G}_k \) must also be related to \( \mathbf{G}_j \) by some \( (\mathbf{R}_\alpha, \mathbf{t}_\alpha) \): \( \mathbf{G}_k = \mathbf{G}_j \cdot \mathbf{R}_\alpha \) and \( c_k = e^{i\mathbf{G}_j \cdot \mathbf{t}_\alpha} / \sqrt{N_j} = c_j e^{i\mathbf{G}_j \cdot \mathbf{t}_\alpha} \). By closeness of the space group, the product \( (\mathbf{R}_\alpha, \mathbf{t}_\alpha) \) and the inversion, \( (-\mathbf{R}_\alpha, -\mathbf{t}_\alpha) \), is also a group element, which relates \( -\mathbf{G}_k \).
Section 2.3. Symmetry Adapted Basis Functions

to $G_j$. Thus we find another relation $c_{-k} = c_j e^{-iG_j \cdot t_\alpha} = c_k^*$. This is possible only if $c_k = c_{-k} = \pm c_j$. So $f(r)$ is a real and even function, all coefficients being equal to either $1/\sqrt{N_j}$ or $-1/\sqrt{N_j}$. For symmorphic space groups (those having no gliding planes and skew axes), e.g., $Im3m$ for BCC packed spheres, obviously all coefficients are $1/\sqrt{N_j}$. Otherwise, negative coefficients may appear, e.g., $Ia\overline{3}d$ for gyroid phase.

For the non-centrosymmetric phase, one wave and its opposite do not necessarily belong to the same star. But for a given star, it may contain all or none of the opposites of its component waves, since if two waves $G_k$ and $G_j$ are connected by some symmetry element, so are their opposites, for $-G_k = (-G_j) \cdot R_\alpha$ if $G_k = G_j \cdot R_\alpha$. We call the former case a closed star and the latter case an open star. For the latter case, the opposite waves themselves form another open star. In both cases, the coefficient ratios of two waves are conjugate to those of the opposites: $c_{-k}/c_{-j} = e^{i(G_j \cdot t_\alpha)} = (c_k/c_j)^*$.

For closed stars in non-centrosymmetric phase, the basis functions generated using Eq. (2.3.3) is generally complex, but can be made real. By construction, $c_j = 1/\sqrt{N_j}$. We further denote $c_{-j} = e^{i\phi_j} c_j$. The phase factor $\phi_j$ is determined by the space group and choice of $G_j$. For instance, it may be 0 or $\pi$ for $I4_132$ (alternating gyroid phase, see Chapter 3), and may be 0 or $\pi/2$ for $P4_132$. As we have noted, for any other wave $G_k$ in the star, $c_{-k}/c_{-j} = (c_k/c_j)^*$ (the specifications of $k$ and $-k$ are arbitrary). We group all terms involving $G_k$ and $G_j$ together, and denote their summation by $g(r)$, then Eq. (2.3.3) may be written as $g(r) + e^{i\phi_j} g^*(r)$. Factoring $e^{i\phi_j}/2$ out, we find:

$$f_{j,\text{real}}(r) \equiv f_j(r) e^{i\phi_j/2} = e^{-i\phi_j/2} g(r) + e^{i\phi_j/2} g^*(r)$$  \hspace{1cm} (2.3.4)

which is a real function. For $\phi_j = 0$, $f_{j,\text{real}}(r)$ is an even function under inversion; for $\phi_j = \pi$, it is odd; otherwise, not determined. The centrosymmetric case corresponds to $\phi_j = 0$.

For two closely related open stars, the basis functions generated using Eq. (2.3.3) can be made conjugate to each other by choosing, e.g., $G_j$ and $-G_j$ as generators. Denote them by $f_j(r)$ and $f_{-j}(r)$, respectively, then the two orthogonal real basis
Section 2.3. Symmetry Adapted Basis Functions

functions can be generated by:

\[ f_{j,\text{even}}(r) = \frac{f_j(r) + f_{-j}(r)}{\sqrt{2}}, \quad f_{j,\text{odd}}(r) = \frac{if_j(r) - f_{-j}(r)}{\sqrt{2}}. \] (2.3.5)

Subscripts “even” and “odd” denote the transformation properties under inversion.

If follows that we can group all accessible plane waves into stars, and use them to generate a set of orthogonal real basis functions, each one being the eigenfunction of the Laplacian, \( i.e., \nabla^2 f_j(r) = -|G_j|^2 f_j(r) \) (for open stars \( f_j \) is replaced by \( f_{j,\text{even}} \) or \( f_{j,\text{odd}} \)). The expansion of an arbitrary symmetric function in terms of these symmetry adaptive basis functions has been used by Tyler and Morse for designing spectral solutions.\(^{29}\) In their case, no discretization of the unit cell is needed, and the complete stars are created naturally by construction: they kept waves with wavelengths below an isotropic cutoff. However, in the pseudo-spectral method, the waves are confined into the FBZ, whose boundary does not have a regular shape. The above mechanism of generating basis functions needs to be slightly generalized, especially for stars close to the FBZ boundary. In the following, we summarize the steps of generating basis functions and comment on the modification.

1. Group waves connected by symmetry operations into stars. First choose a wave \( G_j \), then apply every possible rotation \( R_\alpha \) to it and keep track of all distinct waves of the form \( G_j \cdot R_\alpha \). If \( G_j \cdot R_\alpha \) falls outside of the FBZ (subject to our convention), shift it by some \( \tilde{G} \) and use the one inside. For instance, if a 1-D unit cell has even number of grid points. The inversion operation rotates the wave \( N_1 b_1/2 \) to \(-N_1 b_1/2\). But \(-N_1 b_1/2\) is identical to \( N_1 b_1/2 \) and should not be counted. So the star has only one wave \( N_1 b_1/2 \). There is no such problem for odd number \( N_1 \), in which case, \((N_1 - 1)b_1/2\) and \(-(N_1 - 1)b_1/2\) are distinct and are related by inversion. For the irregular FBZ in the 2-D or 3-D cases, a policy must be made to consistently use one of the equivalent waves on boundaries.

2. Check if the stars are incompatible with the symmetry. If any wave \( G_k \) is connected to \( G_j \) by more than one symmetry operations, compare and check if the phase factors \( e^{i R_j \cdot t_\alpha} \)s are identical. The incompatible star should not be used to generate basis functions. We call the waves in the same star \( G_j \)s partners. To
Section 2.3. Symmetry Adapted Basis Functions

prevent any mutual incompatibility between two partners, it suffices to check that no partner is incompatible with $G_j$ itself. More precisely, wave $G_j$ is either compatible or incompatible with all its partners at the same time. If a partner $G_k$ is incompatible with $G_j$, there exist $(R_\alpha, t_\alpha)$ and $(R_\beta, t_\beta)$ such that $G_k = G_j \cdot R_\alpha = G_j \cdot R_\beta$ but $e^{iG_j \cdot t_\alpha} \neq e^{iG_j \cdot t_\beta}$. If the second partner $G_l$ is related to $G_k$ by $(R_\gamma, t_\gamma)$, then symmetry operations $(R_\alpha, t_\alpha)(R_\gamma, t_\gamma) = (R_\alpha R_\gamma, R_\alpha \cdot t_\gamma + t_\alpha)$ and $(R_\beta, t_\beta)(R_\gamma, t_\gamma) = (R_\alpha R_\gamma, R_\beta \cdot t_\gamma + t_\beta)$ must relate $G_l$ to $G_j$ since $G_l = G_j \cdot R_\alpha \cdot R_\gamma = G_j \cdot R_\beta \cdot R_\gamma$. The ratio of the corresponding phase factors

$$\frac{e^{iG_j \cdot (R_\alpha \cdot t_\gamma + t_\alpha)}}{e^{iG_j \cdot (R_\beta \cdot t_\gamma + t_\beta)}} = \frac{e^{iG_j \cdot t_\alpha}}{e^{iG_j \cdot t_\beta}} \neq 1. \quad (2.3.6)$$

So it suffices to check if $G_j$ is compatible with just one partner. In particular, this partner can be $G_j$ itself. The star does not cancel if $G_j$ is compatible with itself: all symmetry operation $(R_\alpha, t_\alpha)$ leaving $G_j$ unchanged ($G_j \cdot R_\alpha = G_j + ˜G$ for some $˜G$) produces a phase factor $e^{iG_j \cdot t_\alpha} = 1$.

(3) Check if the stars are closed. The star is closed if the opposite of every wave is also in the star. The opposite of a wave $G_j$ is said to be in the star if there exists some wave $G_k$ in the star, such that $G_j + G_k = ˜G$ for some $˜G$. We use the earlier example to illustrate this: a 1-D unit cell is discretized into even number of grid points. The star at boundary includes only one wave, $N_1 b_1/2$, but it is closed since $-(N_1 b_1/2) + N_1 b_1$ lies in the star. This possibility must be explicitly tested for more complicated cases.

(4) Generate one basis function from closed stars (Eq. (2.3.4)) and two basis functions from open stars (Eq. (2.3.5)). Recall that if two waves $G_j$ and $G_k$ on the FBZ boundary are equivalent ($G_j = G_k + ˜G$ for some $˜G$), we make an arbitrary choice and use one of them, say, $G_j$. Then when using Eq. (2.3.3) to create basis functions, we need to compute the phase factors: $e^{iG_j \cdot t_\alpha}$. Using $G_k$ and $G_j$ may result in phase factors differ by $e^{iG \cdot t_\alpha}$ (Same ambiguity exists when testing if a star is cancelled.). To remove this difference, a simple solution is to choose the discretization such that $t_\alpha$ lie on the grid. This is especially important for the space groups with screw axes or glide planes. For examples, the translation vector $[1/4, 1/4, 1/4]$ is present in $Fddd$.
Section 2.4. Iteration

phase of space group #70, we need to set the number of grid points \( N_1, N_2, N_3 \) to be integer multiples of 4. This supplement the requirement we mentioned in Section 2.2.1 that the ratios \( N_1 : N_2 : N_3 \) should be as close as possible to the ratios of the lengths of the unit cell. If the symmetry of the crystal system requires that two or all cell lengths to be equal, e.g., \( a_1 = a_2 \) for tetragonal system, the corresponding \( N_i \) must be identical \( (N_1 = N_2) \): otherwise the waves on the FBZ boundaries may be rotated outside the FBZ which after being shifted into the FBZ does not have the same wavelength as the original one so it is impossible to construct a basis function.

To summarize, when the stars are created, tested to eliminate cancellation, used to generate basis functions, the following questions are examined subject to a free \( \tilde{G} \) factor: whether or not two waves are related by some rotation and whether or not one wave lies in a particular star. The problem of non-unique phase factor associated with gliding planes and screw axes can be resolved by discretizing the unit cell such that the translation vectors lie on the grid.

Each function defined on the grid has three different representations: real space values, Fourier space coefficients, and basis function coefficients. The first two are easily converted to each other by FFT. The third one can be converted from the Fourier coefficients, denoted \( z_j \), by mapping them to the coefficients of an arbitrary wave in the star. For a basis function generated from a closed star, \( f_j(r) \), we first pick up any wave in the star, its coefficient being \( c_k \). Then the projection of the underlying function onto \( f_j(r) \) has a real coefficient: \( a_j = z_j/c_j \). For two open stars connected by inversion, we compute two real coefficients to \( f_{j,\text{even}} \) and \( f_{j,\text{odd}} \), respectively:

\[
\begin{align*}
    a_{j,\text{even}} &= \sqrt{2} \text{Re}\left[ \frac{z_j}{c_j} \right], \\
    a_{j,\text{odd}} &= \sqrt{2} \text{Im}\left[ \frac{z_j}{c_j} \right].
\end{align*}
\]

\[ (2.3.7) \]

2.4 Iteration

In section 2.2.3, we mentioned that solving SCFT equations can be viewed as solving non-linear differential equations for \( q(r, s) \) and \( q^\dagger(r, s) \). It can also be viewed as finding the roots of a set non-linear equations. Consider that Eq. (2.1.3) defines \( q \) and \( q^\dagger \) as functionals of \( \omega_\alpha(r) \). The constraints are really non-linear functions of
Section 2.4.1. Newton-Raphson and Broyden’s Method

\( \omega_\alpha(r) \). The question is how to find the roots, for which the standard approach is to use the Newton-like search.

### 2.4.1 Newton-Raphson and Broyden’s Method

For systems having \( N_m \) different monomers and \( N_c \) independent cell parameters, we define two types of residues from the self-consistent constraints and the stress free condition

\[
R_I(r; i) = \begin{cases} 
\sum_{\alpha=1}^{N_m} \phi_{\alpha}(r) - 1, & i = 1, \\
\omega_{\alpha}(r) - \sum_{\beta \neq \alpha} \chi_{\alpha\beta} \phi_{\beta}(r) - \xi(r), & 2 \leq i \leq N_m 
\end{cases}
\] (2.4.1)

\[
R_{II}(i) = \frac{df}{d\theta_i}, \quad 1 \leq i \leq N_c. \tag{2.4.2}
\]

In Eq. (2.4.1), the Lagrangian field \( \xi(r) \) is calculated from the SCF equation for \( \omega_1 \):

\[
\xi(r) = \omega_1(r) - \sum_{\beta \neq 1} \chi_{1\beta} \phi_{\beta}(r). \tag{2.4.3}
\]

Equations \( R_I(r; i) = 0 \) and \( R_{II}(i) = 0 \) fit the framework of Newton-Raphson machine naturally. Denote the residues collectively by \( R_\alpha \), and the potential fields and unit cell parameters collectively by \( X_\alpha \). Expanding the \( r \) dependent functions by symmetry adaptive basis, these vectors have dimension \( N_m N_b + N_c \). For canonical ensemble calculations, the homogeneous components \( (G = 0) \) of \( \phi_\alpha \) are known to be equal to the compositions, so need not be calculated. That of \( \omega_\alpha \) can be calculated from Eq. (2.1.2) by setting \( \xi(G = 0) = 0 \) (this choice is arbitrary since SCFT solutions are invariant to the constant shift of \( \xi \): its effects cancels when evaluating \( \phi_\alpha \)). Excluding this, the dimension of \( R_\alpha \) and \( X_\alpha \) is \( N_r \equiv N_m(N_b - 1) + N_c \). If \( R_\alpha \) does not vanish for \( X_\alpha^{(n)} \), the next \( X \) is calculated by

\[
X_\alpha^{(n+1)} = X_\alpha^{(n)} - J_{\alpha\beta}^{(n)} R_\beta^{(n)}, \quad J_{\alpha\beta}^{(n)} \equiv \frac{\delta R_\alpha^{(n)}}{\delta X_\beta}, \tag{2.4.3}
\]

where \( J \) is the Jacobian matrix, of dimension \( N_r \times N_r \). This representation of the residue and Jacobian matrix has the virtue that the updated fields, \( \omega_\alpha^{(n+1)} \), still have the underlying phase symmetry.
Section 2.4.1. Newton-Raphson and Broyden’s Method

Typical iterations starting from a good initial guess for $X_\beta$ converges in less than 10 steps, and the cell parameters converge faster than the potential fields.

Numerically evaluating of $J_{\alpha\beta}$ requires solving the modified diffusion equations $N_r$ times, each time generating one column of $J$ matrix. A modest calculation for diblock gyroid phase uses about 500 basis functions, giving $N_r = 2(500 - 1) + 1 = 999$. This number easily explodes if multiblock copolymers are studied in relatively high segregation regime so that more basis functions are needed. We use Broyden’s method\(^{30}\) to avoid solving too many equations. The method starts from a crude guess for the slope ($J^{(0)}$) and improves it at each iteration step using a least square fit for $\delta J = J^{(n+1)} - J^{(n)}$ applied to the secant equation that connects $X^{(n)}$ and $X^{(n+1)}$. As iterations proceed, the Jacobian becomes closer to the correct one, and the convergence is accelerated.

![Diagram](Image)

**Figure 2.3:** Approximation to the Jacobian matrix. Regions shaded with green and blue colors needs to be computed numerically. The block diagonal regions are approximated with RPA.
Section 2.4.1. Newton-Raphson and Broyden’s Method

When solving Eq. (2.4.3), only $J^{(0)}$ needs to be inverted. Because each update of the Jacobian includes only a rank 1 matrix, using the Sherman-Morrison formula, the formalism can be modified to update the inverse of $J^{(n+1)}$ from that of $J^{(n)}$.

A good initial guess for $J^{(0)}$ is essential for the successful application of Broyden’s method. We note that the derivative of $R_I$ is solely determined by $\delta \phi_{\alpha}/\delta \omega_{\beta}$, whose large $|G|$ components may be approximated by those of the homogeneous phase calculated using RPA. We design $J^{(0)}$ as such: a few (typically, 50) of the leading long wavelength components in $R_I$ and $R_{II}$ are evaluated numerically; the remaining short wavelength components of $R_I$ are approximated using RPA. The actual arrangement of Jacobian is shown in Figure 2.3.

This hybrid method in our practice appears to be highly effective for iterating SCF equations. However, the inherent pitfall of the approach is that as the size of the problem grows, the storage and the initial inversion of Jacobian matrix become the bottleneck. The Jacobian free iterations, e.g. GMRES, may be a better strategy for those problems.
The phase behavior of non-frustrated ($F^0$) triblock copolymer melts\textsuperscript{32} is studied using the weak segregation theory and SCFT calculations. The spinodal instability of the homogeneous phase is first examined and used to guide systematic SCFT studies. The phase diagrams in the representative parameter domains are presented for symmetric triblock copolymers with varying relative interaction strengths, and for an asymmetric triblock copolymer, poly(isoprene-styrene-ethylene oxide), in the relatively strong segregation regime. The results remove certain gaps existing in the previous works regarding the sequence of the ordered phases near the ODT and the continuity of the ODT. For the asymmetric model, the results indicate that the $O^70$ phase remain stable as the segregation strength is increased, consistent with the experimental discovery.

### 3.1 Introduction

While the self-consistent field theory (SCFT) of diblock copolymer melts is well established, understanding of more complicated multiblock architectures remains much less mature. A few groups have now used different variants of SCFT\textsuperscript{33–42} to study
limited regions of the large parameter space of ABC triblocks. The present study focuses on so-called “unfrustrated” ABC triblocks, in which the Flory-Huggins parameter $\chi_{AC}$ associated with the interaction between the end blocks is larger than parameters $\chi_{AB}$ and $\chi_{BC}$ between middle and end blocks. We focus more specifically on nearly symmetric systems, in which $\chi_{AB} \simeq \chi_{BC}$. This work builds on and unifies previous studies of such systems by our group, Matsen, and Erukhimovich.

Our group, Matsen, and Erukhimovich have all reported results for idealized symmetric ABC triblocks, with $\chi_{AB} = \chi_{BC}$ and equal statistical segment lengths for all three monomer types. The space of SCF solutions for this class of systems can be parameterized by a ratio $k \equiv \chi_{AC}/\chi_{AB}$, a dimensionless measure of segregation $\chi_{AC}N$, and the block volume fractions $f_A$, $f_B$, and $f_C$. The present study focuses on how phase behavior varies with $k$ and $\chi_{AC}N$ along the isopleth $f_A = f_C$, and also extends our earlier study of the full phase triangle ($f_A \neq f_B$) of two experimentally motivated model systems to the significantly higher segregation strength.

Erukhimovich and coworkers have used a form of weak-segregation theory, analogous to Leibler’s theory of diblock copolymers, to study symmetric ABC triblock copolymer melts. This weak segregation theory is valid in the vicinity of a critical point at which a symmetric nonfrustrated ABC triblock can undergo a continuous order-disorder transition (ODT), for which the critical mode involves a modulation of the $A$ and $C$ monomer concentrations. To reduce the relevant parameter space, Erukhimovich and coworkers have focused on systems that obey the Hildebrand or solubility-parameter approximation, $\chi_{ij} \propto (\delta_i - \delta_j)^2$, in which $\delta_i$ is a solubility parameter for monomer $i$. Within this approximation, a system with $\chi_{AB} = \chi_{BC}$ must have $\delta_B = (\delta_A + \delta_C)/2$, which yields $\chi_{AC} = 4\chi_{AB}$, or $k = 4$. This group constructed a weak segregation phase diagram for symmetric triblocks with $k = 4$.

Matsen used numerical SCFT to study symmetric ABC triblocks with $\chi_{AB} = \chi_{BC}$ and $f \equiv f_A = f_C$, without using the Hildebrand approximation to constrain $k$. He showed a complete phase diagram only for systems with $k = 1$, for which the phase diagram was presented in a plot of $\chi_{AC}N$ vs. $f$, and for $\chi_{AB} = 50$ and $k = 0.0 - 2.0$, for which the phase diagram is shown as a function of $k$ vs. $f$.

We used numerical SCFT to study two closely related models in which the choice
Section 3.1. Introduction

of parameters was chosen to approximate those appropriate to an extensive series
of experimental studies of polyisoprene-b-polystyrene-b-polydimethylsiloxane (ISO)
by Bates and coworkers.\textsuperscript{43,44} We considered the entire composition triangle for an
idealized symmetric model with fixed values of $\chi_{AC} = 35$ and $\chi_{AB}N = \chi_{BC}N = 13$,
and also studied a more realistic asymmetric model in which we used literature values
for all statistical segment lengths and interaction parameters. For both models, the
structures found in the most interesting parts of the phase diagram remained rather
weakly segregated.

Several important differences emerge from a comparison of these three studies.
Erukhimovich predicted a continuous (second order) ODT for symmetric systems
with $k = 4$, while Matsen found only discontinuous (first order) order-disorder transi-
tions. For systems with $k = 1$ and $f = 0.08 - 0.24$, Matsen found the phase sequence
disordered $\rightarrow$ alternating (CsCl) spheres $\rightarrow$ alternating cylinders on a face centered
square lattice $\rightarrow$ alternating gyroid $\rightarrow$ lamellar upon increasing $f$ or decreasing $T$,
with a first order ODT. Matsen found that an alternating cylinder phase with a
square lattice was generally lower in free energy than a phase with hexagonal sym-
metry. For the symmetric system that we studied, we obtained sequence disordered
$\rightarrow$ alternating gyroid $\rightarrow$ lamellar, with a second order ODT. Erukhimovich allowed
for a cylinder phase with hexagonal symmetry but not for one based on a square
lattice, and generally found a continuous ODT to an alternating CsCl sphere phase.
One goal of the present work is to reconcile the results obtained in these three earlier
studies, by considering how the phase sequence changes with changes in the ratio $k$.

Another goal of this work is to extend our earlier study to stronger segregations.
In that work, we found that a novel orthorhombic network phase with space group
Fddd was stable over a rather wide range of compositions in the more realistic of
the two model systems that we considered. This prediction agreed reasonably well
with the results of experimental studies of ISO triblock copolymer melts by Bates and
coworkers, who first identified this phase. We also predicted that the Fddd structure
should be a stable phase of diblock copolymer melts with a very narrow region of the
phase diagram. The fact that the Fddd phase is predicted to be stable in diblock
copolymer melts only in the weak segregation regime raised the question in our mind
if the phase might also become less stable with increasing segregation strength in ABC triblock copolymer melts.

We studied several $F^0$ systems with SCFT, whose parameters were chosen based on Erukhimovich’s weak segregation theory, which is reviewed in the next section. In the third section, we present SCFT phase diagrams for these systems along the AC isopleth (“vertical cut” in the phase prism), study the continuity of the ODT, and elucidate the sequence of the emerged ordered phases near the ODT. In the fourth section, we present phase diagrams in the composition triangle (“horizontal cut”) at the intermediate segregation strength, for two representative systems, one symmetric and one asymmetric. The last section concludes with a short summary and perspective.

Throughout our study, the SCFT equations are solved with the pseudo-spectral method, and the free energy of each candidate phases is also optimized with respect to the unit cell dimension using the method described previously, as explained in Chapter 2.

3.2 Weak Segregation Theory

The spinodal instability relevant to microphase separation in three component ter-polymer melts was first analyzed by Erukhimovich, using a method similar to that for two component heteropolymers. This theory successfully identified two competing composition fluctuation modes, which is absent in diblock copolymers. Here we follow the approach described in reference and the key results will be recapitulated and used to guide SCFT studies.

3.2.1 The Free Energy and Spinodal

The underlying assumption of polymer SCFT and the random phase approximation (RPA) for the structure function $S(k)$ is that the free energy density can be decom-
Section 3.2.1. The Free Energy and Spinodal

posed into the ideal chain part and the interaction part:

\[ F[\phi] = F_{\text{chain}}[\phi] + F_{\text{int}}[\phi]. \] (3.2.1)

Here \( \phi = \{ \phi_i \} \) measures the departure of the monomer densities from that of the spatially homogeneous mixture and \( i \) is the monomer index; \( F_{\text{chain}}[\phi] \) is the free energy of a hypothetical system of ideal chains producing the specified density field; \( F_{\text{int}}[\phi] \) is an additional interaction free energy accounting for the non-ideality. By invoking a Taylor expansion of the ideal chain contribution, the difference of the overall free energy and that of a homogeneous melts can be represented as:

\[
F - F_0 = \delta F_{\text{int}}[\phi] + \frac{V}{2} \int \frac{d\mathbf{q}}{(2\pi)^3} \Gamma_{ij}^{(2)}(\mathbf{q}) \phi_i(\mathbf{q}) \phi_j(-\mathbf{q}) \\
+ \frac{V^2}{3!} \int \frac{d\mathbf{q}_1 d\mathbf{q}_2}{(2\pi)^6} \Gamma_{ijk}^{(3)}(\mathbf{q}_1, \mathbf{q}_2, -\mathbf{q}_1 - \mathbf{q}_2) \cdot \phi_i(\mathbf{q}_1) \phi_j(\mathbf{q}_2) \phi_k(-\mathbf{q}_1 - \mathbf{q}_2) + \cdots
\] (3.2.2)

Here \( \delta F_{\text{int}} \) represents the difference of the interaction free energy between the inhomogeneous and the homogeneous phase; the summation over repeated indices is assumed. For dense polymer melt, the interaction part comes from the pressure field needed to impose the incompressibility and the short-range monomeric repulsions. Both of them can be assumed to be quadratic and point-like in the real space:

\[
\delta F_{\text{int}}[\phi] = \frac{V}{2} \int \frac{d\mathbf{q}}{(2\pi)^3} U_{ij}(\mathbf{q}) \phi_i(\mathbf{q}) \phi_j(-\mathbf{q})
\]

\[
U_{ij}(\mathbf{q}) = B + \chi_{ij}.
\] (3.2.3)

Here a huge positive compressibility constant \( B \) is introduced to suppress the deviation of the overall monomer density from that of the uniform value. The incompressible case is realized when \( B \) is set to infinity. \( \chi_{ij} \) are the dimensionless Flory-Huggins parameters and vanish when \( i = j \). Neither \( B \) nor \( \chi_{ij} \) depends on \( \mathbf{q} \).

This explicit representation of \( \delta F_{\text{int}} \) immediately leads to the conclusion that the Taylor expansion coefficients of the overall free energy are the same as those of the
ideal part at all orders except two. Thus if the expansion coefficients for the overall free energy is denoted by $\Gamma^{(m)}$, one finds $\Gamma^{(m)} = \bar{\Gamma}^{(m)}$ for $m \geq 3$, and

$$\Gamma_{ij}^{(2)}(q) = \bar{\Gamma}_{ij}^{(2)}(q) + B + \chi_{ij}. \quad (3.2.4)$$

For chains obeying Gaussian statistics, standard results exist relating the $\bar{\Gamma}^{(m)}$ (known as vertex functions) to the multi-point correlation functions $\tilde{\Omega}^{(m)}$ of Gaussian chains. The relation for $m = 2$ is particularly simple: $\bar{\Gamma}_{ij}^{(2)}(q) = \tilde{\Omega}_{ij}^{-1}(q)$, where $\tilde{\Omega}_{ij}(q) = \langle \phi_i(q)\phi_j(-q) \rangle$ is the two point single chain correlation function, which is the generalization of the Debye function.

For the incompressible liquid, $B \to \infty$, a simple compressing mode $\varepsilon = (1,1,1)$ of $\Gamma^{(2)}$ with eigenvalue $B$ can be identified, which is not related to the thermodynamic instability. The relevant unstable modes thus can be sought in the two dimensional subspace orthogonal to $\varepsilon$, i.e., in the subspace defined by $\sum_i \phi_i(q) = 0$. To be explicit, consider two basis vectors $e^{(1)}$ and $e^{(2)}$ in the incompressible subspace, such that $\varepsilon \cdot e^{(1)} = \varepsilon \cdot e^{(2)} = 0$. Any vector in this subspace can be expressed as a linear combination of the two bases, i.e., $\phi_i = \varphi_1 e_i^{(1)} + \varphi_2 e_i^{(2)}$. This enables us to rewrite the quadratic sum in the free energy expansion as

$$\Gamma_{ij}^{(2)}(q) = \left( \Gamma_{ij}^{(2)} e_i^{(\alpha)} e_j^{(\beta)} \right) \varphi_\alpha \varphi_\beta \equiv \gamma_{\alpha\beta}^{(2)} \varphi_\alpha \varphi_\beta. \quad (3.2.5)$$

Here $\gamma^{(2)}$ is a symmetric and $B$-independent 2 by 2 matrix.

The system is locally stable when both eigenvalues of $\gamma^{(2)}(q)$ are positive for all $q$. The spinodal surface is the surface along which $\lambda_{\min}(q, \chi_{ij}N) = \lambda(q^*, \chi_{ij}^*N) = 0$. We have implemented two sequential Newton-like searches, one for $q^*$ and one for $\chi_{ij}^*N$, which is more stable than optimizing $q$ and $\chi_{ij}^*N$ simultaneously. The solutions of $q^*$ and $\chi_{ij}^*N$ as functions of compositions for triblocks are generally not smooth surfaces, unlike diblocks. Several competing eigenvalues may vanish simultaneously at different values of $q^*$'s and $\chi_{ij}^*N$. These situations were termed “two-length scale” phenomena by Erukhimovich \cite{38,39} since the values of $q^*$ are reciprocal to the period of the incipient density modulation. The corresponding points on the spinodal surface are termed “Double Spinodal Points” (DSPs) by Kuchanov.\cite{50}
Section 3.2.2. Spinodal in AC Isopleth

Each point on the spinodal surface is accompanied by an eigenvector $\varepsilon(q) = \varepsilon(q^*)$, which may be appropriately called the most “dangerous” mode. By contracting it with the third order vertex function, one may identify critical compositions by looking for the solutions to:

$$\Gamma_{ijk}^{(3)}(q_i, q_j, q_k)\varepsilon_i(q^*)\varepsilon_j(q^*)\varepsilon_k(q^*) = 0. \quad (3.2.6)$$

Here the wave vectors complete an equilateral triangle, namely, $|q_i| = |q_j| = |q_k| = q^*$ and $q_i + q_j + q_k = 0$. The solution to Eq.(3.2.6) defines at least two curves on the spinodal surface, since at least two curves are needed to connect the three critical points on the diblock edges. We found, except in very rare situations, where three curves are needed, two is the usual case.

The topology of the critical curves and the spinodal surface strongly depends on the relative magnitudes of the interaction parameters. In the following discussion, we will focus on the symmetric triblocks with $b_A = b_B = b_C$ and $\chi_{AB} = \chi_{BC}$, and will study the effect of $k \equiv \chi_{AC}/\chi_{AB}$ on the shape of the spinodal surface and critical lines.

3.2.2 Spinodal in AC Isopleth

In the AC-isopleth, the relabeling symmetry of A and C components implies that the A and C indices of eigenmodes of $\gamma^{(2)}$ have the same magnitudes, which, combined with the orthogonality condition, enables us to identify the eigenmodes: $e^{(1)} = (1, 0, -1)$ and $e^{(2)} = (1, -2, 1)$. The $e^{(1)}$ mode is critical (Eq.(3.2.6)) at all compositions in the AC isopleth, since $e_i^{(1)} e_j^{(1)} e_k^{(1)}$ is anti-symmetric with respect to the relabeling of A and C block but $\Gamma^{(3)}$ is symmetric. The $e^{(2)}$ mode is critical at only $f_B = 0.49$.

The eigenvalues of $\gamma^{(2)}$, multiplied by $N/2$ and labeled as $\lambda_{AC}$ and $\lambda_B$, read:

$$\lambda_{AC}(q) = \bar{\omega}_{11}^{-1}(q) - \chi_{AC}N; \quad (3.2.7)$$
$$\lambda_B(q) = \bar{\omega}_{22}^{-1}(q) + \chi_{AC}N - 4\chi_{AB}N \quad (3.2.8)$$
where \( \bar{\omega}^{-1}_{\alpha\beta} \equiv \tilde{\Omega}^{-1}_{ij} e^{(\alpha)}_i e^{(\beta)}_j N/2 \). \( \lambda_B \) corresponds to eigenmode \( e^{(2)} \), for which the A and C components tend to mix, and separate from the B component. \( \lambda_{AC} \) corresponds to \( e^{(1)} \), for which the A and C components tend to separate from each other and the B component tends to stay at the interface. The spinodal conditions “\( \min_q \lambda_B = 0 \)” and “\( \min_q \lambda_{AC} = 0 \)” yield two linear functions of \( \chi_{AC} \) and \( \chi_{AB} \):

\[
\begin{align*}
\chi_{AC}N &= \bar{\omega}^{-1}_{11}(q_{AC}^*); \\
\chi_{AC}N &= \frac{k}{4-k} \bar{\omega}^{-1}_{22}(q_{B}^*).
\end{align*}
\]

Eq.(3.2.9) is independent of \( \chi_{AB} \) and gives the AC-modulated spinodal; Eq.(3.2.10) gives the B-modulated spinodal.

Since \( \lambda_B(q) > 0 \) as \( N \to 0 \) for which the homogeneous phase is stable, \( \bar{\omega}^{-1}_{22}(q_{B}^*) > 0 \). Then Eq.(3.2.10) has solution only if \( k < 4 \). In other words, a B-modulated spinodal exists only if \( k < 4 \). The value of \( \chi_{AC}N \) for B-modulation at a fixed composition is a decreasing function of \( k \) and that for AC-modulation is independent of \( k \) since Eq.(3.2.9) is independent of \( \chi_{AB} \). In Figure 3.1, we have plotted the AC-modulated spinodal and the B-modulated ones at \( k = 0.2, 1, 2 \). The AC-modulated spinodal increases monotonically as the fraction of middle block increases, and approaches infinity as \( f_B \to 1 \). The B-modulated one approaches infinity at both \( f_B = 0 \) and \( f_B = 1 \), and has a minimum at the fixed composition \( f_B = 0.47 \) regardless of the value of \( k \).

For cases when \( k < 2 \), the two spinodals intersect at a certain composition \( f_{DSP} \). The nature of the true spinodal is AC modulated if \( f_B < f_{DSP} \) and is B modulated if \( f_B > f_{DSP} \). \( f_{DSP} \) increases as \( k \) increases and approaches 1 eventually at infinite \( \chi_{AC} \). Near that limit, both \( \bar{\omega}^{-1}_{11}(q) \) and \( \bar{\omega}^{-1}_{22}(q) \) are dominated by \( N\tilde{\Omega}^{-1}_{AC}(q) \) as can be shown by analyzing the asymptotes. The two identities Eq.(3.2.10) and Eq.(3.2.9) thus yield \( k = 2 \).

For cases when \( 2 \leq k < 4 \), the curve defined by Eq.(3.2.10) is always above that defined by Eq.(3.2.9), the true spinodal is AC modulated for any value of \( f_B \).
Section 3.3. Phase Diagrams along AC-isopleth

Figure 3.1: Spinodals along the AC isopleth for different k’s. AC modulated and B modulated lines are shown in different colors. The singular cusps occur at the intersection of the two branches for k < 2, labeled with circles. The portions of B modulated spinodals preceded by AC modulated one are shown as dashed lines. The critical point (f_B = 0.49) on B modulated spinodal is labeled with star.

3.3 Phase Diagrams along AC-isopleth

We present the phase diagrams in the AC-isopleth for three symmetric triblock copolymers with ratios k = \(\chi_{AC}/\chi_{AB}\) = 1, 2, 4, respectively. For these systems, previous experimental and theoretical work have suggested that the competing morphologies should include: \(L\), \(G^A\), \(C^A\), \(S^A\) and \(F^A\). \(L\) stands for lamella. \(G^A\) (I4_132) is called the single gyroid phase by Erukhimovich, in which A and C rich domains each occupy a gyroid network. \(C^A\) is a two dimensional phase in which the A and C cylinders are packed onto two inter-weaving simple square unit cells within B matrix. \(S^A\) is a simple cubic phase in which A and C spheres are packed onto a CsCl lattice and B block forms the matrix. \(F^A\) is analogous to the \(S^A\) phase in which the A and C
spheres are instead packed onto NaCl lattice. $F^A$ phase lies on the same free energy surface as the close packed FCC spheres in AB and BC diblock copolymers. This can be explained by imaging a continuous evolution of the $F^A$ solution towards the FCC solutions on both diblock edges: the size of either A or C spheres can be smoothly turned to 0 without changing the symmetry of the lattice. We did not consider the $G_2$ and $BCC_3$ phases which were suggested in reference,\textsuperscript{39} and have commented on the reason in a previous paper.\textsuperscript{40}

All these alternating phases may be properly called AC-modulated in that their morphologies are characterized by the repelling A and C rich domains. In the previous section, it has been noted that the AC-modulated spinodal points are also critical points. However the ODT’s close to these points are not necessarily continuous because they might be preempted by the other discontinuous transitions. The true behavior can only be found by the full SCFT calculation.

Matsen\textsuperscript{37} previously studied the system with $k = 1$ using SCFT, and found that the sequence of the ordered phases along the AC isopleth near the ODT is $L \rightarrow G^A \rightarrow C^A \rightarrow S^A$ as $f_B$ increases. He also noted that the ODT for compositions from $f_B = 0.4$ to $f_B = 1.0$ is discontinuous, which differs from our conclusion in reference \textsuperscript{40} for the system with $k \simeq 2.7$. Our results in the composition triangle includes one continuous ODT point in the AC-isopleth. On the other hand, Erukhimovich\textsuperscript{39} studied the system with $k = 4$, the value required by the Hildebrand approximation. He assumed that the AC modulated critical line is also the ODT line and is not preceded by any discontinuous phase transition. Around the selected point on this ODT line, he formulated a weak segregation theory by isolating the most “dangerous” mode and predicted that the correct sequence of the ordered phases near the ODT is $L \rightarrow G^A \rightarrow F^A \rightarrow S^A \rightarrow BCC_3$ as $f_B$ increases. Erukhimovich then commented that the system considered by Matsen remains AC-modulated only for compositions from $f_B = 0$ to $f_B \simeq 0.51$.

Apparently, the sequence and type ($C^A$ and $F^A$, in particular) of the ordered phases and the continuity of the ODT’s varies with the value of $k$. In order to bridge the pictures provided by Matsen and Erukhimovich, we have prepared SCFT phase diagrams along the AC-isopleth for systems with $k = 1$ (since Matsen did not consider
Section 3.3. Phase Diagrams along AC-isopleth

the $F^A$ phase), $k = 4$ (to compare with Erukhimovich’s prediction directly) and $k = 2$ (to see the transition).

![Phase diagram of symmetric ABC triblock copolymer in AC-isopleth, with $k = \chi_{AC}/\chi_{AB} = 4$. The dashes line is the spinodal with AC modulated unstable mode and is also a critical line. The stable ordered phases near this spinodal include $L, G^A, C^A, S^A$. All order-disorder transitions appear to be continuous.](image)

Figure 3.2: Phase diagram of symmetric ABC triblock copolymer in AC-isopleth, with $k = \chi_{AC}/\chi_{AB} = 4$. The dashes line is the spinodal with AC modulated unstable mode and is also a critical line. The stable ordered phases near this spinodal include $L, G^A, C^A, S^A$. All order-disorder transitions appear to be continuous.

In Figure 3.2 we have shown the phase diagram and the AC-modulated critical curve (dashed line) for the system with $k = 4$. The sequence of the ordered phases near the ODT is $L \rightarrow G^A \rightarrow S^A \rightarrow F^A$. We verified that the ODTs are continuous by plotting the magnitude of the strongest density modulation harmonics of each phase versus the distance from the ODT line and by verifying that the $q^*$ in the vicinity of ODT is the same for all the phases. Deviations from the quadratic shape were never observed near the ODT, so the ODT overlaps with the AC-modulated critical line. By rendering the morphologies of the ordered phase, we also found that the interface of different domains becomes very diffuse and (in the calculation) only a few harmonics is needed to resolve the structure, so that we can actually access the window with very large value of $\chi_{AC}N$. The order-order transition (OOT) boundary near the ODT is not co-tangent to the ODT, very different from that encountered near the critical
Section 3.3. Phase Diagrams along AC-isopleth

Figure 3.3: Phase diagram of symmetric ABC triblock copolymer in AC-isopleth, with \( k = \chi_{AC}/\chi_{AB} = 2 \). The dashes line is the spinodal with AC modulated unstable mode and is also a critical line. The stable ordered phases near this spinodal include \( L, G^A, C^A, S^A \) and \( F^A \).

point of the diblock copolymer. These two types of continuous transitions have been distinguished by Landau\(^{51,52}\) and the co-tangent shape is mathematically justified only for the latter case. Our results are consistent with Erukhimovich’s prediction, as regarding the stable window of \( L, G^A \) and \( S^A \) phases, but are not with that of \( F^A \) phase. We found that \( F^A \) always has higher free energy than \( S^A \) in the window where he predicts \( F^A \) to be stable. Further, we identified a stable window of \( C^A \) phase which terminates at a \( G^A/C^A/S^A \) triple point slightly off the critical line. Its stable window becomes broader as \( \chi_{AC}N \) increases.

In Figure 3.3 we have shown the phase diagram for the systems with \( k = 2 \). The topology of the phase diagram is similar to that of the system with \( k = 4 \), except that the overall scale of \( \chi_{AC}N \) decreases. The sequence of the ordered phase near the ODT now becomes \( L \rightarrow G^A \rightarrow S^A \rightarrow F^A \rightarrow S^A \). The ODT is obviously discontinuous for compositions with \( f_B \gtrsim 0.6 \), but seems to be still continuous for the \( L\)-Dis and \( G^A\)-Dis
Section 3.3. Phase Diagrams along AC-isopleth

Figure 3.4: Phase diagram of symmetric ABC triblock copolymer in AC-isopleth, with \( k = \chi_{AC}/\chi_{AB} = 1 \). The dashes line is the spinodal with AC modulated and B modulated unstable mode. The stable ordered phases near this spinodal include \( L, G^A, C^A, S^A \). The order disorder transitions for \( G^A, C^A \) and \( S^A \) are discontinuous.

transitions, for which the ODT overlaps with the critical line. The \( G^A/C^A/S^A \) triple point is still present but moves closer to the critical line.

In Figure 3.4 we have shown the phase diagram for the system with \( k = 1 \). We did not find the stable window for \( F^A \) phase so that the phase diagram is the same as Matsen’s except that we now have completed the stable window for \( L, G^A \) and \( C^A \), and have shown the stability limits for the disordered phase. The sequence of the ordered phase near the ODT now becomes \( L \rightarrow G^A \rightarrow C^A \rightarrow S^A \). Besides the \( L-\text{Dis} \) transition, all ODT’s are discontinuous. The \( C^A/G^A/S^A \) triple point has disappeared so that direct \( C^A-\text{Dis} \) transition is possible. It implies that an intermediate value of \( k \) exists between 1 and 2, for which the triple point lies right on the ODT. The \( C^A \) phase is stable near ODT only if \( k \) is smaller than this value.

These phase diagrams and Figure 8 of reference\(^{37} \) indicate that the width of the stable window of the ordered phases is roughly constant at fixed value of \( \chi_{AB}N \).
Section 3.4. $N$-dependence of Phase Triangle

(or $\chi_{BC}N$). This is consistent with the picture that in the AC-modulated phases, the incompatible A, C pair is well separated from each other, so that the enthalpic contribution to the free energy is dominated by the amount of AB and BC contacts.

Regarding the stable window of the $F^A$ phase, our results do not agree with Erukhimovich’s weak segregation theory. We are confident with our results on this phase because its stable window is very close to the ODT where SCFT have no problem of resolving the structure, and because we could reproduce Matsen’s result on the close packed spheres in diblocks by continuously evolving the $F^A$ solution to the diblock edge.

3.4 $N$-dependence of Phase Triangle

In reference 40, we reported the phase diagrams in the composition triangle of two $F^0$ triblock copolymers: one symmetric with $k = \chi_{AC}N/\chi_{AB}N = 35/13 = 2.7$, and another asymmetric, of which the statistical segment lengths ($b_I=6.0\text{Å}, b_S=5.5\text{Å}, b_O=7.8\text{Å}$) and the interaction parameters ($\chi_{IS} = 0.044, \chi_{SO} = 0.0496, \chi_{IO} = 0.1832, N = 250$) were chosen to represent an experimentally extensively studied system, poly(isoprene-styrene-ethylene oxide) (ISO).43,44 For a polymer with fixed values of $\chi_{ij}$’s, each phase triangle corresponds to a horizontal cut in the phase prism, at certain value of $N$. These choices of parameters enable us to avoid the complexity encountered in the triangle cut at lower value of $N$: for symmetric case, the critical line connecting the AB diblock C.P. and BC diblock C.P. is below our cut, so that only one AC-modulated critical point is present (see Figure 3.5(a)); for ISO case, the critical line connecting the C.P.’s at the IO and SO edges are below our cut, so that only one critical point on the critical curve starting from the IS edge and ends at S corner is present (see Figure 3.6(a)).

In both systems, near the end block corners, we have found the core-shell like morphology: e.g., near A corner of the symmetric case, the C phase can be described as C-core cylinders/B-shell/A-matrix. Near the middle block rich corner and near one of the diblock edges, we found the morphologies in which one of the end block domain occupies the regular lattice sites (e.g., the hexagonal sites in C phase), and
Section 3.4. $N$-dependence of Phase Triangle

the other end block occupies the interstitial sites (e.g., the honeycomb lattice sites in $C$ phase). In the region close to the critical point, the two types of solutions extended from both diblock edges are separated by the alternating phases, where we find $G^A$ and $S^A$ phases in the symmetric case, and $G^A$ phase in the ISO case.

Based on the study in the previous section (perpendicular cut), we now understand that if the phase prism is cut at a higher value of $N$, the other alternating phases, $C^A$ in particular, will become stable in the AC isopleth of the symmetric case, and may become stable near the critical point of the ISO case. However it is not clear how the stable domains of each ordered phase will evolve when the overall chain length is increased, which will eventually help us to visualize the topology in the 3-dimensional phase prism. So we have prepared the phase triangles for the two systems with overall chain length doubled, shown in Figure 3.5(b) and Figure 3.6(b), respectively.

In Figure 3.5(b) we have shown phase diagram, the spinodals, and projected critical lines for the symmetric case. The topology of the diagram is analogous to the one with shorter chain length. Near the A and C corner, the stable window of the core-shell like ordered phases moved closer to the corners, which results in a greatly enlarged $L$ domain in the center of the triangle. Two narrow channels of $FCC$ phases also show up, similar to what is happening in diblock phase diagrams increased chain length. The spinodal near these two corners appears to be a good guide of the ODT. Near the B corner, the intersection of the spinodal and the symmetry line along which $f_A = f_C$ (which is also the projected AC modulated critical line) gives the critical point on this cut: $f_B = 0.735$, which is closer to the B corner as compared to the lower chain length cut. The alternating phases along the AC isopleth now appear in the sequence $L \rightarrow G^A \rightarrow C^A \rightarrow S^A \rightarrow F^A$ as $f_B$ increases. The free energy differences of these phases are very small near the critical point, which is reflected by the crowded triple points and by the narrow stable window of $F^A$ phase. These phases remain stable only near the symmetry line. For relatively larger asymmetric compositions, they lose the stability to the ordered phases extended from the diblock edges. Along the ODT’s near the B corner, two thin slices of $FCC$ window emerges. As we have commented, they belong to the same free energy surface as the $F^A$ phase, but the stable windows of the two phases were separated by the BCC packed spheres.
Section 3.4. $N$-dependence of Phase Triangle

Figure 3.5: Phase diagram in the composition triangle of symmetric an ABC triblock copolymer with $b_A = b_B = b_C$ and for: (a) $\chi_{AC}N = 35$, $\chi_{AB}N = \chi_{BC}N = 13$; (b) $\chi_{AC}N = 70$, $\chi_{AB}N = \chi_{BC}N = 26$. The dashed lines near the corners of the triangle are spinodals. The intersection of the spinodal near the B corner and the line along which $f_A = f_C$ indicates the critical point. The ordered phase near the critical point directly accessed from the disordered phase is $S^4$ for (a) and is alternating FCC spheres with sodium chloride packing type for (b).
Section 3.4. \(N\)-dependence of Phase Triangle

Figure 3.6: Phase diagram in the composition triangle for poly(isoprene-styrene-ethylene oxide), with statistical segment lengths \(b_I = 6.0 \text{Å}, b_S = 5.5 \text{Å}, b_O = 7.8 \text{Å}\), and interaction parameters: (a) \(\chi_{IS}N = 11.0, \chi_{SO}N = 14.2, \chi_{IO}N = 45.8\); (b) \(\chi_{IO}N = 91.6, \chi_{IS}N = 22.0\) and \(\chi_{SO}N = 28.4\). The dashed lines near the corners of the triangle are spinodals. The purple lines are projection of the critical lines. The intersection of the spinodal line near the S corner and the critical line indicates the position of the critical point. The ordered phase near the critical point directly accessed from the disordered phase is \(G^A\) for (a) and becomes \(S^A\) for (b).
In Figure 3.6(b) we have shown the similar results for the ISO case. The dashed purple lines represent projected critical curves. One of them connects the two diblock C.P.’s at the IO and SO edge, with relatively small values of \((\chi N)^*\), and is irrelevant to this cut. Another one starts from the IS diblock C.P. and extends towards the S-rich corner. The critical point lies at the intersection of this critical line with the spinodal near the S corner. Near the critical point, the alternating phases appear in the sequence: \(G^A \rightarrow C^A \rightarrow S^A\) as \(f_S\) increases, and \(S^A\) is the phase which melts at the critical point. Right between the boundaries of \(S^A\) and two BCC packed sphere phases, we have also identified two extremely narrow stable domains for \(F^A\) phase. Four different spherical phases (BCC packed I spheres in S matrix, BCC packed O spheres in S matrix, alternating spheres on NaCl lattice, and alternating spheres on CsCl lattice) are competing closely with each other near the critical point. For this asymmetric system, there is no symmetry line as the \(f_A = f_C\) line in symmetric case, but the projection of the critical line seems to be a good guide of the stable windows of the alternating phases.

One of our primary interests of studying this ISO system is to show that the \(O^{70}\) phase identified experimentally is indeed the thermodynamically stable one at the intermediate segregation strength. The narrow \(O^{70}\) window near the IS diblock edge identified in our previous work vanishes in this new diagram, implying that it is only a stable solution in the weak segregation regime. However, the \(O^{70}\) window in the middle of the triangle does not change significantly, and become closer to the composition region where it was found experimentally to be stable. Since the incompatibility of this new system is relatively stronger, it also implies that the “disordered” network reported by Epps\textsuperscript{53} for very long chains, could actually be a developing \(O^{70}\) phase.

3.5 Conclusions

By combining Erukhimovich’s weak segregation theory for spinodal instability with full SCFT calculation for several triblock copolymers within AC-isopleth, we clarified partially the sequence of the alternating ordered phases near the ODT and examined
the smoothness of ODT (Figure 3.2, 3.3 and 3.4). We also explored the chain length-
dependence of phase triangles for two model $F^0$ triblocks (Figure 3.5 and 3.6). The
results are consistent with the stability analysis, and could be viewed as a useful guide
for visualizing the three-dimensional topology of phase prism.

As a continuation of our previous work, we also studied the ISO triblock copolymers
with relatively large segregation strengths, and found that the stability window
of the $O^{70}$ phase is enlarged slightly, and appear to be in better agreement with the
experimental finding.

Our study of the phase diagrams were limited to $F^0$ systems, where the number
of the candidate phases is moderate, and the screening of the different phases with
accurate spectral method is efficient. For the $F^1$ and $F^2$ systems, in which the
end block interaction strength is less than one or both of the neighboring blocks
interaction strengths,$^{32}$ the morphological behavior can be quite complex, and it is
not clear whether or not the spectral method is the most efficient way of studying
the phase behavior for those systems. Combining the spectral method with the more
explorative real space screening method$^{54,55}$ in a large simulation cell may render the
exploration of parameter space less arbitrary.
We study the fluctuation effects by using the Edwards’ auxiliary field theory. In this chapter, we introduce the model and common notations, describe how the SCFT and RPA can be adopted into this more general framework, and summarize how the fluctuation corrections can be studied. The application of the theory to binary homopolymer blends and diblock copolymers will be elaborated in the next two chapters.

4.1 Model and Notation

We consider a coarse-grained model of dense polymer liquids containing one or more species of polymer constructed from two or more types of monomer. For a nearly incompressible liquid, we assume a common reference volume $v$ for all types of monomers.

Let $c_i(r) \equiv \sum_{sma} \delta(r-R_{ami}(s))$ be the fluctuating concentration field for monomers of type $i$, where $R_{ami}(s)$ is the position of monomer number $s$ of monomer type $i$ on
Section 4.1. Model and Notation

chain \( m \) of molecular species \( a \). The structure factor is defined by

\[
S_{ij}(r, r') \equiv \langle \delta c_i(r) \delta c_j(r) \rangle, \quad (4.1.1)
\]

where \( \delta c_i(r) \equiv c_i(r) - \langle c_i(r) \rangle \). Let \( \Omega_{ij}(r - r') \) be the corresponding intramolecular correlation function, arising from correlations between pairs of monomers on the same chain. This is explicitly expressed as a sum

\[
\Omega_{ij}(r, r') \equiv \sum_{am} \langle c_{ami}(r)c_{amj}(r) \rangle \quad (4.1.2)
\]

where \( c_{ami}(r) \equiv \sum_s \delta(r - R_{ami}(s)) \).

To study the statistical properties, we use the effective Hamiltonian in which the potential energy is taken to be of the form

\[
U = U_{\text{chain}} + U_{\text{int}} + U_{\text{ext}}[h], \quad (4.1.3)
\]

where \( U_{\text{chain}} \) is an intramolecular bonding potential, and

\[
U_{\text{int}} = \frac{1}{2} \sum_{ij} \int dr \int dr' U_{ij}(r - r')c_i(r)c_j(r') \quad (4.1.4)
\]

\[
U_{\text{ext}} = - \sum_i \int dr h_i(r)c_i(r). \quad (4.1.5)
\]

Here, \( U_{ij}(r - r') \) is a nonbonded pair potential, and \( h_i(r) \) is an external field that is introduced for mathematical convenience. As in reference 56, we assume a pair interaction matrix \( U_{ij}(r, r') = B_0 + \chi_{0,ij} \). For the binary case, it is of the form

\[
U_{ij}(r - r') = \begin{pmatrix} B_0 & B_0 + \chi_0 \\ B_0 + \chi_0 & B_0 \end{pmatrix} \delta_\Lambda(r - r') \quad (4.1.6)
\]

in which \( \chi_0 \) is microscopic interaction parameter and \( B_0 \) is a bare non-dimensional compression modulus. \( \delta_\Lambda(r - r') \) is a softened Dirac \( \delta \)-function with a cutoff length \( \Lambda^{-1} \).
Section 4.1. Model and Notation

Let $F[\langle c \rangle]$ denote the free energy of this coarse-grained model as a functional of the order parameter $\langle c_i(r) \rangle$. It is defined by a Legendre transform

$$F[\langle c \rangle] \equiv - \ln Z[h] + \sum_i \int d\mathbf{r} \ h_i(\mathbf{r}) \langle c_i(\mathbf{r}) \rangle,$$

in which

$$Z[h] \equiv \int D[\mathbf{R}] e^{-U[\mathbf{R}]},$$

is the corresponding partition function. By construction, $F[\langle c \rangle]$ satisfies

$$h_i(\mathbf{r}) \equiv \frac{\delta F}{\delta \langle c_i(\mathbf{r}) \rangle}.$$

The correlation functions are derived from the functional derivatives:

$$S_{i,j}(\mathbf{r}, \mathbf{r}') = \frac{\delta^2 \ln Z[h]}{\delta h_i(\mathbf{r})\delta h_j(\mathbf{r}')}$$

and satisfies the standard identity:

$$S_{i,j}^{-1}(\mathbf{r}, \mathbf{r}') = \frac{\delta^2 F[\langle c \rangle]}{\delta \langle c_i(\mathbf{r}) \rangle \delta \langle c_j(\mathbf{r}') \rangle}.$$

Most of these conclusions apply equally well to calculations carried out in the canonical or grand-canonical ensemble, and so we use $Z$ and $F$ to denote either the canonical or grand-canonical partition function and free energy functionals, interchangeably. In the canonical ensemble, $\int D[\mathbf{R}]$ denotes an integral over particle positions. In grand-canonical ensemble, $\int D[\mathbf{R}]$ also implies a sum over the numbers of molecules.

In the remainder, we simplify notation by using the following shorthand convention: in expressions for functionals that involve convolution of two functions, by integrating over a shared position and summing over a shared type index, we use *
Section 4.2. Mean Field Theory

to denote convolution. In this notation,

\[ U_{\text{int}} = \frac{1}{2} c * U * c, \quad (4.1.12) \]
\[ U_{\text{ext}} = -h * c, \quad (4.1.13) \]

and \( F = -\ln Z + h * \langle c \rangle \).

Edwards’ method uses a Stratonovich-Hubbard transformation to change the Boltzmann factor arising from nonbonded interactions into an integration over the auxiliary fields:

\[ e^{-\frac{1}{2} c^* U c} = \mathcal{N}^{-1} \int D[J] e^{-\frac{1}{2} J^* U^{-1} J + i J^* c}, \quad (4.1.14) \]

in which

\[ \mathcal{N} \equiv \int D[J] e^{-\frac{1}{2} J^* U^{-1} J} = \sqrt{\det 2\pi U} \quad (4.1.15) \]

is a normalization factor. Substituting this expression into the definition of \( Z \) yields

\[ Z[h] \equiv \mathcal{N}^{-1} \int D[J] e^{L[iJ,h]}. \quad (4.1.16) \]

where

\[ L[iJ,h] \equiv \ln \tilde{Z}[iJ+h] - \frac{1}{2} J^* U^{-1} * J. \quad (4.1.17) \]

Here, \( \tilde{Z}[h + iJ] \) is the partition function for an ideal gas subjected to a fluctuating field \( \tilde{h} = h + iJ \). It contains the configuration space integral:

\[ \tilde{Z}[h] \equiv \int D[R] e^{-U_{\text{chain}}[R] + (h + iJ)^* c}. \quad (4.1.18) \]

4.2 Mean Field Theory

A saddle point approximation to Eq. 4.1.16 yields the mean field theory. Note that \( \langle c \rangle = \delta \ln \tilde{Z} / \delta iJ \), where \( \langle c \rangle \) is the average density fields established in a gas of ideal chains under the external fields \( h + iJ \). The field \( J \) at the saddle point satisfies

\[ iJ^s = -U * \langle c \rangle. \quad (4.2.1) \]
Section 4.2. Mean Field Theory

and \( h + iJ^s \) is the mean molecular field. It can also be shown that \( \langle iJ \rangle = -U * \langle c \rangle \) is generally true, by evaluating \( \langle c \rangle \) from the differentiation of \( \ln Z[h] \) with respect to \( h \) and integrating the functional by part (ignoring the boundary terms).

We now turn off the external potential and evaluate the ideal gas as partition function (Eq. (4.1.18)) at the saddle point condition, in a grand canonical ensemble

\[
\Xi[iJ^s] = \prod_a \left\{ \sum_{M_a=0}^{\infty} \frac{(\lambda_a z_a[iJ^s])^{M_a}}{M_a!} \right\} = \prod_a e^{\lambda_a z_a[iJ^s]},
\]

where \( a \) is the type of, \( M_a \) the number of, \( \lambda_a \) the activity of the distinct molecules, and

\[
z_a[iJ^s] \equiv \int D[R_a] e^{-U_{\text{chain}}[R_a] + iJ^s c_a} \quad (4.2.3)
\]

Note that the average molecule number is given by

\[
\langle M_a \rangle = \frac{\delta \ln \Xi[h]}{\delta \ln \lambda_a} = \lambda_a z_a,
\]

so \( \ln \Xi[iJ^s] = \sum_a \langle M_a \rangle \), which is the ideal gas law.

The grand potential at the saddle point then becomes

\[
\Phi = -\ln \Xi[h = 0] = -\sum_a \langle M_a \rangle^s + \frac{1}{2} \langle c \rangle^s * U * \langle c \rangle^s.
\]

Notice further that \( \mu_a = \ln(\langle M_a \rangle / z_a[iJ^s]) \), the corresponding Helmholtz free energy in canonical ensemble reads:

\[
F = \Phi + \sum_a \mu_a \langle M_a \rangle^s + iJ^s * \langle c \rangle^s
\]

\[
= \sum_a \langle M_a \rangle^s \ln \left( \frac{\langle M_a \rangle^s}{z_a[iJ^s] e} \right) + iJ^s * \langle c \rangle + \frac{1}{2} \langle c \rangle^s * U * \langle c \rangle^s.
\]

Replacing \( iJ^s \) by \( \omega \), the single chain version of this equation becomes essentially identical to Eq. (2.1.7) in Chapter 2. They both reduce to the continuum version of the Flory-Huggins theory if \( z_a = N_a \).

We now write \( \ln Z_s[h] = \ln \tilde{Z}[\tilde{h}] + \frac{1}{2} \langle c \rangle * U * \langle c \rangle \) and use Eq. (4.1.10) to derive the
mean field prediction for $S$. The first derivative:

$$\frac{\delta \ln Z_s[h]}{\delta h} = \frac{\delta \ln \tilde{Z}[\tilde{h}]}{\delta \tilde{h}} \ast \delta \tilde{h} \ast \langle c \rangle \ast U \ast \frac{\delta \langle c \rangle}{\delta \tilde{h}} \ast \frac{\delta \tilde{h}}{\delta h} = \left( \langle c \rangle + \langle c \rangle \ast U \ast \tilde{\Omega} \right) \ast \frac{\delta \tilde{h}}{\delta h} \quad (4.2.6)$$

where substitutions $\langle c \rangle = \delta \ln \tilde{Z}[\tilde{h}]/\delta \tilde{h}$, and $\tilde{\Omega} = \delta \langle c \rangle/\delta \tilde{h}$ being the ideal gas intramolecular correlations, have been made. $\delta \tilde{h}/\delta h$ may be derived from the saddle point condition, which we write as $\tilde{h} = h - U \ast \langle c \rangle$. Differentiating both sides with respect to $\tilde{h}$ yields: $\delta h/\delta \tilde{h} = 1 + U \ast \tilde{\Omega}$. This leads to

$$\frac{\delta \ln Z_s[h]}{\delta h} = \langle c \rangle , \quad (4.2.7)$$

and that

$$\bar{S} = \frac{\delta^2 \ln Z_s[h]}{\delta \tilde{h}^2} = \frac{\delta \langle c \rangle}{\delta \tilde{h}} \ast \frac{\delta \tilde{h}}{\delta h} = \tilde{\Omega} \ast \left( 1 + U \ast \tilde{\Omega} \right)^{-1} = \left( \tilde{\Omega}^{-1} + U \right)^{-1} . \quad (4.2.8)$$

This is the familiar RPA expression for the correlation function.

### 4.3 Loop Expansions

Fluctuation corrections to the mean field theory can be worked out using the standard perturbative expansion.\textsuperscript{4} We expand the effective Hamiltonian for $iJ$ fields with a Taylor functional series around the saddle point,\textsuperscript{56} and denote the coefficients functions to $(iJ - iJ^s)^n$ by $L^{(n)}$. It is straightforward to show that $L^{(2)} = \tilde{\Omega} + U^{-1}$, and that $L^{(n)} = \tilde{\Omega}^{(n)}$ for $n \geq 3$, where $\tilde{\Omega}^{(n)} = \delta^n \ln \tilde{Z}[h + iJ^s]/\delta(iJ^s)^n$ are ideal gas $n$-point intramolecular correlation functions evaluated at the saddle point (had we been working in canonical ensemble, these need to be replaced with the corresponding cumulants\textsuperscript{56}).

As shown in reference\textsuperscript{56}, using $\tilde{G} \equiv (L^{(2)})^{-1} = \left( \tilde{\Omega} + U^{-1} \right)^{-1}$ as the propagator, the perturbation series for the free energy and various correlation functions can be
Section 4.3. Loop Expansions

expressed as functional integrals involving $\hat{\Omega}^{(n)}$ ($n \geq 3$) and $\hat{G}$. The series may be ordered according to the number of independent integration (internal) variables, which is conventionally called a loop expansion. The mean field approximation involves no such integrations; the one-loop approximation involves a single integration variable; and so on. At the level of power counting, it has been shown that, in this hierarchical series, the $(n+1)$-loop terms are “smaller” than the $n$-loop terms by a factor $\bar{N}^{-1/2}$, $\bar{N} \equiv N b^6/v^2$ being the invariant degree of polymerization.

Within this hierarchical framework, the one-loop theory for the free energy may be obtained by approximating the difference $\delta L$ between $L[iJ,h]$ and its saddle-point value by just the harmonic functional. This yields a (Gaussian) correction to the free energy, including a contribution arising from the constant $\mathcal{N}$ (Eq.(4.1.15)),

$$\delta \ln Z = -\frac{1}{2} \text{Tr} \ln (\hat{G}^{-1} U) = -\frac{1}{2} \text{Tr} \ln (1 + \hat{\Omega} U), \quad (4.3.1)$$

Differentiating this term with respect to $h$, the one-loop correction to the correlation function at fixed chemical potential can be exactly recovered. The corresponding expressions for fixed compositions may be obtained by compensating for the composition difference between mean field and one-loop results.

The loop expansion for the multi-point correlation functions to arbitrary orders in systems involving multiple species and multiple monomers was worked out by Morse. The one-loop corrections have been carefully examined for binary homopolymer blends and diblock copolymers. Like many coarse grained theories (in particular, those in polymer science), the integrals involved are ill-defined at short length scale, showing strong dependences on the microscopic details of the fluids (UV divergence). The standard theoretical tool to resolve this is to isolate and absorb the terms that depend strongly on the local fluid structures into quantities that are measurable in some reference system or states – renormalization (See Section 5.1.1 for a discussion in the blends case). It has been shown that the one-loop theory, for the binary systems examined, is renormalizable, meaning that the dependence on the short length physics can be absorbed (thus removed) into the $\chi$-parameter inferred from the scattering measurements and into the statistical segment lengths (See Section 5.7 and Section 53).
Section 4.3. Loop Expansions

5.8 in Chapter 5 for an explanation of the divergence originating from the correlation hole effects).

We examine the quantitative consequence of this renormalized one-loop theory as applied to binary homopolymer blends and diblock copolymers in the next two chapters. Correlation functions are the central quantities we studied, which includes both intra- and inter- molecular contributions. The theory enables us to study them separately, and as a result, also enables us to examine the single molecule properties such as the structure factor and the geometric dimensions. The explicit expressions will be given in the relevant discussions.
The renormalized one-loop theory is a coarse-grained theory of corrections to the random phase approximation (RPA) theory of composition fluctuations. We present predictions of corrections to the RPA for the structure function $S(k)$ and to the random walk model of single-chain statics in binary homopolymer blends. We consider an apparent interaction parameter $\chi_a$ that is defined by applying the RPA to the small $k$ limit of $S(k)$. The predicted deviation of $\chi_a$ from its long chain limit is proportional to $N^{-1/2}$, where $N$ is chain length. This deviation is positive (i.e., destabilizing) for weakly non-ideal mixtures, with $\chi_aN \simeq 1$, but negative (stabilizing) near the critical point. The positive correction to $\chi_a$ for low values of $\chi_aN$ is a result of the fact that monomers in mixtures of shorter chains are slightly less strongly shielded from intermolecular contacts. The predicted depression in $\chi_a$ near the critical point is a result of long-wavelength composition fluctuations. The one-loop theory predicts a shift in the critical temperature of $\mathcal{O}(N^{-1/2})$, which is much greater than the predicted $\mathcal{O}(N^{-1})$ width of the Ginzburg region. Chain dimensions are found
5.1 Introduction

Equilibrium properties of polymer mixtures that involve correlations over distances greater than a few Angstroms are rather well described by a family of related self-consistent field theories. Among these are the Flory-Huggins (FH) theory of homogeneous mixtures and the random phase approximation (RPA) theory of composition fluctuations. Both the FH and RPA theories are special cases of a more general self-consistent field theory (SCFT) of inhomogenous polymer liquids.

Theoretical treatments of polymer mixtures that go beyond SCFT may be generally classified as either microscopic liquid state theories or coarse-grained theories of correlation effects. Liquid state theories such as the polymer reference interaction site model (PRISM)\textsuperscript{58} and Born-Green-Yvon theories\textsuperscript{59} attempt to predict all details of dense liquid structure from first principles. Coarse-grained theories that go beyond SCFT are based on more idealized models of chain conformations and interactions, \textit{e.g.}, as continuous Gaussian chains with point-like interactions.

Over the past 20 years, a series of coarse-grained theories of correlation effects in polymer mixtures have been based on a functional integral representation of the partition function that was originally introduced by Edwards.\textsuperscript{60–66} All such “field theoretic” studies of mixtures have thus far used an approximation in which the distribution of field fluctuations is approximated by a Gaussian. This approximation is referred to in the jargon of field theory (which we have adopted) as a “one-loop” approximation.

5.1.1 Coarse-Graining and Renormalization

The reason for studying correlations in coarse-grained models is the hope that, by doing so, one might describe the essential features of phenomena that are not captured...
by SCFT, but that are, in some sense, independent of short-wavelength details. The first several studies of coarse-grained models of blends, however, were plagued by a sensitivity of all predictions to the treatment of very short wavelength correlations, at length scales that the coarse-grained Hamiltonian was never intended to describe. The only way around this problem, which was first applied to this problem by Wang, is a renormalization procedure in which the sensitivity to monomer scale structure is (if possible) absorbed into the values of a few phenomenological parameters. Wang considered the one-loop prediction for the free energy of a homogeneous polymer blend. He showed that the sensitivity of this quantity to local fluid structure could be absorbed into an appropriate renormalization of the Flory-Huggins interaction parameter. More recently, we showed how to generalize this procedure to obtain unambiguous results for one-loop corrections to both collective and single-chain correlation functions at nonzero wavenumbers, in both polymer blends and diblock copolymer melts.

The development of this renormalization procedure required two insights that were absent from earlier analyses of the one-loop theory in blends:

The first was the realization that the SCF approximation that has proven useful in describing experimental data should not be identified with a simple random-mixing approximation. Prior to Wang’s work, the SCF approximation had often been conceptually identified with a simple mean-field approximation that is obtained from a saddle-point approximation for the underlying functional integral. The resulting mean-field theory ignores all correlations except those arising from the intramolecular connectivity, and is not a useful starting point for describing a dense liquid. Wang was the first to make a clear conceptual distinction between the “bare” interaction parameter $\chi_0$ that appears in this mean-field theory, and an “effective” interaction parameter $\chi_e$ that is implicitly used when experimentalists compare data to SCF and RPA predictions. Wang defined a one-loop approximation for the effective interaction parameter by identifying a contribution to the free energy of a homogeneous liquid that depends sensitively on short-wavelength correlations, but is independent of overall chain lengths, and absorbed this into a redefinition of $\chi$. We later emphasized that this effective SCF interaction parameter could also be defined by considering the
behavior of predicted free energy in the limit of infinitely long chains. Defining SCF parameters by a process of extrapolation to the infinite chain limit takes advantage of the fact that the local correlations in liquids of long polymers depend only weakly on chain length, even in strongly correlated liquids. The difference between the free energy of a system of finite chains and that of a hypothetical reference system of infinite chains is primarily the result of subtle differences in long-wavelength correlations. Only these differences can be adequately described by a coarse-grained model. By treating the interaction free energy of an infinite-chain reference system as an input to the theory (which must be inferred from experimental or simulation data), one can obtain a renormalized theory that makes unambiguous predictions of corrections to SCF phenomenology.

The second new insight was the realization that the one-loop prediction for the structure factor $S(k)$ at nonzero wavenumber $k$ is affected by a renormalization of statistical segment length, as well as of the interaction free energy. The value of the statistical segment length $b$ of a flexible polymer in a dense mixture is generally different than the “bare” value required as an input to a coarse-grained theory. One-loop predictions for the magnitude of this difference are sensitive to short-wavelength correlations. This renormalization of $b$ has no effect upon the predicted value of structure factor $S(k)$ at exactly $k = 0$, and so did not need to be taken into account in Wang’s interpretation of one-loop predictions for $S(k = 0)$. It becomes an unavoidable complication, however, in calculations of single-chain correlations, and in applications to diblock copolymer melts, for which the dominant fluctuations occur at nonzero $k$.

In our previous work, we focused primarily on clarifying the physical reasoning underlying the renormalization procedure, and on demonstrating that it yields a physically consistent interpretation of the one-loop theory. In this work, we present predictions for binary homopolymer blends. Predictions for diblock copolymer melts will be presented elsewhere.
5.1.2 Related Prior Work

The analysis given here has several particularly close antecedents.

Our analysis of the free-energy density of a homogeneous blend and the long wavelength limit of \( S(k = 0) \), which is given in Secs. 5.2 and 5.3, is closely related to that of Wang.\(^6\) The main differences arise from mathematical approximations that Wang introduced in order to an analytic approximation for behavior near the spinodal. We have avoided all approximations other than the one-loop approximation itself, at the cost of some additional numerical analysis. The additional rigor has allowed us to calculate some additional quantities (e.g., the absolute shift in the critical point) and to discuss physical phenomena that remain important far from the spinodal.

Our analysis of corrections to Gaussian chain statistics in blends, given in Section 5.5, is closely related to the recent theoretical analysis of chain statistics in one-component melts by Beckrich, Johner, Semenov, and coworkers (Strasbourg group).\(^67,68\) Like us, but prior to our work, these authors introduced a renormalized statistical segment length, defined by extrapolation to \( N = \infty \), as part of a systematic calculation of small corrections to random-walk statistics. We initially failed to notice the connection to our own work,\(^2\) or to cite their work. These authors presented a beautiful analysis of universal corrections to Gaussian statistics in an incompressible melt at intermediate wavelengths, less than the coil size but greater than a monomer size. They also obtained analytic results for one-loop corrections to the intramolecular correlation function at all wavelengths in melts of equilibrium polymers, with an exponential distribution of chain lengths. Here, we consider single chain correlations in blends, in which chain conformations are influenced by composition fluctuations, using a numerical procedure that allows us to evaluate one-loop predictions for blends of monodisperse homopolymers and (in Chapter 6) for block copolymer melts.

The most important antecedent of both our work and the recent work of the Strasbourg group is the older, larger, and (generally) more sophisticated theoretical literature on correlations in semi-dilute polymer solutions.\(^69\) At a technical level, the closest analog of our approach within this literature seems to be the analysis of monodisperse semi-dilute solutions by Ohta and Nakanishi.\(^70,71\)
5.1.3 Outline

The chapter is organized as follows: Section 5.2 provides a brief review of the renormalized one-loop theory for the free energy density, and of our notation. Section 5.3 presents predictions for corrections to the RPA theory of composition fluctuations. Section 5.4 presents corrections to the binodal curves. Section 5.5 presents predictions for corrections to random walk statistics in polymer blends. Section 5.6 presents comparisons of theoretical predictions to results of published lattice Monte Carlo simulations. Section 5.7 discusses the physical relationship between the one-loop theory for the free energy and RPA theory of correlations. Section 5.8 clarifies the physical origin of some features of the one-loop theory by relating them to corresponding features of the underlying RPA theory.

5.2 Theoretical Formulation

5.2.1 Model and Notation

We consider a coarse-grained model of a binary homopolymer blend. Let $v$ be the average volume per monomer, for either species. Let the volume fraction, degree of polymerization, statistical segment length and packing length for species $i$ be denoted by $\phi_i, N_i, b_i$, and $l_i \equiv v/b_i^2$, respectively, for species $i = 1$ and 2.

Let the potential energy be the sum of an intramolecular potential $U_{\text{chain}}$ and a monomer-monomer pair interaction

$$U_{\text{int}} = \frac{1}{2} \int dr \int dr' U_{ij}(r - r') c_i(r)c_j(r') \ .$$

(5.2.1)

Here, $c_i(r) = \sum_{ms} \delta(\mathbf{r} - \mathbf{R}_{mi}(s))$ is the concentration of monomers of type $i$, in which $\mathbf{R}_{mi}(s)$ is the position of monomer $s$ on molecule $m$ of species $i$. The strength of the pair interaction is taken to be of the form

$$U_{ij}(r - r') = v \left(\begin{array}{cc} B & B + \chi_0 \\ B + \chi_0 & B \end{array}\right) \delta_\Lambda(r - r') \ .$$

(5.2.2)
Section 5.2.1. Model and Notation

Here, $\delta_\Lambda$ is a function $\delta_\Lambda \equiv \Lambda^3 F(\Lambda|\mathbf{r} - \mathbf{r}'|)$ with a range $\Lambda^{-1}$ and an integral $\int d\mathbf{r} \delta_\Lambda = 1$, so that $\delta_\Lambda$ approaches a Dirac $\delta$-function as $\Lambda \to \infty$. $B$ is a dimensionless compression energy and $\chi_0$ is a dimensionless “bare” interaction parameter. The incompressible limit may be obtained by considering the large $B$ limit.

Let

$$S_{ij}(\mathbf{r}) = \langle \delta c_i(\mathbf{r}) \delta c_j(0) \rangle$$  \hspace{1cm} (5.2.3)

where $\delta c_i(\mathbf{r}) = c_i(\mathbf{r}) - \langle c_i \rangle$, and let $S_{ij}(\mathbf{k}) = \int d\mathbf{r} e^{i\mathbf{k} \cdot \mathbf{r}} S_{ij}(\mathbf{r})$ denote the Fourier transform. Let $\Omega_i(\mathbf{k})$ be the intramolecular contribution to $S_{ii}(\mathbf{k})$ from chains of type $i$. A continuous random walk model yields

$$\Omega_i(\mathbf{k}) = \phi_i N g(k^2 R_{g,i}^2)/v$$  \hspace{1cm} (5.2.4)

where $R_{g,i}^2 = N_i b_i^2/6$ is the radius of gyration for species $i$ and $g(x) = 2(e^{-x} - 1 + x)/x^2$ is the Debye function.

Composition fluctuations in an effectively incompressible blend may be described by a scalar correlation function

$$S(k) = S_{11}(k) = S_{22}(k) = -S_{12}(k) \quad .$$  \hspace{1cm} (5.2.5)

Here, we follow Schweizer and Curro and our previous work, by expressing this scalar correlation function in terms of what we (and Wang$^{66}$) refer to as an “apparent” interaction parameter $\chi_a(\mathbf{k})$, by defining

$$S^{-1}(k) = \Omega_1^{-1}(k) + \Omega_2^{-1}(k) - 2v\chi_a(\mathbf{k}) \quad .$$  \hspace{1cm} (5.2.6)

This is, of course, a generalization of the RPA expression for $S(k)$. The usual incompressible RPA is recovered by assuming that chains are random walks and that $\chi_a(\mathbf{k})$ is independent of $k$, $N$, and $\chi N$. 

61
5.2.2 One-loop Free Energy

The Helmholtz free energy $f$ per volume for this coarse-grained model may be expressed, in the incompressible limit, as a sum

$$f = f_{id} + e_{mf} + f_{corr},$$

where

$$f_{id} \equiv \frac{\phi_1}{N_1 v} \ln \phi_1 + \frac{\phi_2}{N_2 v} \ln \phi_2.$$  \hspace{1cm} (5.2.8)

is the ideal Flory-Huggins entropy of mixing, and

$$e_{mf} = \frac{1}{2} \int dr U_{ij}(r) \langle c_i \rangle \langle c_j \rangle = v^{-1} \chi_0 \phi_1 \phi_2$$ \hspace{1cm} (5.2.9)

is a simple mean-field approximation for the interaction energy density. The remainder, denoted $f_{corr}$, is a correlation free energy. Here, and throughout the remainder of this chapter except Section 5.6, where we compare to simulation results, we set $kT = 1$.

The one-loop approximation for $f_{corr}$ has been obtained in previous work by considering a Gaussian approximation for the distribution of fluctuations of a complex chemical potential field within the context of the Edwards auxiliary field formalism. In Section 5.7, we discuss an alternative derivation in which this approximation is instead obtained by thermodynamic integration of the RPA correlation function. However it is obtained, the resulting approximation for $f_{corr}$ is given, in the general case of a compressible liquid, by a Fourier integral

$$f_{corr} = \frac{1}{2} \int_q \ln \left| \det \left[ \mathbf{I} + \mathbf{\Omega}(q) \mathbf{U}(q) \right] \right|$$ \hspace{1cm} (5.2.10)

Here, the bold faced symbols $\mathbf{\Omega}(q)$ and $\mathbf{U}(k)$ indicate $2 \times 2$ matrices with elements $\delta_{ij} \Omega_i(q)$ and $U_{ij}(q)$, respectively, $\mathbf{I}$ denotes the identity, and $\det \left| \cdots \right|$ is a determinant. Here and hereafter, we use the shorthand $\int_q \equiv \int d^3q/(2\pi)^3$ for Fourier integrals.
Section 5.2.3. Divergence and Renormalization

In the nearly-incompressible limit of interest here, Eq. (5.2.10) for $f_{\text{corr}}$ may be approximately reduced to

$$f_{\text{corr}} = \frac{1}{2} \int_{\mathbf{q}} \ln \left[ \left( \Omega_{1} + \Omega_{2} - 2\chi_{0}v\Omega_{1}\Omega_{2} \right) v \right].$$  \hfill (5.2.11)

To obtain the integrand of Eq. (5.2.11), in a model with a pair interaction of the form given in Eq. (5.2.2), we have taken the limit $B \gg 1$ in Eq. (5.2.10), and also replaced the Fourier transform of $\delta_{\Lambda}$ by unity. This yields an expression for the integrand that is valid for $|\mathbf{q}| \ll \Lambda$. In what follows, we regularize the one-loop approximation for $f_{\text{corr}}$ by treating $\Lambda$ as a cutoff wavenumber, and simply restricting the integral in Eq. (5.2.11) to $|\mathbf{q}| < \Lambda$. This is equivalent to the use of a pair potential in which the Fourier transform of $\delta_{\Lambda}(\mathbf{r} - \mathbf{r}')$ is taken to be unity for $\mathbf{q} < \Lambda$, and zero for $\mathbf{q} > \Lambda$. The purpose of the renormalization procedure discussed below is to extract predictions that are independent of such details of our treatment of short-wavelength correlations.

5.2.3 Divergence and Renormalization

It has long been known that, in a model of continuous Gaussian chains, the idealized limit $\Lambda \rightarrow \infty$ of point-like interactions yields a one-loop expression for $f_{\text{corr}}$ that diverges as the cube of $\Lambda$.\textsuperscript{60–62,66} In previous work, both Wang\textsuperscript{66} and we\textsuperscript{2} have analyzed the structure of the high-$q$ divergence of this free energy density, and its physical significance. We found that Eq. (5.2.11) for $f_{\text{corr}}$ can be expressed as a sum

$$f_{\text{corr}} = f_{\text{corr}}^{\Lambda} + f^{*}$$  \hfill (5.2.12)

of an “ultra-violet” (UV) divergent contribution $f_{\text{corr}}^{\Lambda}$, which increases with increasing $\Lambda$, and a contribution $f^{*}$ that is independent of $\Lambda$. The UV divergent contribution $f_{\text{corr}}^{\Lambda}$ may be expressed as a sum\textsuperscript{2}

$$f_{\text{corr}}^{\Lambda} = f_{\text{bulk}}^{\Lambda} + f_{\text{end}}^{\Lambda}$$  \hfill (5.2.13)
Section 5.2.3. Divergence and Renormalization

where

\[ f_\text{bulk}^\Lambda = \frac{1}{12\pi^2} \left[ \ln \left( \frac{12l}{v\Lambda^2} \right) + \frac{2}{3} \right] \Lambda^3 - \frac{6\chi_0}{\pi^2v} \frac{L}{l} \phi_1\phi_2\Lambda \]

\[ f_\text{end}^\Lambda = -\frac{3}{2\pi^2v} \left( \frac{\phi_1l_1^2}{N_1} + \frac{\phi_2l_2^2}{N_2} \right) \Lambda. \]  

(5.2.14)

and where \( \bar{l} \equiv \phi_1l_1 + \phi_2l_2 \). The contribution \( f_\text{end}^\Lambda \), which is proportional to \( 1/N \), was identified\(^2\) as an excess free energy for chain ends. The quantity \( f_\text{bulk}^\Lambda \), which is independent of \( N \), is instead a correction to the “bulk” interaction free energy density of a hypothetical reference system of infinitely long chains.

To remove the explicit cutoff dependence, we re-interpret the one-loop free energy as a sum

\[ f = f_{id} + f_{int} + f_\text{end}^\Lambda + f^* \]  

(5.2.15)

in which

\[ f_{int} \equiv e_{mf} + f_\text{bulk}^\Lambda \]  

(5.2.16)

is identified as the interaction free energy of the relevant form of SCFT. The contribution \( f_\text{end}^\Lambda \) is a non-universal chain end contribution that could (and generally should) be added to SCFT, to reflect the fact that the fluid structure is perturbed in the immediate vicinity of any chain end. The remaining cutoff-independent contribution \( f^* \) is a universal correction to SCF phenomenology.

Eq. (5.2.16) for \( f_{int} \) simplifies considerably in the case of structurally symmetric polymers, with \( l_1 = l_2 = l \). In this case, \( f_{int} \) is given to within a composition-independent constant by a function of the form

\[ f_{int} = v^{-1}\chi_e(\Lambda)\phi_1\phi_2. \]  

(5.2.17)

where

\[ \chi_e(\Lambda) = \left[ 1 - \frac{6}{\pi^2}\Lambda \right] \chi_0 \]  

(5.2.18)

is an effective Flory-Huggins interaction parameter. This UV divergent expression for \( \chi_e \) was first obtained by Olvera de la Cruz et al.\(^60\). The physical origin of the UV
Section 5.2.3. Divergence and Renormalization

divergence of this quantity is discussed in Section 5.8.

We focus in the remainder of this chapter on the UV convergent correction $f^*$. It is convenient to introduce a notation for $f^*$ and related quantities, in which we use $\int_q^* A(q)$ to denote a renormalized Fourier integral. The renormalized Fourier integral of an integrand $A(q)$ is defined by a difference

$$\int_q^* A(q) \equiv \int_q A(q) - \int_q^\Lambda A(q) \tag{5.2.19}$$

between the unrenormalized integral $\int_q A(q)$ and the UV divergent part of the integral, denoted by $\int_q^\Lambda A(q)$. In a theory of continuous chains, the “UV divergent” part of Fourier integral is obtained by constructing a high-$q$ asymptotic expansion of the integrand, in decreasing powers of $qR$, and retaining only those terms in the expansion that lead to a UV divergent integral.\(^2\)

In this notation,

$$f^* = \frac{1}{2} \int_q^* \ln \left[ (\Omega_1 + \Omega_2 - 2v\chi\Omega_1\Omega_2) v \right]. \tag{5.2.20}$$

The $N$-dependence of $f^*$ may be isolated by non-dimensionalizing the renormalized integral in terms of a reference length $R$, which we take to be the root-mean-squared radius of gyration $R = R_{g1}$ of species 1. It may then be shown that all of the quantities in the integrand can be expressed as functions of $qR$ and of a set of dimensionless parameters $\phi_1, \chi N, N_2/N_1, R_2/R_1$. By doing so, we find that $f^*$ may be expressed as a function of the form

$$f^* = \frac{1}{R^3} \hat{f}^*(\chi N, \phi_1, N_2/N_1, R_2/R_1) \tag{5.2.21}$$

in which $\hat{f}^*$ is a dimensionless function given by the value of the non-dimensionalized renormalized integral. The required set of dimensionless parameters is the same as that required by the standard non-dimensionalized SCFT for an incompressible blend. Note that, in Eqs. (5.2.20) and (5.2.21), we have written $f^*$ as a function of a parameter $\chi N$, but have not specified whether by $\chi$ we mean $\chi_0$, $\chi_c$, or (perhaps)
Section 5.2.4. Structure Function

the low-$q$ limit of $\chi_a$. In fact, different choices lead to different variants of the theory, as discussed in more detail below.

Results for $f^*$ and related quantities that are reported here have all been obtained by numerically evaluating the relevant renormalized Fourier integrals. To do this, for each quantity of interest, we first numerically evaluate the unrenormalized integral with a large but finite cutoff $|q| < \Lambda$, then subtract an analytic result for the UV divergent part of the regularized integral. The Fourier integrals required as inputs to the one-loop theory may all be expressed as either one dimensional integrals with respect to a wavenumber $q$ (for free energy density and its derivatives) or two-dimensional integrals with respect to $q$ and a polar angle $\theta$ (for correlation functions at nonzero wavenumber). Subtraction of the UV divergent part from an unrenormalized integral yields an estimate of the renormalized integral that depends only weakly on the numerical cutoff $\Lambda$. Our final result for the value of a renormalized integral is obtained by repeating this procedure for several values of $\Lambda R \gg 1$, and numerically extrapolating to $\Lambda = \infty$.

5.2.4 Structure Function

The long-wavelength limit of $S(k)$ is related to the composition dependence of the free energy density $f$ by a statistical mechanical theorem:

$$\lim_{k \to 0} S^{-1}(k) = v^2 \frac{\partial^2 f}{\partial \phi^2_1} . \quad (5.2.22)$$

The quantity $S^{-1}(0)$ is also related to the long-wavelength limit of $\chi_a(k)$ by

$$\lim_{k \to 0} S^{-1}(k) = 2v(\chi_s - \chi_a) . \quad (5.2.23)$$

Here, and hereafter, we use $\chi_a$ to denote the $q \to 0$ limit of the quantity $\chi_a(k)$ defined in Eq. (5.2.6). The quantity $\chi_s$ is the spinodal value of $\chi_a$, given by

$$2\chi_s \equiv v \frac{\partial^2 f_{id}}{\partial \phi^2_1} = \frac{1}{N_1 \phi_1} + \frac{1}{N_2 \phi_2} . \quad (5.2.24)$$

66
Section 5.2.4. Structure Function

Using decomposition (5.2.15) for $f$, and hereafter neglecting the explicit end effects, the one-loop approximation for $\chi_a$ may be expressed as a sum

$$\chi_a = \chi_e + \chi^*, \quad (5.2.25)$$

in which

$$\chi_e \equiv -\frac{v}{2} \frac{\partial^2 f_{\text{int}}}{\partial \phi_1^2} \quad (5.2.26)$$

is the interaction parameter of phenomenological SCFT, and

$$\chi^* = -\frac{v}{2} \frac{\partial f^*}{\partial \phi_1^2} \quad (5.2.27)$$

is a correction to SCFT arising from long-wavelength fluctuations.

An explicit Fourier integral expression for $\chi^*$ may be obtained by differentiating the integrand of Eq. (5.2.20) for $f^*$ twice with respect to $\phi_1$. The resulting approximation for $\chi^*$ may be expressed in terms of either Edwards’ screened interaction$^2$ or in terms of the correlation function

$$S^{-1}(k; \chi) = \Omega_1^{-1}(k) + \Omega_2^{-1}(k) - 2v\chi \quad . \quad (5.2.28)$$

When expressed in terms of $S(k)$, it is found that

$$\chi^* = \frac{v}{4} \int_q^* \left[ \mu(q)S^2(q; \chi) - \lambda(q)S(q; \chi) + \eta \right] \quad (5.2.29)$$

where

$$\mu(q) = \frac{1}{\phi_1 \Omega_1(q)} - \frac{1}{\phi_2 \Omega_2(q)}$$

$$\lambda(q) = -2 \left( \frac{1}{\phi_1^2 \Omega_1(q)} + \frac{1}{\phi_2^2 \Omega_2(q)} \right)$$

$$\eta = 1/\phi_1^2 + 1/\phi_2^2. \quad (5.2.30)$$

The quantities $\mu(0)$ and $\lambda(0)$ are proportional to the third and fourth derivatives of
Section 5.2.4. Structure Function

$f_{id}(\phi_1)$ with respect to $\phi_1$, respectively. Since $\mu(q), \lambda(q)$ and $\eta$ are independent of $\chi$, the proximity to the spinodal in this expression is controlled by $S(q)$ alone.

By non-dimensionalizing the integral in Eq. (5.2.29), we may show that it yields a correction to $N\chi_a$ of the form

$$N\chi^* = \frac{1}{N^{1/2}} \tilde{\chi}^*(\chi N, \phi_1, N_2/N_1, R_{g2}/R_{g1})$$, \hspace{1cm} (5.2.31)

in which $\tilde{\chi}^*$ is a non-dimensional function that is defined by the non-dimensionalized integral. Here,

$$\tilde{N} \equiv Nb^6/v^2$$ \hspace{1cm} (5.2.32)

is an invariant degree of polymerization, in which (by convention) $N = N_1$ and $b = b_1$.

In Eqs. (5.2.20), (5.2.21), and (5.2.31), we have intentionally expressed $f^*$ and $\chi^*$ as functions of an interaction parameter $\chi$, without specifying whether this input parameter should be taken to be the bare parameter $\chi_0$ or some type of a renormalized value. In fact, different variants of the renormalized one-loop theory can be obtained by different choices for the interaction parameter used within these Fourier integrals. If we define $f^*$ by simply subtracting the UV divergent part of the one-loop expression for $f_{corr}$, we obtain a theory that is no longer UV divergent, but that retains an explicit dependence upon the unmeasurable “bare” parameter $\chi_0$. Following the logic used to construct renormalized expansions of field theories, however, we may also replace $\chi_0$ by a renormalized parameter within each integrand to obtain a theory from which all reference to the bare parameter have been removed. This substitution may be formally justified, within the context of a one-loop approximation, by observing that the difference between approximations obtained by using a bare or renormalized parameter in the one-loop theory differ only at second order in a systematic loop expansion.

In the remainder of this chapter, we follow Wang\textsuperscript{66} by considering a self-consistent one-loop approximation. In this approximation, also known as a “Hartree” approximation, $\chi$ is replaced within the Fourier integral expression for $\chi^*$ by $\chi_a \equiv \chi_a(q = 0)$. 

68
In the resulting theory, $\chi_a$ is given by a function of the form

$$\chi_a = \chi_e + \chi^*(\phi_1, \chi_a).$$

(5.2.33)

Here, $\chi_e$ is related to the SCF (i.e., $N \to \infty$) interaction free energy $f_{\text{int}}(\phi)$ by Eq. (5.2.26). For purposes of numerical evaluation, it is convenient to rewrite Eq. (5.2.33) as an explicit expression $\chi_e = \chi_a - \chi^*(\phi_1, \chi_a)$ for $\chi_e$ as an explicit function of $\chi_a$.

5.3 Collective Fluctuations

5.3.1 Symmetric Blends, Critical Composition

Figs. 5.1 displays predictions of the renormalized Hartree theory for $\chi_a$ in blends of structurally symmetric polymers ($b = b_1 = b_2$ and $N = N_1 = N_2$) at their critical composition ($\phi_1 = 1/2$). It shows predictions for $\chi_a N$ as a function of $\chi_e N$ in blends with three different chain lengths, corresponding to $N = 64, 128, \text{ and } 512$. The difference between $\chi_a N$ from $\chi_e N$ is largest for the shortest chains, and vanishes in the limit $N \to \infty$. The SCF predicts a critical point for a symmetric $\chi_e N = 2$. The actual critical point for such a blend is reached when $\chi_a N = 2$.

Figure 5.2 shows the underlying dimensionless function $\hat{\chi}^* \equiv (\chi_a N - \chi_e N)\sqrt{N}$ as a function of $\chi_a N$. Note that both $\chi_a$ and $\chi^*$ vanish in the limit $\chi_e = 0$ for any structurally symmetric mixture, with $b_1 = b_2$ and $N_1 = N_2$, because this is an exact result for such a ideal mixture, in which the two species are physically indistinguishable.

Notably, the dependence of $\chi^*$ upon $\chi_a N$ is not monotonic: for small values of $\chi_a N$, the deviation $\chi^* = \chi_a - \chi_e$ is positive and increases with increasing $\chi_a$. Closer to the critical point, $\chi^*$ begins to decrease with increasing $\chi_a N$, changes sign at $\chi_a N \simeq 1.7$, and is negative at the critical point. Note that all the curves in Figure (5.1) intersect at $\chi_a N = \chi_e N \simeq 1.7$, where $\chi^* = 0$. For any structurally symmetric
Figure 5.1: Self-consistently calculated $\chi_a N$ versus $\chi_e N$ for symmetric binary blends with $\phi_1 = 1/2$ for $\bar{N} = 64, 128, 512$ respectively (solid lines). The dotted line shows where $N\chi_a = N\chi_e$, which corresponds to the limit $\bar{N} \to \infty$. Solid dots along the line $\chi_a N = 2$ indicate critical points for finite chains.

blend, with $b_1 = b_2$ and $N_1 = N_2$, we find that the initial slope is

$$\lim_{\chi_a N \to 0} \frac{\partial (\chi^* N)}{\partial (\chi_a N)} = \frac{(6/\pi)^{3/2}}{\bar{N}^{1/2}}, \quad (5.3.1)$$

for any composition.

At the critical point of such a blend ($\phi_1 = 1/2$ and $\chi_a N = 2$), the one-loop prediction for $\chi^* N$ approaches a negative limiting value

$$\lim_{\chi_a N \to 2} \chi^* N = -3.7\bar{N}^{-1/2}, \quad (5.3.2)$$

with a slope that diverges at the critical point. In the Hartree approximation, this yields a predicted critical value of

$$(\chi_e N)_c = 2 + 3.7\bar{N}^{-1/2}. \quad (5.3.3)$$
Figure 5.2: The deviation $\bar{N}^{1/2}N(\chi_a - \chi_e)$ as a function of $\chi a N$ for symmetric binary blends at the critical composition, $\phi_1 = 1/2$.

If $\chi_e$ is a decreasing function of temperature, this corresponds to a depression in the critical temperature $T_c$ by an amount $\delta T_c \propto N^{-1/2}$.

The predicted decrease in $\chi^*$ near the critical point is not surprising: near the critical point, long wavelength correlations decrease the level of local mixing between $A$ and $B$ monomers, thereby decreasing the apparent interaction parameter $\chi_a$ and stabilizing the homogeneous phase.

The origin of the positive values obtained for $\chi^*$ at small values of $\chi_a$ is less obvious. In Section 5.8 of this chapter we show that this prediction is the result of a subtle dependence of local correlations in a polymer liquid upon overall chain length, which is discussed in much greater detail in reference 73. In a dense liquid of long polymers, the immediate vicinity of each monomer is crowded with monomers that belong to the same chain. This intramolecular “self-concentration” reduces the space available for monomers from other chains, creating a so-called correlation hole in the intermolecular correlation function. In a mixture, the correlation hole reduces the magnitude of the potential energy of interaction between monomers of types 1 and 2. It was shown in the reference 73 that the depth of the correlation hole decreases slightly
with decreasing chain length. Far from the spinodal, this simple packing effect causes $\chi_a$ to increase with decreasing chain length, reflecting the fact that shorter chains are less strongly shielded from intermolecular contacts. Because we define $\chi_e$ to be the limiting value of $\chi_a$ in the limit of infinitely long chains, this effect makes a positive contribution to the difference $\chi_a(N) - \chi_e$ for any finite $N$. In reference, this effect was analyzed without reference to the one-loop theory, and the prefactor in Eq. (5.3.1) is derived by very different reasoning than that used here.

A shift in the critical temperature by an amount $\delta T_c \propto \bar{N}^{-1/2}$ was predicted previously by Holyst and Vilgis. The one-loop theory of Holyst and Vilgis did not use a systematic renormalization procedure, but instead introduced an *ad hoc* cutoff $\Lambda \sim 1/R$ to avoid the UV divergence. This approach captures the correct scaling, but does not allow a meaningful calculation of numerical values for one-loop corrections, because it yields corrections whose values are sensitive to the exact numerical value chosen for an arbitrary cutoff length.

### 5.3.2 Vicinity of the Spinodal

We now discuss the behavior of the Hartree theory near the spinodal. This part of our analysis is similar to that given by Wang, who focused on behavior near the spinodal, but who made several approximations that we avoid.

A rigorous asymptotic expansion of the behavior of $\chi_a$ near the spinodal may be obtained by expanding $S(q; \chi_a)$, $\mu(q)$ and $\lambda(q)$ in Eq. (5.2.29) around their values at $q = 0$ and $\chi_a = \chi_s$. Let

$$
\begin{align*}
    r &= 2(\chi_s - \chi_a) \\
    \tau &= 2(\chi_s - \chi_e).
\end{align*}
$$

(5.3.4)

The required asymptotic expansion of $S(q)$ is

$$
S^{-1}(q) \simeq r + q^2 \xi_s^2.
$$

(5.3.5)
Section 5.3.2. Vicinity of the Spinodal

where

$$\xi_0^2 \equiv v \bar{l} / (18 \phi_1 \phi_2 l_1 l_2) .$$  \hspace{1cm} (5.3.6)

By also expanding $\mu(q)$ and $\lambda(q)$ around $q = 0$, we obtain an asymptotic expansion of the form

$$r = \tau + \frac{v}{\xi_0^2 N^{3/2}} \left[ \frac{A}{\sqrt{N} r} + B + C \sqrt{N} r + \cdots \right]$$  \hspace{1cm} (5.3.7)

where $A$, $B$, and $C$ are dimensionless coefficients that are independent of $r$, but that depend upon $\phi_1$, $N_2/N_1$, and $R_2/R_1$. Here, $N$ is an arbitrary choice of a reference degree of polymerization, which could be taken to be $N_1$ or $N_2$ or an appropriate average of the two.

The coefficients $A$ and $C$ in this expansion can be calculated analytically, by considering the singular behavior of the integral near $q = 0$ as $r \to 0$. The coefficient $A$ is given by

$$A(\phi_1) = \frac{-N^2}{16 \pi \nu^2} \mu^2(0)$$

$$= -\frac{N^2}{32 \pi} \left( \frac{1}{\phi_1^2 N_1} - \frac{1}{\phi_2^2 N_2} \right)^2 .$$  \hspace{1cm} (5.3.8)

Here, $\mu(q = 0)$ is the third derivative with respect to $\phi_1$ of the ideal mixture free energy per monomer $v f_{1d}(\phi_1)$. This quantity vanishes at the Flory-Huggins critical composition, at which $\phi_1^2 N_1 = \phi_2^2 N_2$, and so (as noted by Wang$^{66}$) $A(\phi_1)$ also vanishes at the critical composition $\phi_{1c}$. At the critical composition, we find

$$C(\phi_{1c}) = \frac{-1}{4 \pi \phi_{1c}^2 \phi_{2c}^2} \frac{N}{\sqrt{N_1 N_2}} .$$  \hspace{1cm} (5.3.9)

These expressions for $A$ and $C$ agree with corresponding results of Wang.$^{66}$

In the Hartree approximation, the value $\tau_c$ of $\tau$ (the reduced “temperature”) at the critical point is determined by the value of the constant $B$ at the critical composition: The critical point occurs when $r = 0$ at $\phi_1 = \phi_{1c}$, or when

$$\tau_c = -v B(\phi_{1c}) \xi_0^{-3} N^{-3/2} .$$  \hspace{1cm} (5.3.10)
Section 5.3.2. Vicinity of the Spinodal

If $B$ is nonzero, an expansion of this form thus yields a shift in the critical value of $\chi_eN$ of order $\bar{N}^{-1/2}$.

The coefficient $B$ cannot be obtained from an asymptotic analysis of the low-$q$ behavior of the integral in the Eq. (5.2.29). To understand why, recall that the problem actually involves three length scales: the monomer size (or cutoff length $\Lambda^{-1}$), the coil size $R \propto \sqrt{N}$, and correlation length $\xi = \xi_0/\sqrt{r}$. Very near the spinodal, $\xi \gg R$. Our renormalization procedure removes all dependence on $\Lambda^{-1}$, but leaves a dependence on both $R$ and $\xi$. Away from the critical composition, the integral in Eq. (5.2.29) develops an infra-red (IR) divergence of the form $A/\sqrt{r}$ as $r \to 0$. This divergence is the result of fluctuations with wavenumbers $q \sim \xi^{-1}$, and so its prefactor can be obtained by considering the behavior of the integrand near $q = 0$. At the critical composition, the coefficient $C$ can be isolated by considering the IR divergence of the derivative of Eq. (5.2.29) for $\chi^*$ with respect to $\chi_a$, which then diverges as $r^{-1/2}$. The actual value of $\chi^*$, however, converges even at the critical point, and is dominated by fluctuations with $qR \sim 1$. As a result, the one-loop prediction for the shift in the critical point can only be calculated by numerically evaluating the renormalized integral, as done here, without introducing approximations for $\Omega_1(q)$ and $\Omega_2(q)$ that are valid only for $qR \ll 1$.

At the critical composition, the asymptotic expansion of the Hartree theory may be expressed more compactly as a sum

$$Nr = N\delta\tau + \frac{Cv}{\xi_0^{3/2}\bar{N}^{1/2}}\sqrt{Nr}$$

(5.3.11)

where $\delta\tau \equiv \tau - \tau_c$, with $C < 0$. The theory exhibits strongly non-classical critical behavior for values of $\delta\tau$ less than a crossover value $\delta\tau^*$. Approximating $\delta\tau^*$ by the value at which the $\sqrt{r}$ fluctuation correction is equal to $\delta\tau$ yields a reduced crossover temperature

$$N\delta\tau^* \sim \bar{N}^{-1}$$

(5.3.12)

as first noted by de Gennes$^{74}$. As noted by Holyst and Vilgis,$^{63}$ the predicted $O(1/N)$ width of the critical region is thus much less than the predicted $O(\bar{N}^{-1/2})$ magnitude of the shift of the critical temperature from its SCF value.
Section 5.3.3. Off-Critical Blends

Very close to the critical point, $\tau \ll \tau_c + \delta \tau^*$, the Hartree theory yields $r \propto \tau^2$, or $S(q = 0) \propto \tau^{-2}$. The predicted critical exponent of $\gamma = 2$ is much larger than the known Ising critical exponent of $\gamma \approx 1.26$. This is a well known defect of the Hartree theory.

Using the low $\chi$ asymptotics, $\bar{N}^{1/2} \delta \chi N \approx h_0(x) = (6/\pi)^{3/2} \chi N$, and the high $\chi$ one discussed in this section, $N^{1/2} \delta \chi N \approx h_0(x) = (6/\pi)^{3/2} \chi N \approx h_1(x) = -3.71 + 27(2 - \chi N)^{1/2}/\pi$, and introducing the appropriate weight, we found the following functional form can fit the curve shown in Figure 5.2 adequately:

$$h_0(x) (1 - \chi N/2)^{m_1} + (h_1(x) - m_2(2 - \chi N)) (\chi N/2)^{m_3}$$

with $m_1 = 1.30$, $m_2 = 3.86$, $m_3 = 1.30$.

5.3.3 Off-Critical Blends

At any composition except the critical composition, the Hartree theory considered here does not have a spinodal: at off-critical compositions, because $\chi^*$ diverges like $r^{-1/2}$ with decreasing $r$, there is no value of $\tau$ for which $r = 0$. As noted by Wang, in the Hartree approximation, this causes $\chi_e$ to become a non-monotonic function of $\chi_a$ or (equivalently) $\chi_a$ to become a multi-valued function $\chi_e$. An example of this behavior is shown in Figure 5.3, which shows predictions of renormalized Hartree theory for $\chi_a$ vs. $\chi_e$ in a series of off-critical blends of various compositions with $b_1 = b_2$, $N_1 = N_2$, and $\bar{N} = 4000$. Wang referred to the turning point at which $\chi_e$ reaches its maximum value, which is also where $S(q = 0)$ is maximum, as a “pseudo-spinodal”. The appearance of a pseudo-spinodal is a symptom of the inadequacy of a Hartree theory of equilibrium fluctuations. Wang also noted, however, that this pseudo-spinodal corresponds to a point at which the barrier to nucleation is a few times $k_B T$, and may thus have some dynamical significance.
Section 5.4. Coexistence Curve

We present results on the miscibility of symmetric binary blends obtained with the one-loop theory corrected free energy. We computed coexistence (binodal) curves for various chain length, in the region far away from the mean field spinodal, using Eq.(5.2.7). The first two terms $f_0$ and $\delta f^λ$ of Eq.(5.2.7) are combined and replaced with the normal Flory-Huggins expression, Eq.(5.2.8), in which $\chi_0$ is replaced with the $\chi_e$. $\delta f^*$ is interpreted as the meaningful one-loop correction.

The coexisting curves for $\bar{N} = 466$, $1176$, $2126$ and $\infty$, and the mean field spinodal curve (dashed) computed from the Flory-Huggins free energy alone are shown in Figure 5.4. All binodal curves except the $\bar{N} = \infty$ one are outside the Ginzburg region around the spinodal. The prediction for the finite chains is different from that of the infinite chain in two qualitatively distinct ways. In the region with nearly symmetric compositions and close to the spinodal, the stability of the miscible blend is increased.

Figure 5.3: Self-consistently computed $\chi_a$ versus $\chi_e$ for off-critical blends with $b_1 = b_2$ and $N_1 = N_2$ and $\bar{N} = 4000$ at various values of $\phi = \phi_1$. Both axes are rescaled by the spinodal value $\chi_s$. Note that the spinodal line $\chi_a/\chi_s = 1$ is actually reached only at the critical composition of $\phi_1 = 1/2$. The computed locus of turning points is depicted with dashed line.

5.4 Coexistence Curve
Section 5.4. Coexistence Curve

Figure 5.4: Coexisting curves calculated from the one-loop theory corrected free energy $\bar{N} = 466, 1176, 2126$ and $\infty$ (Flory-Huggins prediction). All curves intersect at a common composition $\phi \simeq 0.71$. The dashed line is the mean field spinodal.

by the fluctuation correction, such that the value of $\chi_e N$ needed to induce the phase separation is increased. On the other hand, in the region where the compositional asymmetry is large and the binodal curve is far away from the spinodal, the correction is dominated by the correlation hole effect, which, for finite chains, tends to increase the inter-chain contacts and as a result increase the interaction energy. Thus the miscible blend is destabilized and the value of $\chi_e N$ on the binodal curve becomes smaller. Consequently the shape of the one-loop theory corrected binodal curves become flatter and broader as compared to the mean field one, and they intersect the mean field curve at an intermediate composition (around 0.7 or 0.3). The departure from the mean field curve increases as $\bar{N}$ decreases. But they all intersect at the same composition, a generic feature of the one-loop theory.

Since $\chi_a$ is the experimentally probed $\chi$ parameter, the shape of the one-loop theory corrected coexisting curve also implies that the ratio $\chi_a/\chi_e$ (small for symmetric compositions but large for asymmetric ones) as determined from phase separation measurements as a function of blending composition will display the parabolic shape.
5.5 Single Chain Properties

The one-loop theory\(^2,75\) also predicts slight deviations from random-walk statistics for individual chains. The one-loop approximation for the intramolecular correlations function is a form of renormalized perturbation theory in which each pair of monomers on a chain interact via Edwards’ screened interaction, and in which the effect of this interaction is taken into account to first order in powers of the strength of the screened interaction.\(^76\)

We consider the single-chain correlation function \(\omega_i(k)\). This is given for a Gaussian homopolymer by

\[
\omega_i(k) = N^2 g(k^2 R_{g,i}^2),
\]

(5.5.1)

where \(R_{g,i} = \sqrt{N_i b_i^2/6}\) is the radius of gyration of species \(i\) and \(g(x) = 2(e^{-x} - 1 + x)/x^2\) is the Debye function. The one-loop correction to \(\omega_i(k)\) in a homopolymer blend is given by\(^2,75\)

\[
\delta \omega_i(k) = -\frac{1}{2} \int dq \, \psi_i^{(4)}(k, -k, q, -q) G_{ii}(q). \tag{5.5.2}
\]

Here, \(G_{ii}(q)\) is the screened interaction between any two \(i\) monomers, which is given in an incompressible blend at wavelengths \(q \ll \Lambda\) by

\[
G_{ii} = \frac{1 - 2v\chi_1 \Omega_1 \Omega_2 \Omega_i^{-1}}{\Omega_1 + \Omega_2 - 2v\chi_1 \Omega_1 \Omega_2}. \tag{5.5.3}
\]

The function \(\psi_i^{(4)} = \psi_i^{(4)}(k, -k, q, -q)\) is given by

\[
\psi_i^{(4)} = \omega_i^{(4)}(k, -k, q, -q) - \omega_i(k) \omega_i(q),
\]

where \(\omega_i^{(4)}\) is the 4-point intramolecular correlation function for an ideal Gaussian chain.\(^2\) It is straightforward to verify that \(\delta \omega_i(k)\) vanishes in the limit \(k = 0\), as required to retain consistency with the exact result \(\omega_i(0) = N_i^2\).

If the high-\(q\) behavior of the above integral is regularized by introducing a sharp
Section 5.5.1. Monodisperse Melt

cutoff at \( q = \Lambda \), and using Eq. (5.5.3) for all \( q < \Lambda \), the resulting integral is found to increase linearly with \( \Lambda \) as \( \Lambda \) is increased. We\(^2\) and Beckrich \textit{et al.}\(^{67}\) have shown, however, that this UV divergence can be absorbed into the renormalization of statistical segment length. After this UV divergent part is subtracted, the remaining UV convergent correction, which we will call \( \delta \omega_i^*(k) \), may be used to characterize the deviation from random-walk statistics. More precisely, \( \delta \omega_i^*(k) \) is the deviation of the intramolecular correlation function \( \omega_i(k) \) from that of a Gaussian chain with a renormalized statistical segment length \( b_{\infty,i} \) characteristic of a dense one-component liquid of infinitely long chains. The correction \( \delta \omega_i^*(k) \) is found to be smaller than \( \omega_i(k) \) by a factor proportional to \( \bar{N}^{-1/2} \), and exhibits a nontrivial dependence on \( k \).

The fractional deviation of the polymer radius gyration is given (appendix B.1) by

\[
\frac{\delta R_g^2}{R_g^2} = -\frac{3}{N_i^2 b_{\infty,i}^2} \lim_{k \to 0} \frac{\partial \delta \omega_i(k)}{\partial (k^2)}. \quad (5.5.4)
\]

where \( R_g^2 \equiv N_i b_{\infty,i}^2 / 6 \) is the prediction for a Gaussian chain with statistical segment length \( b_{\infty,i} \). This fractional deviation is proportional to \( \bar{N}^{-1/2} \).

### 5.5.1 Monodisperse Melt

We first consider the case of a monodisperse one-component melt, which we obtain by setting \( \phi_2 = 0 \). The one-loop approximation used here reduces in the case of one-component liquids to that investigated by Semenov \textit{et al.}\(^{67,68,77,78}\) The only difference in our treatment of this case is our use of a numerical integration and renormalization procedure to obtain accurate results for monodisperse polymers.

Figure 5.5 shows the predicted correction to the single chain correlation function in a monodisperse melt. From the low \( k \) behavior (see appendix B.1) we find that the predicted fractional change of the radius of gyration is

\[
\frac{\delta R_g^2}{R_g^2} = -\frac{1.42}{\sqrt{N}}. \quad (5.5.5)
\]

We thus predict a contraction of finite chains, relative to a hypothetical Gaussian.
Section 5.5.2. Bidisperse Melt

chain with a statistical segment length $b_\infty$, in agreement with the conclusions of references\textsuperscript{68} (Eq. (20)).

![Graph showing predicted correction to the single chain correlation function (Debye function).](image)

Figure 5.5: Predicted correction to the single chain correlation function (Debye function).

5.5.2 Bidisperse Melt

We next consider the behavior of a trace concentration of a species of chains of length $N_1$ in a matrix of chemically homologous shorter chains of length $N_2$. This limit is obtained by calculating the limit $\phi_1 \to 0$ of $\delta \omega_1(q)$. To represent chemically similar species, we set $l_1 = l_2$ and $\chi_e = 0$. This case reduces to that of a monodisperse melt when $N_2 = N_1$, and to a dilute solution of polymer in oligomeric solvent when $N_2 \ll N_1$.

In the previous subsection, we noted that the size of a single chain in the pure melt is smaller than the unperturbed value. It is also well known that a single chain will swell when dissolved in a liquid of chemically similar oligomers, which provides a good solvent. In Figure (5.6), we show one-loop predictions for the fractional change of the radius of gyration of a test chain of length $N_1$ in a matrix of chains of length $N_2 \leq N_1$. The change is indeed negative for $N_2 = N_1$, and becomes positive for $N_2 \ll N_1$, passing through zero at $N_2/N_1 \simeq 0.17$. 

80
Section 5.5.2. Bidisperse Melt

Figure 5.6: The fractional change of the radius of gyration of an isolated chain of length \(N_1\) in a matrix of short chains of length \(N_2\), rescaled with \(\bar{N}_1^{1/2}\).

The limit \(N_2 \ll N_1\) corresponds to a polymer solution in a good small-molecule solvent. The curve in Figure 5.6 diverges as \(0.31N_1/N_2\) in this limit (appendix B.1). Also in this limit, where the matrix chains are point-like, Eq. (5.5.3) for the screened interaction between a pair of monomers on a longer chain reduces to a constant \(G_{11}(q) = v/N_2\). Recall that the definition of a “monomer” in an incompressible coarse-grained theory is simply the length of a chain that occupies an arbitrary reference volume \(v\). If, to simplify notation, the reference volume is taken to be equal to the excluded volume of a solvent \((i.e.,\) matrix\) molecule, thus setting \(N_2 = 1\), we obtain an interaction \(G_{11}(q) = v\) characterized by an excluded volume parameter equal to the solvent volume. Predictions of the theory in this limit are thus identical to those obtained in the first order perturbation theory for a single chain with a point-like interactions \(v\delta(r)\).\(^79\) It is straightforward to show that this perturbative result is consistent with the prediction\(^80\) that the longer chain will undergo substantial expansion if \(N_2 \ll \sqrt{N_1}\), signalling a breakdown of first order perturbation theory.
5.5.3 Binary Blends

We now consider binary blends with $\chi \neq 0$. For simplicity, we focus on symmetric systems, with $N_1 = N_2 = N$ and $b_1 = b_2 = b$. Figure 5.7 shows the one-loop predictions for the fractional change of the radius of gyration squared, rescaled by $\sqrt{N}$, as function of $\chi eN$ for various compositions. Increasing $\chi$ always causes both species in a blend to contract. The dependence of $R_{g1}$ upon $\chi$ is strongest when species 1 is a tracer in a matrix of 2 ($\phi_1 \ll 1$). There is no dependence of $R_{g1}$ upon $\chi$ in the opposite limit $\phi_2 \ll 1$ of essentially pure homopolymer 1. In the dilute limit, $\phi_1 \to 0$, the one-loop theory predicts a deviation $\delta R_{g1}^2$ that is a strictly linear function of $\chi N$. Furthermore, it can be shown that the slope of the limiting line is -0.62, which is -2 times that of the coefficient to the $1/\alpha$ divergence for the bidisperse melt in the limit of small-molecule good solvent discussed in the previous subsection (appendix B.1).

It is interesting to note that at the critical composition, $\phi_1 = 1/2$, the deviation induced by increasing $\chi$ always remains less than the chain-length dependent deviation from ideal chain statistics that is already present in the one-component melt ($\chi = 0$). Also note that the radius of gyration is a smooth, nearly linear function of $\chi$ even near the critical point. This reflects the fact that the long-wavelength composition fluctuations that appear near the critical point have characteristic wavelengths much larger than the radius of gyration, and so couple very weakly to the conformations of individual chains.

5.6 Comparison to Simulation

Here, we compare the predictions of the one-loop theory to the results of lattice Monte-Carlo simulations. We compare to bond-fluctuation model (BFM) simulations of symmetric blends at $\phi_1 = 1/2$ by Binder, Deutsch, and Müller,\textsuperscript{81–83} and to BFM simulations of single-chain properties by Beckrich \textit{et al.}\textsuperscript{67} The bond fluctuation model is a lattice model on a simple cubic lattice in which each monomer occupies a set of 8 sites at the vertices of a cube. In all of the simulations discussed here, the
monomer concentration is 1/16 monomer per lattice site, which is half the maximum possible concentration for this model. The statistical segment length extrapolated for the infinitely long chain is 3.244, as reported in reference 84. In simulations of polymer blends, monomers of types $i$ and $j$ on neighboring sites interact with an energy $u_{ij}$, with $u_{11} = u_{22}$ and $u_{12} > u_{11}$. Binder and coworkers have carried out semi-grand canonical ensemble simulations using two different variants of the rules for what constitute a “neighbor”: one in which each monomer can interact only with monomers located at the 6 closest allowed sites, and another in which each monomer can interact with monomers at any of the 54 closest allowed sites.

5.6.1 Determining $\chi_e$

To compare predictions of a coarse-grained theory to simulation data, one must somehow establish a relationship between the parameters used in the simulations and the phenomenological interaction parameters required as inputs to both Flory-Huggins
Section 5.6.1. Determining $\chi_e$

theory and the one-loop theory. The method of doing this was proposed in reference 73, where we justify and refine a form of “modified Flory-Huggins theory” that was originally proposed by Müller and Binder. In reference 73, a perturbation theory for a lattice model of the type described above was considered, in which the free energy of mixing is expanded in powers of a perturbation parameter $\alpha = u_{12} - u_{11}$. We identify the SCF interaction free energy per monomer $f_{\text{int}}$ by considering the behavior of the free energy of mixing in the limit of infinitely long chains. We show there that $f_{\text{int}}$ is given to first order in a power series in $\alpha$ by a function

$$f_{\text{int}}(\alpha, \phi_1) = kT \chi_e \phi_1 (1 - \phi_1)$$ (5.6.1)

in which

$$\chi_e = z^\infty [u_{12} - u_{11}] / kT .$$ (5.6.2)

Here, $z^\infty$ is an “effective coordination number” that is obtained by evaluating a value $z(N)$ of the average number of inter-molecular nearest neighbors per monomer in a one-component reference liquid, with $\alpha = 0$, and extrapolating the value to the limit of infinitely long chains. The values of $z^\infty$ used here were reported by Müller and Binder: $z_{c}^\infty = 2.1$ for the model with 54 interacting sites, and $z_{c}^\infty = 0.307$ for the model with 6 interacting sites.

Our use of a first order perturbation theory to estimate $f_{\text{int}}$ in the one-phase region of the phase diagram is justified by the fact that the critical value of $\alpha$ decreases as $1/N$ with increasing chain length. The fractional error in our estimate of $\chi_e$ arising from the use of a first order expansion is thus expected to be of order $1/N$ near the critical point. For $N \gg 1$, this error is expected to be much smaller than the corrections to $\chi_a$ predicted by the one loop theory, which are of order $N^{-1/2}$. The resulting $O(1/N)$ errors in our estimate of the “bulk” interaction parameter $\chi_e$ are expected to be comparable in importance to the $O(1/N)$ corrections that arise from end effects.
5.6.2 Composition Fluctuations in Blends

Figure 5.8 shows the results of Müller for $NS^{-1}(0)/2$ plotted vs. $\chi_eN$ for bond-fluctuation model simulations of chains of length $N = 64$. These simulations used a variant of the BFM in which interactions extend over 54 neighboring sites, and in which $u_{11} = -u_{12}$. Values of $S^{-1}(0)$ were extracted from the semi-grand equation of state. We have calculated the SCF effective $\chi_e$ parameter for each simulation from Eq. (5.6.2) using the value of $z^\infty = 2.1$ reported by Mueller and Binder.\(^{85}\)

Figure 5.8: Comparison of the results of Müller’s bond-fluctuation model lattice simulations $NS^{-1}(0)/2$ (circles) to corresponding one-loop 1-loop predictions (dashed line), for $N = 64$ and $\bar{N} = 290$, for a half-filled lattice.\(^{86}\) The calculation of values of $\chi_e$ for simulation results is discussed in the text.

In the left panel of Figure 5.8 the solid line is the RPA prediction and the dashed line is the one-loop prediction obtained using the appropriate value of $\bar{N} = 290$ (the value was reported as 240, which was computed from the apparent statistical segment length of chains with $N = 64$). The right panel shows a comparison of simulation results for the difference $\chi^*N = (\chi_a - \chi_e)N$ multiplied by $\sqrt{\bar{N}}$ to the universal curve shown in Figure 5.2. We see that the self-consistent one-loop theory gives an extremely accurate description of deviations from SCFT far from the critical point, for $\chi_aN \approx 1$, but appears to overestimate the stabilizing effect of critical fluctuations. For this system, the suppression of $\chi_a$ by long-wavelength fluctuations near the critical point is almost exactly cancelled by the enhancement of $\chi_a$ at smaller values of $\chi_e$, giving a critical value of $\chi_eN$ that is closer to the SCFT value than to the value.
predicted by the one-loop theory.

Figure 5.9 compares the predictions of the one-loop theory for the ratio \( T_c^\infty / T_c(N) \) for different values of \( N \) to the results of simulations by Deutsch and Binder.\(^87\) Here, \( T_c^\infty \equiv \alpha z^\infty N/(2k) \) is the critical temperature that is predicted by SCF if we use Eq. (5.6.2) for \( \chi_e \). The critical temperatures reported by Deutsch and Binder were identified for each chain length by a finite-size scaling analysis of simulations with different simulation cell sizes. Simulation results are shown for variants of the BFM model in which the neighbor interactions extend over 6 neighbors (circles) and over 54 neighbors (triangles). For both versions of the models, \( T_c^\infty / T_c(N) \) extrapolates to unity as \( N \to \infty \). This confirms that first order perturbation theory prediction for \( T_c \) is indeed asymptotically exact in the limit \( N \to \infty \).

For both versions of the BFM, however, the measured deviations of \( T_c^\infty / T_c(N) \) are significantly smaller than those predicted by the one-loop theory. This quantitative discrepancy must be, in part, a result of the inadequacy of the one-loop theory as a theory of critical phenomenon, and the need for a renormalization group approach near the critical point. This data suggests that, if it is indeed possible to express universal corrections to \( T_c^\infty / T_c(N) \) that arise from critical fluctuations as a power series in \( 1/\sqrt{N} \), the coefficient of any \( O(N^{-1/2}) \) correction must be much smaller than predicted by the one-loop theory.

It is important to also note that the slight deviations of \( T_c^\infty / T_c(N) \) from unity in Figure 5.9 are not the same for the two variants of the BFM, and appear to be of opposite sign. This model-dependence cannot be so easily explained as a failure of the one-loop approximation near the critical point, since we expect that a more sophisticated treatment of critical phenomena in a simple coarse-grained model would also predict a universal dependence of \( T_c^\infty / T_c(N) \) on the dimensionless parameter \( \bar{N} \). The observed non-universality could, however, be the result of corrections arising from contribution to \( f_{\text{int}} \) that are second order in \( \alpha \), which are neglected in our estimate of \( \chi_e \), and/or the result of end effects. Both of these effects are neglected in our analysis, and both are expected to yield model dependent corrections to \( T_c/T_c^\infty \) that are proportional to \( 1/N \). It appears to us that the dominant contribution to the deviation \( T_c^\infty / T_c(N) - 1 \) for this data may well be a nonuniversal correction proportional to
Section 5.6.3. Single-Chain Correlations

$1/N$ (which appears to provide a better description of the $N$ dependence, as originally suggested by Deutsch and Binder) rather than a universal correction proportional to $1/\sqrt{N}$.

Figure 5.9: Chain length dependence of the shift in the critical temperature. Comparison between one-loop theory prediction and Deutsch and Binder’s lattice simulation. Simulation results are shown for variants of the BFM in which interactions extend over 6 nearest neighbors (circles) and 54 neighbors (triangles).

5.6.3 Single-Chain Correlations

In Figure 5.10 we compare one-loop predictions and simulation results of Beckrich et al.\textsuperscript{67} for the deviation $\delta \omega(k)$ of the correlation function for a monodisperse melt from the Debye function. Simulation results for 5 different chain lengths were taken from reference\textsuperscript{67}. As noted by Beckrich et al., the collapse of data for different chain lengths when $\sqrt{N} \delta \omega(q)$ is plotted vs. $kR_g0$ already shows that the deviation is proportional to $1/\sqrt{N}$, as predicted by the one-loop theory. Simulations and predictions agree quite well, although there do appear to be some small systematic discrepancies in the high $k$ regime. The agreement is somewhat better than that obtained by the Strasbourg group using a more approximate treatment of a monodisperse melt. A similar level of agreement was obtained previously by that group in comparisons of the one-loop
theory to simulations of polydisperse equilibrium polymers, for which they obtained analytic predictions for $\delta \omega(q)$.\textsuperscript{67,68,77,78,88}

Figure 5.10: One-loop correction to the single chain correlation function (Debye function). The data points are gleaned from Figure 6 of reference\textsuperscript{67}. Different symbols are lattice simulation ($\rho = 1/16$, $b \approx 3.24$) results for chains with different lengths: + ($N = 2048$), $\circ$ (1024), $\Diamond$ (512), $\nabla$ (256), $\triangle$ (128). Near $k = 0$ the data points for various chain lengths overlap and can not be distinguished from the original figure, so are symbolized as $\ast$.

Müller has examined the dimension of homopolymer chains of various lengths in binary blends with varying compositions and interactions\textsuperscript{89}, using Monte Carlo simulations of the BFM with the same parameters as the one used to study composition fluctuations.\textsuperscript{86} In Figure 5.11 we re-plotted $\sqrt{N}$ times his results for the fractional deviation of the mean-squared end-to-end vector $R^2$ for component $A$ over a range of values of $\phi = \phi_A$ for a fixed value $\alpha N/k_BT = 0.32$, corresponding to $\chi e N = 0.672$, for 6 different chain lengths, adapted from Figure 5b in reference\textsuperscript{89}. Here $\delta R^2$ represents the deviation of $R^2$ in a mixture from the ideal Gaussian chain value calculated using the statistical segment length of a sufficiently long chain. The original results were presented as the difference between the value in the blend and that in a melt of chains of the same length. We have switched the normalization by assuming that the mean-
squared end-to-end vector measured in the melt is smaller compared to the ideal value by the amount $1.40/\sqrt{N}$. The fact that results for different chain lengths collapse confirms by itself that these deviations are proportional to $1/\sqrt{N}$. The method of obtaining the theoretical curve in Figure 5.11 is sketched in appendix B.2. One-loop predictions exhibit very rough agreement with these simulation results.

Figure 5.11: Composition dependence of the fractional change of the mean squared end-to-end distance for homopolymer chains in a binary blends for systems with $\chi_eN = 0.672$ and variable composition. Simulation data were adapted from Müller’s data for $\langle R^2 \rangle$. Solid line is the one-loop prediction.

### 5.7 Thermodynamic Integration of the RPA

The one-loop approximation has most often been presented within the context of the Edwards formalism, as a Gaussian approximation for the functional integral representation for the partition function. Here, we discuss an alternative derivation that makes no reference to the Edwards formalism, in which the one-loop free energy is obtained by the thermodynamic integration with respect to the strength of either
Section 5.7.1. Variation of the Pair Potential

the pair potential or the bare interaction parameter, while using the RPA approximation for $S_{ij}(q)$. The derivation is closely analogous to the usual derivation of the Debye-Hückel approximation for the excess free energy of an electrolyte solutions, which is obtained by combining an expression for the free energy as an integral with respect to a “charging” parameter with the Debye-Hückel linear self-consistent field approximation for the correlation function (see, e.g., McQuarrie’s book\(^{90}\)).

5.7.1 Variation of the Pair Potential

Our analysis starts with the following exact expression for the dependence of the free energy $F = -\ln Z$ upon the pair potential $U_{ij}(r - r')$ in any model with a pair potential: The perturbation $\delta F$ in the free energy induced by an infinitesimal perturbation $\delta U_{ij}(r - r')$ in the pair potential is given by an integral

$$\delta F = \frac{1}{2} \int dr \int dr' \langle c_i(r)c_j(r') \rangle \delta U_{ij}(r - r') \tag{5.7.1}$$

The corresponding perturbation of the correlation free energy density $f_{\text{corr}}$ may be expressed as an integral

$$\delta f_{\text{corr}} = \frac{1}{2} \int dr \ S_{ij}(r) \ \delta U_{ij}(r) \tag{5.7.2}$$

or as a Fourier integral

$$\delta f_{\text{corr}} = \frac{1}{2} \int_q S_{ij}(q) \ \delta U_{ij}(q) \tag{5.7.3}$$

where $S_{ij}(r) \equiv \langle c_i(r)c_j(0) \rangle - \langle c_i \rangle \langle c_j \rangle$.

By explicitly evaluating the corresponding variation of Eq. (5.2.10) for the one-loop correlation free energy for a compressible liquid, we find that, in this approximation,

$$\delta f_{\text{corr}} = \frac{1}{2} \int_q \tilde{S}_{ij}^{RPA}(q) \delta U_{ij}(q) \tag{5.7.4}$$
Section 5.7.2. Variation of $\chi_0$

where

$$S_{ij}^{RPA}(q) = [\Omega^{-1}(q) + U(q)]_{ij}^{-1} \quad (5.7.5)$$

is the RPA (or mean-field) approximation for $S_{ij}(q)$ in a compressible liquid. We thereby find that the one-loop approximation for the free energy density is thermodynamically consistent with an RPA approximation for $S_{ij}(q)$.

It follows that the one-loop free energy may be obtained by a thermodynamic integration similar to that used to obtain the free energy in the Debye-Hückel theory of electrolytes: Consider a sequence of systems with a reduced pair potential $\lambda U_{ij}$, with a charging parameter $\lambda$ in the range $0 < \lambda < 1$. The one-loop correlation energy (which vanishes in the $\lambda = 0$ ideal gas state) may be expressed as an integral

$$f_{corr} = \frac{1}{2} \int_0^1 d\lambda \int_q U_{ij}(q)S_{ij}^{RPA}(q; \lambda) \quad (5.7.6)$$

in which $S_{ij}^{RPA}(q; \lambda)$ is the RPA correlation function for a compressible mixture with a reduced pair potential $\lambda U_{ij}$. It is straightforward to confirm that Eq. (5.2.10) is recovered by explicitly completing the integral with respect to $\lambda$.

5.7.2 Variation of $\chi_0$

For many purposes, it is useful to consider the simple special case of a symmetric mixture of structurally identical chains, with $b_1 = b_2$ and $N_1 = N_2$, and with a pair potential of the form given in Eq. (5.2.2). In this case, the limit $\chi_0 = 0$ yields a true ideal mixture, for which $f_{corr}$ is independent of composition. In a nearly-incompressible symmetric mixture, with $Bv \gg 1$, the composition dependence of $f_{corr}$ may thus be obtained by starting from a nearly incompressible reference state with $\chi_0 = 0$, and calculating how $f_{corr}$ varies as $\chi_0$ is increased. As a special case of Eq. (5.7.3), it is straightforward to show that

$$\frac{\partial f_{corr}}{\partial \chi_0} = v \int d\mathbf{r} S_{12}(\mathbf{r})\delta_\Lambda(\mathbf{r}) \quad (5.7.7)$$
Section 5.8. Correlation Hole Effects

If we take the incompressible limit, for which \( S_{12}(r) = -S(r) \), and the limit \( \Lambda \to \infty \) of point-like interactions, Eq. (5.7.7) reduces to

\[
\lim_{\Lambda \to \infty} \frac{\partial f_{\text{corr}}}{\partial \chi_0} = -v \lim_{r \to 0} S(r),
\]

or

\[
\frac{\partial f_{\text{corr}}}{\partial \chi_0} = -v \int q S(q),
\]

in Fourier space.

The one-loop theory may be obtained by using the incompressible RPA approximation for \( S(q) \) in Eq. (5.7.9). In a symmetric blend, the incompressible RPA yields

\[
S_{\text{RPA}}(q; \chi) = \phi_1 \phi_2 \Omega(q) - \frac{2v \chi \phi_1 \phi_2}{\Omega^{-1}(q)}. \tag{5.7.10}
\]

An idealized IRPA model of Gaussian chains with point-like interactions, however, yields a UV divergent integral in Eq. (5.7.9). This may be regularized by restricting the integral to \( q < \Lambda \). The regularized (but unrenormalized) one-loop free is then given, to within a composition independent constant, by an integral

\[
f_{\text{corr}} = -v \chi_0 \int_0^1 d\lambda \int q S_{\text{RPA}}(q; \lambda \chi_0), \tag{5.7.11}
\]

where the Fourier integral is constrained to \( |q| < \Lambda \).

### 5.8 Correlation Hole Effects

Several features of the one-loop approximation for \( f_{\text{corr}} \) may be understood by relating them to corresponding features of the incompressible RPA description of correlations. To show this, it is useful to consider the derivative \( \partial f_{\text{corr}}/\partial \chi_0 \) in an ideal statistical mixture, which is obtained in our model by setting \( b_1 = b_2, N_1 = N_2, \) and \( \chi_0 = 0 \). In this limit, Eq. (5.7.10) for \( S(q) \) reduces to

\[
S(q) = \phi_1 \phi_2 \Omega(q). \tag{5.8.1}
\]
Section 5.8.1. UV divergence (Unrenormalized Theory)

This expression can also be obtained by the following physical argument: let \( S(r) = \langle \delta c(r) \delta c(0) \rangle \) be the overall correlation function in a one-component reference liquid of either pure 1 or pure 2, and let \( H(r) \) and \( \Omega(r) \) be the inter-molecular and intramolecular correlation functions, so that \( S(r) = \Omega(r) + H(r) \). An ideal mixture may be created by randomly labelling a fraction \( \phi_1 \) of the chains in such a one-component liquid as species “1”, and the remainder as species “2”. In the resulting ideal mixture, the probability that a particular pair of monomers on different chains will be on chains labelled \( i \) and \( j \) is simply \( \phi_i \phi_j \). It follows that the inter-molecular correlation function \( H_{ij}(r) \) in such a mixture is simply \( H_{ij}(r) = \phi_i \phi_j H(r) \). Similarly, because the probability that two monomers on the same chain belong to a chain of type \( i \) is \( \phi_i \), the intra-chain correlation function \( \Omega_{ij}(r) \) in such a mixture is \( \Omega_{ij}(r) = \delta_{ij} \phi_i \Omega(r) \). Thus far, everything we have said is exact.

In the idealized limit of a nominally incompressible liquid, however, we assume that \( S(r) = 0 \), and thus that \( \Omega(r) + H(r) = 0 \). In an incompressible liquid, the inter-chain correlation function \( H(r) \) must thus have a “correlation hole”, which is a mirror image of the intra-chain correlation function \( \Omega(r) \). This implies that, in an incompressible statistical mixture, \( H_{ij}(q) = -\phi_i \phi_j \Omega(q) \). Using this assumption, it is straightforward to show that \( S_{12}(q) = -\phi_1 \phi_2 \Omega(q) \) and that \( S_{11}(q) = +\phi_1 \phi_2 \Omega(q) \) in any incompressible ideal mixture.

5.8.1 UV divergence (Unrenormalized Theory)

The UV divergence of the correlation correction to \( \chi_c \) in Eq. (5.2.18) is the result of a pathological feature that arises from a combination of the assumption of rigorous incompressibility, at all wavelengths, in a model of continuous Gaussian chains. In the limit \( \chi_0 = 0 \) and \( \Lambda \to \infty \), Eqs. (5.7.9) and (5.8.1) may be combined to show that

\[
\frac{\partial f_{\text{corr}}}{\partial \chi_0} = v \phi_1 \phi_2 H(r = 0) = -v \phi_1 \phi_2 \Omega(r = 0) .
\]  

(5.8.2)

In the limit \( \Lambda \to \infty \), the predicted free energy is sensitive to the value of \( H(r) \) only at \( r = 0 \) because the range of the pair interaction \( U_{ij} \) vanishes in this limit.
Section 5.8.2. N-dependence (Renormalized Theory)

It is well known, however, that the intramolecular correlation function $\Omega(r)$ for a continuous Gaussian thread diverges as $\Omega(r) \propto 1/r$ as $r \to 0$. Recall the origin of this divergence: The number of monomers within a region of volume $r^3$ near a test monomer is of order the number of monomers $g$ in a segment of chain of size $r = \sqrt{gb}$, giving an average concentration $g/r^3 \sim 1/(rb^2)$ within a region of size $r$, or $\Omega(r) \propto 1/r$. When combined with an assumption of rigorous incompressibility, however, the divergence in $\Omega(r)$ yields an infinitely deep correlation hole in $H(r)$ at $r = 0$ in the one-component reference liquid. Taken literally, the incompressible RPA would yield negative values of $\langle c(r)c(0) \rangle$ in a region around $r = 0$. This leads to the nonsensical prediction of a divergent reduction in $H(r = 0)$, and thus to a divergent negative correction to $\chi_e$.

The UV divergence obtained from the IRPA that underlies the one-loop theory could be avoided by the use of any model that avoids the use of any of: i) a point-like interaction, ii) a continuous Gaussian thread model, or iii) rigorous incompressibility. For example, in the thread limit of the PRISM theory, one retains a model of continuous Gaussian chains, and a point-like effective interaction (i.e., direct correlation function), but avoids complete nonsense by allowing for some compressibility at short wavelengths.

5.8.2 N-dependence (Renormalized Theory)

In the renormalized one-loop theory, the UV divergent part of the correlation correction to $\chi_a$ is absorbed into the definition of $\chi_e(\Lambda)$. Once the divergence is removed, the renormalized theory can make concrete predictions about the difference $\chi^* = \chi_a - \chi_e$. Because the one-loop expression for $\chi^*$ is proportional to $N^{-1/2}$, $\chi_e$ may be interpreted as the limit of $\chi_a$ extrapolated to the limit $N \to \infty$. We now show that the value of $\chi^*$ is sensitive to the slight difference between the depth of the correlation hole in a system of finite chains and that in a hypothetical system of infinite chains.

To show this, consider the derivative of Eq. (5.2.20) for $f^*(\chi_a)$ with respect to $\chi_a$, evaluated (for simplicity) in a reference state with $\chi_a = \chi_0 = 0$. A straightforward
differentiation yields
\[
\lim_{\chi_a \to 0} \frac{\partial f^*}{\partial \chi_a} = -v\phi_1\phi_2 \int_q \Omega(q) .
\] (5.8.3)

The only differences between Eq. (5.8.3) and the limit \( \chi_0 = 0 \) of Eq. (5.7.9) for \( \partial f_{\text{corr}} / \partial \chi_0 \) are: i) the use of a renormalized integral (denoted by an asterisk) to remove the UV divergence, ii) the use of \( \chi_a \) rather than \( \chi_0 \) as the input parameter in a Hartree approximation.

The UV convergent part of the integral in Eq. (5.8.3) is given by a difference
\[
\lim_{\chi_a \to 0} \frac{\partial f^*}{\partial \chi_a} = -v\phi_1\phi_2 \int_q [\Omega(q) - \Omega^\Lambda(q)] ,
\] (5.8.4)
in which \( \Omega^\Lambda(q) \) is an asymptotic approximation for \( \Omega(q) \) in the limit \( q \gg R^{-1} \). This quantity is given by
\[
\Omega^\Lambda(q) \equiv 12/(vq^2b^2) .
\] (5.8.5)

Let \( \Omega(q; N) \) denote the intramolecular correlation function for a single-component melt of chains of length \( N \). Because \( \Omega^\Lambda(q) \) is an asymptotic expansion of \( \Omega(q; N) \) in the limit \( qR \gg 1 \), it may be interpreted equally well as either:

i) The high-\( q \) behavior of \( \Omega(q; N) \) for chains of fixed length \( N \), or

ii) The asymptotic behavior of \( \Omega(q; N) \) at fixed \( q \) in the limit \( N \to \infty \).

By adopting the latter interpretation, and inverting the Fourier transform, Eq. (5.8.4), may thus be expressed as a difference
\[
\lim_{\chi_a \to 0} \frac{\partial f^*}{\partial \chi_a} = -v\phi_1\phi_2 \lim_{r \to 0} [\Omega(r; N) - \Omega(r; \infty)]
\] (5.8.6)
or, equivalently,
\[
\lim_{\chi_a \to 0} \frac{\partial \chi^*}{\partial \chi_a} = v^2 \lim_{r \to 0} [H(r; N) - H(r; \infty)]
\] (5.8.7)
where \( H(r; N) \) denotes the value of the inter-molecular correlation function \( H(r) \) in a one-component melt of chains of length \( N \).
The renormalization procedure that was originally introduced to remove the UV divergence is thus seen to be equivalent to the subtraction of the $N \to \infty$ limit. The resulting difference relates $\chi^* = \chi_a - \chi_e$ to the difference in the depth of the correlation hole at $r = 0$ in a system of finite chains and that in a hypothetical system of infinite chains. The renormalized coarse-grained theory correctly predicts the behavior for $\chi^*$ for small values of $\chi_a$ because it correctly describes this subtle difference between finite and infinite chains, despite the fact that it predicts a UV divergence of $H(r; N)$ itself.

5.9 Conclusions

We have used the renormalized one-loop theory to analyze corrections to the RPA description of composition fluctuations in binary blends, and to the random walk model of chain conformations.

Our analysis of long-wavelength composition fluctuations is closely related to the earlier analysis by Wang, who focused primarily on behaviors near the spinodal.\textsuperscript{66} Our predictions can be summarized by considering the difference $\chi^* \equiv \chi_a - \chi_e$ between an apparent interaction parameter $\chi_a$ that would be inferred from the magnitude $S(q = 0)$ of long-wavelength composition fluctuations and a parameter $\chi_e$ that we identify as the SCFT interaction parameter, which is the limit of $\chi_a$ as $N \to \infty$.

We show that the deviation from SCFT can be understood as the result of two competing physical effects: in the limit $\chi_e N \ll 1$ of a nearly ideal mixture, $\chi_a$ is greater than $\chi_e$ because of a simple packing effect: monomers on a finite chain are slightly less strongly shielded from contact with monomers of other chains than are monomers on an infinite chain, and are therefore more exposed to unfavorable interactions with chains of the other species in a binary blend. Closer to the spinodal, however, the build up of long-wavelength correlations causes the difference $\chi_a - \chi_e$ to decrease with increasing $\chi_e$. Near the critical point, both effects yield contributions to $\chi_a$ that are proportional to $N^{-1/2}$, and comparable in magnitude. An accurate prediction of the magnitude and sign of the absolute shift in the critical value of $\chi_e N$ thus requires an accurate description of both of these competing effects. A simple
Section 5.9. Conclusions

renormalized Hartree theory predicts an overall enhancement in the critical value of $\chi_e N$ (or a depression in $T_c$) for a symmetric blend by an amount proportional to $\bar{N}^{-1/2}$, as first predicted by Holyst and Vilgis.\textsuperscript{63,64}

Comparisons to the data from lattice Monte Carlo simulations of symmetric blends at the critical composition indicate that the one-loop theory gives an excellent description of the packing effect that dominates corrections to the RPA for $\chi_e N \simeq 1$, but a mediocre description of correlation effects closer to the critical point. It appears that the self-consistent one-loop (or Hartree) theory gives a reasonable semi-quantitative description of deviations from SCFT, but tends to overestimate the magnitude of the depression in $\chi_a$ near the critical point, and thus to predict too high a value for $(\chi_e N)_c$. Predictions for corrections to random-walk statistics were also compared to the available simulation data. Predictions for deviations of the intramolecular correlation function from the Debye function for chains in a monodisperse single-component melt agree very well with the simulation results of Beckrich \textit{et al.},\textsuperscript{67} as did early predictions for poly-disperse polymers by the same group. Predictions of the composition dependence of the mean-squared end-to-end vector in a binary blend with $\chi_e \neq 0$ show somewhat rougher quantitative agreement with lattice Monte Carlo results.
Quantitative corrections to the random phase approximation for the structure factor $S(q)$ of disordered diblock copolymer melts are presented, based on a self-consistent renormalized one-loop theory\textsuperscript{57} (ROL). The variations of the peak position and peak intensity of the $S(q)$, of the radius of gyration of each block and the mean squared center of mass distance of two blocks, as functions of the Flory-Huggins $\chi$ parameter are calculated, for symmetric and asymmetric copolymers. The theory allows a clean separation of intra- and intermolecular contributions to $S(q)$, which demonstrates that the shift in peak position near ODT is primarily due to the intermolecular correlations. The conventional Fredrickson-Helfand theory is shown to be the asymptotic limit of the ROL for the symmetric diblock copolymer.

The work discussed in this chapter is completed in collaboration with a previous graduate student in Prof. Morse’ group, Piotr Grzywacz.
6.1 Introduction

The seminal paper by Leibler\(^7\) is the natural starting point for any analysis of composition fluctuations in block copolymer melts. In this paper, Leibler made some prescient comments about the limitations of his theory, and about the potential importance of fluctuation effects that it neglects. Leibler’s analysis is based on a Landau (or power series) expansion of the self-consistent field theory (SCFT) free energy around the homogeneous state for weakly segregated AB diblock copolymers. This expansion provides predictions for both the structure factor \(S(q)\) in disordered melts, and for phase transitions involving weakly-segregation ordered phases. The SCF approximation that Leibler used to calculate \(S(q)\) is often referred to as a random-phase approximation (RPA).\(^5,6\) SCFT predicts a second-order transition between the disordered and lamellar phase at a critical copolymer composition, and weakly segregated structures near this critical point. (The critical composition corresponds to equal volume fractions of A and B if the two types of monomer have equal statistical segment length.) Leibler noted, however, that Brazovskii\(^92\) had already shown that a transition between a homogeneous and periodic phase that is second order at a mean-field level will actually be first order as a result of the very strong order parameter fluctuations near such a transition. These strong pre-transitional fluctuations were also shown to cause large corrections to the Landau description of correlations near any such weakly-first order crystallization transition. It was thus clear from the outset of interest in this subject that a more sophisticated treatment of fluctuation effects would be needed.

The task of incorporating fluctuation effects into Leibler’s theory was undertaken by Fredrickson and Helfand.\(^93\) Fredrickson and Helfand mapped Leibler’s theory onto Brazovskii’s formalism\(^92\) by identifying the SCFT free energy functional with the effective Hamiltonian used in Brazovskii’s more phenomenological field theory. The resulting theory has successfully explained many discrepancies between Leibler’s theory and experimental observations, as discussed below.

Small angle neutron (SANS) and x-ray (SAXS) scattering from disordered AB diblock copolymer melts probe the structure function \(S(q)\). In the notation used here
Section 6.1. Introduction

for an incompressible melt, \( S(q) = \int d\mathbf{r} (\delta c_A(\mathbf{r})\delta c_A(0))e^{iq\mathbf{r}} \), where \( \delta c_A(\mathbf{r}) \) is the deviation in the number concentration of \( A \) monomers from its spatial average. Leibler’s RPA approximation for \( S(q) \) yields an inverse structure function of the form

\[
S^{-1}(q) = \tilde{F}(q) - 2v\chi N,
\]

(6.1.1)

where \( \chi \) is the Flory-Huggins interaction parameter, \( N \) is degree of polymerization, and \( v \) is a monomer volume. The function \( \tilde{F}(q) \) has a minimum at a wavenumber \( q^* \propto 1/R_g \), where \( R_g \) is the copolymer radius of gyration. The predicted form of \( \tilde{F}(q) \) is based upon an assumption of random walk statistics for each chain. The predicted wavenumber dependence of this function has been found to adequately describe the results of most SANS\(^{94}\) and SAXS\(^{95}\) measurements. The predicted dependence of \( S^{-1}(q) \) on \( \chi \) has been widely used to extract values for the \( \chi \) parameter and its temperature dependence.\(^{95-98}\) Careful comparisons of this RPA prediction to experimental results have also revealed some limitations of the theory, particularly in the vicinity of the ODT.

Leibler’s RPA theory predicts that the inverse peak intensity \( S^{-1}(q^*) \) depends linearly on \( \chi(T) \), a parameter that is assumed to be independent of \( N \) and to vary smoothly with temperature. The temperature dependence of \( \chi(T) \) is often approximated by a function \( \chi(T) \approx A/T + B \). With this approximation for \( \chi(T) \), one expects plot of \( S^{-1}(q^*) \) vs. \( T^{-1} \) to yield a straight line. Studies of diblock copolymers over a wide temperature range that includes the ODT have, however, demonstrated a clear non-linearity in this plot near the ODT.\(^{95,99-106}\) This behavior cannot be accounted for by Leibler’s theory, and is believed to be a result of the fluctuation effects that the Brazovskii\(^{92}\) and FH theory attempt to describe. The molecular weights covered in these studies range from a few kg/mol\(^{102}\) to hundreds.\(^{105}\) Studies that have quantitatively compared the temperature dependence of the peak intensity to predictions of the FH theory\(^{99,106}\) have concluded that the FH theory can fit the data rather well, if one takes \( \chi(T) = A/T + B \) and adjusts \( A \) and \( B \) to the data.

Leibler’s theory predicts a peak position \( q^* \) proportional to the radius of gyration of a Gaussian chain. The peak wavenumber is thus expected to vary very little with
Section 6.1. Introduction

temperature (only as a result of the slight temperature dependence of the statistical segment lengths), and to vary with \( N \) at fixed temperature as \( q^* \propto N^{-1/2} \). Numerous experiments have shown that near the ODT, \( q^* \) varies slightly with temperature, and have shown a molecular weight dependence at the fixed temperature somewhat stronger than the \( N^{-1/2} \) dependence expected for Gaussian coils. The variation of \( q^* \) with \( T \) cannot be explained by the thermal expansion of statistical segment lengths. Independent measurements of \( S(q) \) and the polymer radius of gyration \( R_g \) near the ODT also indicate that the shift in \( q^* \) cannot be fully accounted for by the expansion of \( R_g \).

Simulation studies have provided analogous results. Fried and Binder simulated diblock copolymers on a cubic lattice with relatively high concentrations. They, and many others, reported clear non-Gaussian single chain properties well outside the transition region, non-linear shape of \( S^{-1}(q^*) \) versus the inverse of temperature, and a gradual decrease in \( q^* \) with decreasing temperature. By comparing the temperature dependence of the single chain size directly with that of \( q^* \), Binder et al. also concluded that the shift in \( q^* \) is largely caused by intermolecular correlations, rather than intramolecular stretching alone, in agreement with the conclusions of an analogous experimental comparison by Bartels and Mortensen. The approximations used in the original FH theory did not allow for a shift in \( q^* \) near the transition. Barrat and Fredrickson later refined the FH theory by retaining the full \( q \) dependence of the quartic coefficients of the effective Hamiltonian, and predicted a shift in \( q^* \). Almdal, Bates and coworkers concluded that the resulting theory adequately described the molecular weight dependence of \( q^* \) in a series of homologous copolymers with different molecular weights at the same temperature.

Leibler’s theory assumes (among other things) that chain statistics are adequately described as Gaussian random walks. Universal deviations from the random walk statistics in one-component polymer melts have been convincingly demonstrated in recent simulations and quantitatively explained by a renormalized one-loop theory. We show here that these deviations from random walks statistics cause predictable deviations from the RPA prediction for \( S(q) \) even in the limit \( \chi = 0 \), which would be found in scattering measurements from diblocks with two thermo-
dynamically identical blocks that are labeled to produce a scattering contrast (e.g., idealized diblocks of hydrogenated and deuterated monomers of the same covalent structure).

Despite its successes, the Fredrickson-Helfand-Barrat theory is somewhat unsatisfying as a result of ambiguities and approximations that are inherent in how it was derived. Some of these flaws are discussed in Section 6.4 of this thesis, and are merely noted here: (1) There is no rigorous justification for FH’s use of a mean-field free energy as an effective Hamiltonian. (2) The fact that the theory neglects integrals involving the third-order coefficient in the Landau expansion, which vanishes at the critical composition, makes it inapplicable away from this composition. (3) Fredrickson and Helfand introduced several mathematical approximations in order to approximate the wavevector-dependent coefficients in Leibler’s Landau expansion by the simpler functional forms assumed by Brazovskii. These approximations were intended to capture only the behavior at temperatures very near the transition temperature, and at wave numbers very near $q^*$, and limit the applicability of the theory to this domain. (4) Predictions of the FH theory contain an ultraviolet (UV) divergence (i.e., a strong dependence of all quantities on an arbitrary short-wavelength cutoff length) that Fredrickson and Helfand simply removed, without comments or adequate considerations of its physical meaning or implications. This last problem with the FH theory was highlighted by Kudlay and Stepanow, who attempted to construct a physically motivated renormalization procedure to remove the UV divergence, while keeping the full wavevector dependence of all vertex functions, but were unable to do so.

Recent works by our group and others have provided a more systematic theory of correlations, the renormalized one-loop theory (ROL), that is free of the aforementioned flaws. Here, we present predictions of the ROL theory for both collective and single-chain correlations in disordered diblock copolymer melts.

The quantitative predictions of ROL are presented in the current work: in Section 6.3, we introduce the notations and review the key results of ROL; in Section 6.4, we present the predictions of the ROL to the wavevector and $\chi$ dependence of the correlation function, of various dimensional characterization of the molecules, for
symmetric and asymmetric diblock copolymers; in Section 6.5, we demonstrate numerically that the FH theory and ROL theory are asymptotically equivalent close to the order-disorder transition. The summary is given in Section 6.6.

### 6.2 Notation

We consider a coarse grained model for AB diblock copolymer melts. Each monomer occupies a reference volume $v$, which is the same for A and B monomers. The degree of polymerization, the block volume fractions, the statistical segment lengths, and the packing lengths, are denoted by $N$, $f_i$, $b_i$, $l_i = v/b_i^2$ respectively, where $i = A$ or B. The molecular density $\rho = 1/(vN)$. Let $c_i(r) = \sum_{m,j} \delta(r - R_{mi}(s))$ be the fluctuating concentration of monomers of type $i$, in which $R_{mi}(s)$ is the position of monomer $s$ on block $i$ of molecule $m$.

In this work, we are particularly interested in the behavior of the structure function

$$S_{ij}(r) = \langle \delta c_i(r) \delta c_j(0) \rangle \quad (6.2.1)$$

where $\delta c_i(r) = c_i(r) - \langle c_i \rangle$ is the deviation of the monomer concentration from its mean value. Let $S_{ij}(q) \equiv \int dr \ S_{ij}(r)e^{iqr}$. The intramolecular correlation function $\Omega_{ij}(r)$ and its Fourier transform $\Omega_{ij}(q)$ are defined to be the contributions to $S_{ij}(r)$ and $\Omega_{ij}(q)$, respectively, that arise from correlations between pairs of monomers on the same chain. To distinguish corrections to the RPA that arise from intra- and intermolecular correlations, it is useful to introduce a generalized Ornstein-Zernicke equation $^{57,124-127}$

$$S^{-1}_{ij}(q) = \Omega^{-1}_{ij}(q) - C_{ij}(q), \quad (6.2.2)$$

in which $\Omega_{ij}(q)$ is the true intramolecular correlation function (rather than a random walk approximation), and $C_{ij}$ is a direct correlation function that is defined by this equation. In a dense, nearly-incompressible liquid with monomers of equal volume, we will assume that the eigenmodes of the matrix $S_{ij}(q)$ for values of $q$ of order the inverse coil size are given approximately by fluctuating composition mode, of the form $(\delta c_A(q), \delta c_B(q)) \propto (1, -1)$, and a density fluctuation mode of the form...
Section 6.2. Notation

\((\delta c_A(q), \delta c_B(q)) \propto (1, 1)\), and that fluctuations of the density mode are strongly suppressed by the large compression modulus of the liquid. In the limit of negligible density fluctuations, one can define a scalar structure function \(S(q) = S_{AA}(q) = S_{BB}(q) = -S_{AB}(q) = -S_{BA}(q)\) that is given by references \(^{57,126,127}\)

\[
S(q) = \frac{1}{F(q) - 2v\chi_a(q)}, \tag{6.2.3}
\]

where

\[
F(q) = \varepsilon_i\Omega_{ij}^{-1}(q)\varepsilon_j = \Omega_+(q)/|\Omega(q)| \tag{6.2.4}
\]

\[
\chi_a(q) \equiv \frac{1}{2v}\varepsilon_iC_{ij}(q)\varepsilon_j = \frac{1}{2v}[C_{AA}(q) + C_{BB}(q) - 2C_{AB}(q)], \tag{6.2.5}
\]

where \(\varepsilon \equiv (\varepsilon_A, \varepsilon_B) = (1, -1)\), \(\Omega_+(q) \equiv \sum_{ij} \Omega_{ij}(q)\) and \(|\Omega(q)| \equiv \Omega_{AA}(q)\Omega_{BB}(q) - \Omega_{AB}^2(q)\). Here and hereafter, summation over repeated subscripts is implicit. We refer to the function \(\chi_a(q)\) defined by the above as the “apparent” interaction parameter.

The form of Leibler’s RPA theory that is usually used in comparisons to experiment can be recovered from the above more general expression by assuming random walk statistics to calculate \(\Omega_{ij}(q)\) and \(F(q)\), and by approximating \(\chi_a(q)\) by a value that is independent of chain length \(N\) and wavenumber \(q\), and that depends only on temperature. The random walk model used in the original RPA yields intra-block correlation \(\tilde{\Omega}_{ii}(q)\) for \(i = A\) or \(B\), and an inter-block correlation \(\tilde{\Omega}_{ij}(q)\) for \(i \neq j\),

\[
\tilde{\Omega}_{ii}(q) = \rho N^2 f_i^2 g(q^2 R_{g,i}^2)
\]

\[
\tilde{\Omega}_{ij}(q) = \rho N^2 f_i f_j e(q^2 R_{g,i}^2)e(q^2 R_{g,j}^2), \tag{6.2.6}
\]

where \(R_{g,i}^2 = f_iNb_i^2/6\) is the radius of gyration of the \(i\)-th block, \(g(x) \equiv 2(e^{-x} - 1 + x)/x^2\) is the Debye function, and \(e(x) \equiv (1 - e^{-x})/x\). Here and hereafter, we use \(\tilde{\cdots}\) to denote a property of an ideal Gaussian chains. The function \(\tilde{F}(q)\) used in Eq. (6.1.1) is calculated using these random walk expressions.

Despite its superficial similarity to Leibler’s RPA expression, the expression given in Eq. (6.2.3) allows for the possibility of corrections to the RPA that arise both
from corrections to the random-walk model, which affects the values of the true intramolecular correlation functions $\Omega_{ij}(q)$ that are used to calculate $F(q)$, and from corrections to the SCF treatment of intermolecular correlations, which affects the value of $\chi_a(q)$.

The renormalized one-loop theory yields an expression for $S(q)$ that approaches a form consistent with Leibler’s theory in the limit $N \to \infty$. We will hereafter use $\chi_e$ to denote the limiting value that $\chi_a(q)$ approaches in the limit $q \sim R^{-1}$, $\chi N \sim 1$, and $N \to \infty$. For finite values of $N$, the one-loop theory yields separate predictions for corrections to $\Omega_{ij}(q)$ and $C_{ij}(q)$, or to $F(q)$ and $\chi_a(q)$. The one-loop theory is the first correction to self-consistent field theory in an expansion in powers of $N^{-1/2}$, where

$$\tilde{N} \equiv N b^6 / v^2$$  \hspace{1cm} (6.2.7)

is the invariant degree of polymerization defined by Fredrickson and Helfand.\textsuperscript{93}

## 6.3 Renormalized One-Loop Theory

In this section, we review the renormalized one-loop theory that was derived in reference\textsuperscript{57}, and summarize the results needed to apply the theory to diblock copolymer melts.

The one-loop theory is derived by considering a simple coarse-grained theory in which the potential energy is the sum of intramolecular potential $U_{\text{chain}}$, which is approximated by the free energy of a set of Gaussian chains, and non-bonded pair interaction with short range interactions. We consider a pair potential of the form $U_{ij}(r) = \epsilon_{ij}\delta_{\Lambda}(r)$, where $\delta_{\Lambda}(r)$ is a regularized $\delta$ function with an integral $\int dr \delta_{\Lambda}(r) = 1$ and a characteristic range of interaction $1/\Lambda$. The interaction energies are given by $\epsilon_{ii} = B$, where $B$ is a large compression energy, and $\epsilon_{ij} = B + \chi_0$ for $i \neq j$, where $\chi_0$ is a “bare” interaction parameter.

A systematic method of generating corrections to the RPA approximation for both intramolecular and collective correlation functions was given in reference\textsuperscript{56} and in Chapter 4. A renormalization procedure to remove the otherwise strong dependence
Section 6.3.1. Intramolecular Correlations

on the value chosen for $\Lambda$ was discussed in reference$^{57}$. The renormalized one-loop theory provides separate predictions for corrections to the random-walk model of intramolecular correlations, and for the function $\chi_a(q)$.

6.3.1 Intramolecular Correlations

The one-loop correction $\delta \Omega_{ij} = \Omega_{ij} - \tilde{\Omega}_{ij}$ to the intramolecular correlation function $\Omega_{ij}$ (where $\tilde{\Omega}_{ij}$ is the value of $\Omega_{ij}$ for non-interacting Gaussian chains) is given by a Fourier integral

$$
\delta \Omega_{ij}(q) = -\frac{\rho}{2} \int_k \psi_{ijkl}^{(4)}(q, -q, k, -k) \tilde{G}_{kl}(k) \quad (6.3.1)
$$

Here $\int_k \equiv (2\pi)^{-3} \int dk$. The quantity $\tilde{G}_{kl}(k)$ is a screened interaction that is given for the general case of a compressible liquid by

$$
\tilde{G}^{-1}(k) = U^{-1}(k) + \tilde{\Omega}(k) \quad . \quad (6.3.2)
$$

where $\tilde{G}(k)$, $U(k)$ and $\tilde{\Omega}(k)$ are $2 \times 2$ matrices with elements $\tilde{G}_{ij}(k)$, etc., and where inversion denotes a matrix inverse. We are interested in this work in the limit of mesoscopic wavelengths ($q \sim R^{-1}$ and $q \ll \Lambda$) and negligible compressibility ($B \to \infty$). In this limit, $G_{ij}(q)$ reduces to:$^{57}$

$$
\tilde{G}_{ij}(q) = \frac{1 - 2v\chi_0|\tilde{\Omega}(q)|\tilde{\Omega}^{-1}_{ij}(q)}{\tilde{\Omega}_+(q) - 2\chi_0 v|\tilde{\Omega}(q)|} . \quad (6.3.3)
$$

The four point function $\psi_{ijkl}^{(4)}(q, -q, k, -k)$ is defined by

$$
\psi_{ijkl} = \tilde{\omega}_{ijkl}^{(4)}(q, -q, k, -k) - \tilde{\omega}_{ij}(q)\tilde{\omega}_{kl}(k). \quad (6.3.4)
$$

in which $\tilde{\omega}_{kl}(k) \equiv \tilde{\Omega}_{kl}(k)/\rho$ is a single-chain correlation function, normalized by the molecular density $\rho$, and $\tilde{\omega}_{ijkl}^{(4)}(q, -q, k, -k)$ is an analogous single-chain four point function for monomers within blocks $i$, $j$, $k$, and $l$.$^{57}$

The physical content of Eq. (6.3.1) is shown schematically in the left diagram of Figure 6.1, in which the curve represents a single chain, along which two segments
Section 6.3.1. Intramolecular Correlations

interacts via a “screened” potential $\tilde{G}$.

$$\tilde{G}_{kl}(k)$$

$$\tilde{G}_{mn}(k)$$

$$\tilde{G}_{kl}(-k)$$

Figure 6.1: Diagrams illustrating the effects of the screened intra- (left) and inter- (right) molecular interactions on the correlations of segments of type $i$ and $j$. Additional segmental indices $k, l, m, n$ runs through the whole chain. $k$ and $q$ are wave vectors for the interactions or correlations, and $k_{\pm} = k \pm \frac{q}{2}$, one particular choice made to conserve momentum.

The expression given in Eq. (6.3.1) is the lowest order contribution to $\delta \Omega_{ij}(q)$ in a perturbation theory that was developed more extensively in reference 56. Like most results of this un-renormalized perturbation theory, Eq. (6.3.1) is ultraviolet (UV) divergent: The value of the Fourier integral is dominated by contributions of large wavevectors, $|k| \sim \Lambda$, and increases without bound with increasing cutoff wavenumber $\Lambda$. The integral in Eq. (6.3.1) increases linearly with $\Lambda$ when $\Lambda R_g \gg 1$.

We showed in our previous work, however, that this sensitivity of the one-loop prediction for $\Omega_{ij}(k)$ to short-wavelength correlations is entirely the result of a difference between the value of the statistical segment length of a chain in the dense melt and that in a gas of non-interacting chains, and so could be absorbed into a shift in the value used for this parameter. We showed how the result of Eq. (6.3.1) for $\Omega_{ij}(q)$ can be expressed as a sum

$$\Omega_{ij}(q) = \tilde{\Omega}_{ij}(q) + E\Lambda + \delta \Omega_{ij}^*(q),$$ (6.3.5)

of a UV divergent contribution $E\Lambda$ and a UV convergent contribution $\delta \Omega_{ij}^*(q)$, in which the coefficient $E$ and the function $\delta \Omega_{ij}^*(q)$ are independent of $\Lambda$ in the limit
Section 6.3.1. Intramolecular Correlations

$\Lambda R \gg 1$. Our interpretation of the UV divergence was based on a demonstration that the UV divergent term $E\Lambda$ is of the form

$$E\Lambda = \frac{\partial \tilde{\Omega}_{ij}(\mathbf{q}; b)}{\partial b_k} \delta b_k,$$  \hspace{1cm} (6.3.6)

where

$$\delta b_k = \frac{l_k^2}{\pi^2 \bar{l}}$$  \hspace{1cm} (6.3.7)

is a UV divergent shift in the value of the statistical segment length and $\bar{l} = f_A l_A + f_B l_B$. We thus interpret the UV divergence as a result of shift in the value of the $b$, which can be absorbed into a shift in the value used for this quantity, and interpret $\delta \Omega_{ij}^*(\mathbf{q})$ as the physically relevant prediction of a correction to Gaussian chain statistics.

After the divergence is removed, Eq.(6.3.1) can be expressed as a convergent Fourier integral that can be non-dimensionalized by associating all wavenumbers with a reference length scale $R = (Nb/6)^{1/2}$, in which we take $b = b_A$ as a matter of convention. Non-dimensionalization yields an expression of the form

$$\delta \Omega_{ij}(\mathbf{q}) = \frac{\rho N^2}{N^{1/2}} \delta \tilde{\omega}_{ij}(\mathbf{q}R, \chi_0 N, f_A, b_B/b_A),$$  \hspace{1cm} (6.3.8)

where $\delta \tilde{\omega}$ is the result of dimensionless Fourier integral. Here and hereafter, we use $\delta \Omega_{ij}(\mathbf{q})$ to denote the physically relevant, UV convergent part of $\delta \Omega_{ij}(\mathbf{q})$, and drop our use of an asterisk to denote this quantity. The corresponding correction to $F(\mathbf{q})$, evaluated to the same order in $N^{-1/2}$, is given by

$$\delta F(\mathbf{q}) = -\varepsilon_i \tilde{\Omega}_{\alpha}^{-1}(\mathbf{q}) \delta \Omega_{\alpha\beta}(\mathbf{q}) \tilde{\Omega}_{\beta j}^{-1}(\mathbf{q}) \varepsilon_j.$$  \hspace{1cm} (6.3.9)

This is the expression that we use to evaluate the correction to $S^{-1}(\mathbf{q})$.  

108
6.3.2 Direct Correlation Function

The unrenormalized one-loop theory yields an expression for the direct correlation function as a sum

\[ C_{ij}(\mathbf{q}) = -U_{ij}(\mathbf{q}) + \delta C_{ij}(\mathbf{q}) \]  

(6.3.10)

where

\[ \delta C_{ij}(\mathbf{q}) = \tilde{\Omega}^{-1}_{ik}(\mathbf{q}) \Sigma_{kl}(\mathbf{q}) \tilde{\Omega}^{-1}_{lj}(\mathbf{q}), \]  

(6.3.11)

\[ \Sigma_{ij}(\mathbf{q}) = \frac{1}{2} \int K \tilde{\Omega}^{(3)}_{imk}(\mathbf{q}, \mathbf{k}, -\mathbf{k}, \mathbf{k}) \tilde{G}_{kl}(\mathbf{k}) \times \tilde{\Omega}^{(3)}_{jnl}(\mathbf{k}, -\mathbf{k}, \mathbf{k}) \tilde{G}_{mn}(\mathbf{k}). \]  

(6.3.12)

Here, \( \mathbf{k}_\pm = \mathbf{k} \pm \frac{\mathbf{q}}{2} \), and \( \tilde{\Omega}^{(3)}_{ijk} \) is a three point intramolecular correlation function for monomers within blocks \( i, j \) and \( k \) of a Gaussian diblock. The physical content of Eq. (6.3.12) for \( \Sigma_{ij} \) is shown schematically by the right diagram of Figure 6.1, in which two pairs of segments along two chains are interact via the screened interaction \( \tilde{G} \).

The corresponding correction to \( \chi_a(\mathbf{q}) \) can be evaluated by using Eq.(6.2.5). This yields a UV divergent expression for \( \chi_a \), in which the dependence on \( \Lambda \) for \( \Lambda R_g^{-1} \) has been shown to be of the form

\[ \chi_a(\mathbf{q}) = \chi_0 + A \Lambda^3 + B \chi_0 \Lambda + \frac{H}{N} \Lambda + \delta \chi^*(\mathbf{q}), \]  

(6.3.13)

where the coefficients \( A, B, \) and \( H \) and the UV convergent contribution \( \delta \chi^*(\mathbf{q}) \) are all independent of \( \Lambda \). The coefficients of the UV divergent terms are reproduced below,
Section 6.3.2. Direct Correlation Function

for reference:

\[ A = \frac{(l_A - l_B)^2 \nu}{24\pi^2 l^2}, \]  
(6.3.14)

\[ B = -\frac{6l_A l_B^2}{\pi^2 l^3}, \]  
(6.3.15)

\[ H = \frac{7(q^2 Nb_A b_B)(l_A - l_B)^2 \nu^2}{24\pi^2 b_A b_B l^2} + \frac{3\nu(l_A - l_B)^2 \nu}{2\pi^2 l^3} \left( l_A^2 - l_A l_B + l_B^2 \right) 
- \frac{3(l_A - l_B)}{2\pi^2 l^2} \left( \epsilon_i T_{ik}^{-1} L_k \right). \]  
(6.3.16)

Here, \( L_k = f_k l_k^2 + f_k^2 e_k \left( l_A^2 + l_B^2 - (l_A + l_B) l_k \right) \) and \( e_k = e(q^2 R_{g,k}^2) \) as defined in Section 6.3. \( T \equiv \bar{\Omega}/(\rho N^2) \) is the non-dimensionalized ideal chain correlation function.

Our interpretation of the terms involving the coefficients \( A \) and \( B \) was based on the observation that these two coefficients are independent of wavenumber \( q \), chain length \( N \), and block fraction \( f_A \). Furthermore, it was shown that the same values for these two coefficients were obtained in an expansion of \( \chi_a(q) \) in a binary polymer blend of the same overall composition.\(^57\) We thus interpret the divergent terms involving these two coefficients as contribution to an effective self-consistent field interaction parameter \( \chi_e \) that includes the effects of local correlations that are independent of chain length or architecture. In the one-loop theory, this quantity is given to this order by

\[ \chi_e = \chi_0 + AA^2 + B\chi_0 \Lambda. \]  
(6.3.17)

Simply rewriting the expression in terms of the renormalized interaction parameter \( \chi_e \), rather than \( \chi_0 \), removes most of the UV divergence, except for the contribution \( HA/N \), which is smaller by a factor of 1/N.

Our interpretation of the contribution \( HA/N \) is somewhat more subtle. Unlike the coefficients \( A \) and \( B \), \( H \) exhibits a nontrivial dependence on \( q \), \( N \), and \( f_A \). We showed in reference\(^57\) that the functional form of the resulting contribution to \( S^{-1}(q) \) is exactly consistent with that predicted by a generalized RPA model in which we allow for the existence of excess free energies associated with chain ends and the diblock
Section 6.3.3. Self-Consistent Approximation

The straight perturbative theory can be improved by a self-consistent approximation, analogous to that used in FH theory. Leibler’s mean field theory predicts that \( \rho N S_0^{-1}(q^*) = 2\chi_s N - 2\chi_e N \), where \( \chi_s N = \rho NF(q_0)/2 \) is the mean field spinodal. Mimicking this form, we introduce an “apparent” \( \chi \)-parameter, \( \bar{\chi}_a \), into the one-loop
Section 6.4. Results

theory corrected correlation function at $q^*$:

$$NS^{-1}(q^*) = (2\chi_s N - 2\overline{\chi}_a N)v.$$  \hspace{1cm} (6.3.19)

We further express $S^{-1}$ as the sum of mean field value plus correction term:

$$NS^{-1}(q^*) = NS^{-1}(q_0) + N\delta S^{-1}(q^*, \chi_e)$$
$$= (2\chi_s N - 2\chi_e N)v + N\delta S^{-1}(q^*, \chi_e).$$  \hspace{1cm} (6.3.20)

Compare this equation and Eq.(6.3.19), we have

$$\overline{\chi}_a N = \chi_e N - \frac{\rho N}{2} \delta S^{-1}(q^*, \chi_e).$$  \hspace{1cm} (6.3.21)

This equation offers a convenient way of calculating $\overline{\chi}_a$ using $\chi_e$ as the input to the one-loop theory. The self-consistent approximation amounts to replacing the input to one-loop theory by $\overline{\chi}_a$,

$$\chi_e N = \overline{\chi}_a N + \frac{\rho N}{2} \delta S^{-1}(q^*, \overline{\chi}_a).$$  \hspace{1cm} (6.3.22)

6.4 Results

We first present results for wavevector dependence of correlation function at $\chi_e = 0$ and $\chi_e \neq 0$, respectively. The intra- and inter- molecular components are compared for the later case to clarify the origin of the shift in peak position. Then we introduce a self-consistent approximation and focus on predictions to the $\chi$ dependence of the peak intensity of the correlation function, for both symmetric and asymmetric diblock copolymers. A short subsection then follows presenting results on the dimensions of single chain and blocks, and on their $\chi N$ dependence.

As noted in the previous section, the one-loop corrections to the mean field theory scales with $\tilde{N}^{-1/2}$. We choose the $\tilde{N}$ values ranging from 500 to 10000, corresponding to the typical diblock copolymers with low (10 kg/mol)$^{103}$ and high (200 kg/mol)$^{101}$ molecular weights.
6.4.1 Correlations at $\chi = 0$

At $\chi_e = 0$, the intermolecular contribution, $-2\chi_a(q)$, to the total correlation function vanishes for symmetric diblock copolymers, which implies that all fluctuation effects at $\chi_e = 0$ originate from the intramolecular contribution.

The fact that $\delta\chi_a(q)$ vanishes for symmetric diblocks can be understood by noting that: Eq.(6.3.3) for $\bar{G}_{ij}$ reduces to a scalar $\bar{G}$, so that the summation over $k, m$ and $l, n$ in Eq.(6.3.12) can be carried out separately; then by introducing $\bar{\Omega}_i(q,k) \equiv \sum_{klm} \bar{\Omega}_{ik}^{(3)}(q,k_, -k_+)$, Eq(6.3.11) for direct correlations simplifies to $\delta C_{ij} = \frac{1}{2} \int_k \bar{\Omega}_i(q,k)\bar{\Omega}_j(-q,-k)\bar{G}^{-1}(k+)\bar{G}^{-1}(k_-); -2\nu\chi_a(q) = \varepsilon_i\varepsilon_j\delta C_{ij}$ vanishes since $\varepsilon_i\varepsilon_j\cdot\bar{\Omega}_i(q,k)\bar{\Omega}_j(q,k) = 0$ and $\bar{\Omega}_i(q,k)\bar{\Omega}_j(-q,-k)$ for symmetric diblock copolymer.

![Figure 6.2](image)

Figure 6.2: Calculated correlation functions for symmetric diblock copolymer from RPA and one-loop theory at $\chi_e = 0$, showing wavevector dependence. One-loop results are evaluated at $\bar{N} = 500$. Inset: the difference of the two theories, normalized by $\sqrt{\bar{N}}$, which is an universal function of $qR_g$, independent of $\bar{N}$.

Figure 6.2 shows that the correlation function for symmetric diblock copolymer with $\bar{N} = 500$ and at $\chi_e = 0$, evaluated using the RPA theory (dashed line) and the renormalized one-loop theory (solid line), is shown as functions of the wavevector times the radius of gyration. The results are normalized by chain length $N$ as sug-
Section 6.4.1. Correlations at $\chi = 0$

gested by Eq.(6.2.3). The difference of the two, normalized by $\bar{N}^{1/2}$, is given in the inset, which assumes a universal functional form within one-loop theory. The fluctuation correction, although small for this particular $\bar{N}$, is apparent over the entire $q$ range. As we just mentioned, this difference reflects the intramolecular corrections to ideal chain statistics alone. The shape of the curve is similar to the corresponding one for the correction to intramolecular form factor of a homopolymer in the melt (Figure6 in reference\textsuperscript{121} and Figure9 in reference\textsuperscript{122}) in the intermediate and short wavelength $q$ range. The negative correction in the small $q$ region is related to the shrinkage of the mean squared center of mass distance of two blocks, as will be shown in Section 6.4.5.

As the effective repulsion between unlike monomers is turned on, the correlation increases with $\chi_e$ in the $q$ range corresponding to the molecular size: the peak intensity increases and peak width narrows. This trend fails in the vicinity of the mean field spinodal, where the integrals diverge and the straight perturbative theory fails. For $\bar{N} = 500$, this occurs at $\chi_e N \simeq 8.0$. We can improve the theory by invoking the self-consistent or Hartree approximation,\textsuperscript{92} as discussed in Section 6.3.3.

Figure 6.3: Shift in the peak position of correlation function versus $\bar{\chi}_a N$ (a) and $\chi_e N$ (b) for symmetric diblocks with $\bar{N} = 100$, 1000 and 10000. The sub-figure (b) is prepared using the self-consistent approximation discussed in Section 6.3.3. The dots in (b) are Fredrickson-Helfand predictions for $(\chi N)_{ODT}$. 

\[ 114 \]
6.4.2 Shift in the Peak Wavenumber

ROL also predicts a weak but discernible decrease of the peak position, $q^*$ with increasing $\chi_e N$, as shown in Figure 6.3(b) for symmetric diblocks with $\bar{N} = 100$, 1000 and 10000, where $q^*$ is normalized by the mean field value, $q_0 = 1.946/R_g$. In the small $\chi_e$ regime, $q^*$ is greater than $q_0$, which results from the fluctuation correction to the intramolecular correlations. In the large $\chi_e$ regime, the value of $q^*$ monotonically decreases up to about 80% of $q_0$ for $\chi_e N \approx 15$, for all three chains, which is consistent with experimental results close to ODT$^{95,96,98,100–103,105–109}$.

![Figure 6.4: Wavenumber dependence inter- and intra- molecular components to the total correlation functions from the one loop prediction, evaluated for $\bar{N} = 500$ and at $\chi_e N = 8.0$. Following Eq.(6.2.3), to display contributions from each component, the inverse of $S(q)$ is shown. $\rho NS^{-1}_0$: Leibler’s mean field theory prediction. $\rho NF(q)$: the intramolecular part with one-loop correction. $-2\chi_a(q)N$: the intermolecular part with one-loop correction.](image)

To better understand the origin of the change in $q^*$ with $\chi_e$, in Figure 6.4, we show $q$ dependence of the inverse of correlation functions evaluated with mean field theory.
and with ROL, for $\bar{N} = 500$ and at $\chi_e N = 8.0$. The components of corrections, $\delta F(q)$ and $-2\delta \chi_a(q) N$, are also shown. For $q$ ranging between $q^*$ and $q_0$, $-2\delta \chi_a(q) N$ is increasing whereas $\delta F(q)$ decreases, which shows clearly that the decrease of $q^*$ is related to the intermolecular correlations, in accordance with Binder’s conclusion based on Monte Carlo simulations. In the low $q$ region, both $\delta \chi_a(q)$ and $\delta F(q)$ diverge as $q^{-2}$. Eq.(6.2.5) and (6.3.11) imply that the corrections have $|\tilde{\Omega}(q)|^2$ on the denominator, which scales as $q^4$ in the low $q$ regime. The integrals in Eq.(6.3.11) are equal to $N^2 f_i f_j$ times a $q$-independent constant when $q \to 0$, since $\tilde{\Omega}_{mk}^{(3)}(0, k, -k) = N f_i \tilde{\Omega}_{mk}(k)$ and $\tilde{\Omega}_{jl}^{(3)}(0, -k, k) = N f_j \tilde{\Omega}_{nl}(k)$. These terms cancel after the contractions with $\tilde{\Omega}^{-1}(q \to 0)$ and $\varepsilon$. Thus the dominant term in the numerator scales as $q^2$, which cancels with a $q^2$ in the denominator, leaving a $q^{-2}$ dependence of $\delta \chi_a(q)$. Similar reasoning also applies to the intramolecular correction since $\psi_{ijkl}^{(4)}(q, -q, k, -k) \simeq 0 + O(q^2)$ in the low $q$ regime.

6.4.3 Peak Intensity

The self-consistently evaluated inverse peak intensity, $S^{-1}(q^*)$ as a function of $\chi_e N$ is shown in Figure 6.5 for symmetric diblock copolymer with $\bar{N} = 1000$ and 10000. The straight dashed line represents mean field prediction, in which $S^{-1}(q^*)$ linearly depends on $\chi_e N$. One-loop results show negative deviations from the mean field theory already at $\chi_e = 0$ (see also Figure 6.2), which becomes positive for $\chi_e N \gtrsim 6$. The difference decreases as $\bar{N}$ increases, consistent with the fact that one-loop theory is an asymptotic theory controlled by $\bar{N}^{-1/2}$. The curved dashed lines are predictions of F-H theory, which asymptotically approaches one-loop predictions at large $\bar{\chi}_a N$ (demonstrated in Section 6.5), but are distinctly different from that for intermediate $\chi_e N$’s. The curvature of the predictions from both theories for large $\chi_e N$ agree with experimentally measured scattering peak intensities in nearly symmetric diblock copolymers.95,99,101–103,105,106

Figure 6.6 shows the component contributions to $\delta S^{-1}$ from inter- and intramolecular correlations for $\bar{N} = 1000$. In the small $\bar{\chi}_a N$ region, $-2\delta \chi_a(q^*) N$ vanishes at $\chi_e = 0$, assumes small negative value for $\chi_e N \lesssim 2$, then changes the sign and
Section 6.4.4. Asymmetric Diblocks

Both FH theory and Brazovskii’s theory assumes that the cubic term in the effective Hamiltonian gives negligible contribution to the final results. This, by itself, limits their applicability to symmetric diblocks. The nature of the one-loop correction to $S(q)$ behavior near the spinodal is qualitatively different for asymmetric diblocks, as discussed below, using the renormalized one-loop theory.

The correction to the inverse of $S$ can be written as $N\delta S^{-1}(q_0) = v\bar{N}^{-1/2}f(q_0 R_g, \chi N)$, which diverges as $\chi N$ approaches to $\chi_s N$. For convenience, we define $\tau \equiv 2\chi_a N - 2\chi N$. The dominant divergence can be expressed as powers of $\tau$ (See Appendix D). For the intramolecular contribution, the integral in Eq.(6.3.1) is dominated by a term proportional to $\tau^{-1/2}$. For the intermolecular part, the integral in Eq.(6.3.11) is dom-
Section 6.4.4. Asymmetric Diblocks

Figure 6.6: Component contributions from inter and intra molecular correlations, versus $\bar{\chi}_a N$, for $\bar{N} = 1000$.

Inated by a $\tau^{-1}$ and a $\tau^{-1/2}$ term. It can be shown (Appendix D) that the coefficient to $\tau^{-1}$ term vanishes at the mean field critical composition.

Therefore, close to the spinodal, we can approximate $N\delta S^{-1}(q_0)$ for diblock copolymers with $b_A = b_B$ but with asymmetric compositions by

$$ N\delta S^{-1}(q_0) \simeq \frac{v}{N^{1/2}} \left[ \frac{a(\chi N)^c}{\sqrt{\chi_s N - \chi N}} + \frac{b(\chi N)^c}{\chi_s N - \chi N} + d \right] $$

This expression works very well for block fraction $f$ between 0.35 and 0.65 and for $\chi N$ above 8. We found the following fits for parameters $a, b, c$ and $d$, as functions of $f$:
Figure 6.7: $\delta S^{-1}(q_0)$ versus $\tilde{\chi}_a$ for diblock copolymer with $b_A = b_B$, at various block fractions $f = 0.35, 0.40, 0.45$ and 0.50. Solid lines are fitted results using Eq.(6.4.1). The dash-dotted perpendicular line are ODT calculated from SCFT.
Section 6.4.5. Size of Molecule and Blocks

\begin{align*}
a(f) &= 0.652 - 0.799 \left( \frac{1}{2} - f \right)^2 \\
b(f) &= -20.8 \left( \frac{1}{2} - f \right)^2 \\
c(f) &= 2.50 + 0.857 \left( \frac{1}{2} - f \right)^2 \\
d(f) &= -7.58 - 1460 \left( \frac{1}{2} - f \right)^2.
\end{align*}

(6.4.2)

Coefficients \( b \) vanished for symmetric diblocks, and we recover the behavior that is qualitatively consistent with FH theory. For asymmetric diblocks, however, we obtain a stronger divergence of opposite sign that becomes apparent only very close to the ODT. The quality of the fits are illustrated in Figure 6.4.1, which shows that the above approximation is quantitatively good even close to \( \bar{\chi}_a N = 0 \). For asymmetric diblocks (\( f = 0.35 \) and \( f = 0.40 \)), the stronger \( \tau^{-1} \) divergence can dominate even prior to the order-disorder transition.

6.4.5 Size of Molecule and Blocks

The dimension of diblock molecule is characterized by the radius of gyration of each block (\( R_{g,A}^2 \) and \( R_{g,B}^2 \)) and of the whole molecule (\( R_g^2 \)), and the mean squared distance of the center of mass of two blocks (\( R_{AB}^2 \)), which are related by

\[ R_g^2 = f_A R_{g,A}^2 + f_B R_{g,B}^2 + f_A f_B R_{AB}^2. \]

(6.4.3)

\( R_{g,i}^2 \) is related to the value of intramolecular correlation function \( \Omega_{ii} \) in the Guinier regime through \( \Omega_{ii}(q \to 0) = N f_A^2 (1 - q^2 R_{g,i}^2 / 3) / v. \) \( \Omega_{AB} \) contains the missing information for \( R_g^2 \). The definition of correlation functions can be used to show (Appendix C)

\[ \Omega_+ \simeq \frac{N}{v} \left( 1 - \frac{q^2}{3} R_g^2 \right). \]

(6.4.4)
This equation combined with the low-q expansion of $\Omega_{ii}$ and Eq. (6.4.3) leads to the expansion: $2\Omega_{AB} - f_B\Omega_{AA}/f_A - f_A\Omega_{BB}/f_B \simeq -N f_A f_B q^2 R_{AB}^2/(3v)$. Or, in a more symmetrical form

$$|\Omega| \simeq \left( \frac{N f_A f_B}{v} \right)^2 \frac{q^2}{3} R_{AB}^2.$$  \hspace{1cm} (6.4.5)

This also implies, in the low q regime, $S(q, \chi_e = 0) = |\Omega|/\Omega_+ \simeq N f_A^2 f_B^2 q^2 R_{AB}^2/(3v)$. For non-zero $\chi_e$, the $1/q^2$ term in $\chi_a N$ gives additional contribution to low-q expansion of $S$. For ideal chains, $R_{AB}^2 = 2(R_{g,A}^2 + R_{g,B}^2)$. For ideal symmetric chains, $R_{g,A}^2 = R_{g,B}^2 = R_{g}^2/2$ and $R_{AB}^2 = 2R_{g}^2$.

Figure 6.8: $\chi$ dependence of the fractional change in the radius of gyration of one block ($R_{g,A}^2$) and of whole molecule ($R_{g}^2$), and the center of mass distance of two blocks ($R_{AB}^2$), for a symmetric diblock. The curve labeled with $\delta(q^*)^{-2}$ represents the corresponding fractional change in the length scale $(q^*)^{-1}$, $N^{1/2}/((q_0/q^*)^2 - 1)$, calculated using data for $N = 10000$.

The fluctuation correction is found by analyzing the low q behavior of the corrections to the three intramolecular correlation functions. Figure 6.8 shows the $\chi$ dependence of the predicted size changes for a symmetric diblock copolymer, nor-
Section 6.4.5. Size of Molecule and Blocks

Normalized to be $\bar{N}$ independent. At $\chi = 0$, all corrections are negative, whose origin has been discussed in reference $^{121}$. $R_{AB}^2$ initially decreases slightly with $\chi N$, then increases significantly for $\chi N \gtrsim 5$. Its negative sign for small $\chi N$’s causes the suppression of $S(q)$ in the small $q$ regime (inset of Figure 6.2). $R_{g,A}^2$ ($R_{g,B}^2$) decreases monotonically with $\chi N$. This agrees with the picture that two blocks tend to avoid the increasingly unfavorable contacts by shrinking and by locally segregating from each other. The sum of the two, $R_g^2$, is dominated by $R_{g,A}^2$ for small $\chi N$ and by $R_{AB}^2$ later on. In particular, $\delta R_g^2/R_g^2 = -1.42\bar{N}^{-1/2}$ at $\chi N = 0$, the same as for homopolymers. $^{122}$ For $\bar{N} = 500$, using the values at $\chi N = 0$ as reference, the fractional change of $R_g$, $R_{AB}$, $R_{g,A}$ at $\chi N = 10$ are 2.5%, 9.4% and -5.5% respectively.

![Figure 6.9](image-url)

Figure 6.9: The change of mean squared distance of center of mass of two blocks ($R_{AB}^2$, left) and the radius of gyration of one block ($R_{g,A}^2$, right), for block fraction $f = 0.1, 0.2, ..., 0.9$. The abscissa is $\chi N$ normalized by the mean field spinodal.

The dependence of the size changes on the block fractions is shown in Figure 6.9, in which the $x$-axis ($\chi N$) is normalized by the respective mean field spinodal. Figure
Section 6.5. Relationship of ROL and FH Theory

6.9(a) represents the results for $\delta R_{AB}^2$ and Figure 6.9(b) for $\delta R_{g,A}^2$. Results for $\delta R_{g}^2$ nearly fall onto the same curve (similar to that in Figure 6.8), so are not shown. $\delta R_{AB}^2$ shows a weak $f$ dependence. The correction is slightly more pronounced for asymmetric molecules. For $R_{g,A}^2$, the short blocks shrinks much more than the longer ones and the longer blocks experience an upturn close to the mean field spinodal, the shape becoming similar to that of $R_{g}^2$.

All these quantities diverge as $\tau^{-1/2}$ close to the mean field spinodal, as was discussed in Section 6.4.4.

6.5  Relationship of ROL and FH Theory

The renormalized one-loop theory is related to the FH theory. In reference 128, we show analytically that the FH theory differs from the ROL by terms independent of $\chi N$ at the symmetric composition. In this section, we show that the dominant $\chi$ dependence of the two theories agree with each other close the ODT, but only asymptotically. For systems with moderate $\bar{N}$ values, the use of ROL theory is necessary.

The FH theory works for nearly symmetric diblocks, which mapped Leibler’s free energy onto the Brazovskii model using the composition fields as the order parameter. The effective Hamiltonian reads:

\[
H[\phi] = \frac{1}{2} \int S_0(\mathbf{k}, -\mathbf{k})\phi(\mathbf{k})\phi(-\mathbf{k}) + \\
+ \frac{1}{4!} \int_{\mathbf{k}_1, \mathbf{k}_2, \mathbf{k}_3, \mathbf{k}_4} \Gamma^{(4)}(\mathbf{k}_1, \mathbf{k}_2, \mathbf{k}_3, \mathbf{k}_4)\phi(\mathbf{k}_1)\phi(\mathbf{k}_2)\phi(\mathbf{k}_3)\phi(\mathbf{k}_4)\delta(\mathbf{k}_1 + \mathbf{k}_2 + \mathbf{k}_3 + \mathbf{k}_4)
\]

(6.5.1)

Where the quadratic term is the inverse of mean field $S(q)$ and is approximated by a Lorentzian, $S_0(q) = \tau + \alpha b^2 (q - q_0)^2$. The cubic coefficient vanishes at the symmetric composition. The fourth order coefficient, $\Gamma^{(4)}$, is defined in Leibler’s paper.

Using Brazovskii’s self-consistent expression for the correlation in the homoge-
Section 6.5. Relationship of ROL and FH Theory

Figure 6.10: Correction to $S^{-1}(q_0)$ predicted by the F-H theory (dashed) and by the renormalized one-loop theory (solid) theory in double logarithmic scale. The two theories are asymptotically close as $\bar{\chi}_a$ approaches $\chi_s$.

Coarse-grained phase of a symmetric diblock copolymer, they found:

$$ S^{-1}(q) - S_0^{-1}(q) = \frac{1}{2V\rho} \int_\Gamma^{(4)}(q, -q, k, -k) S(k). \quad (6.5.2) $$

They looked for the solution of the form $S^{-1}(q) = N^{-1}r + ab^2(q - q_0)^2$, which is appropriate for system close to the transition point. Here $r$ denotes $2(\chi_sN - \chi N)$ and $b$ is the statistical segment length. For $\chi$ close to $\chi_s$, the Lorentzian in the integrand of Eq.(6.5.2) is sharply peaked. The dominant $\chi$-dependent term is then given by:

$$ \rho N \delta S^{-1}(q) = \frac{6}{4\pi} \frac{(q_0R_g)^2}{\sqrt{2}} \frac{N\gamma^{(4)}(q_0, q_0)}{\alpha^{1/2}} \cdot \frac{1}{N^{1/2}\sqrt{\chi_sN - \chi N}}. \quad (6.5.3) $$
Section 6.5. Relationship of ROL and FH Theory

where $\gamma^{(4)}$ denotes the angular average of $\Gamma^{(4)}$, defined by

$$
\gamma^{(4)}(q, k) = \frac{1}{4\pi k^2} \int d\mathbf{k}' \delta(|\mathbf{k}'| = k) \Gamma^{(4)}(\mathbf{q}, -\mathbf{q}, \mathbf{k}, -\mathbf{k}). \tag{6.5.4}
$$

For symmetric diblocks we find $N\gamma^{(4)}(q_0, q_0) = 170.795$ and $\alpha = 1.214$, which yields:

$$
\rho N\delta S^{-1}(q) \simeq \frac{198.08}{N^{1/2}\sqrt{\chi N - \chi N}}. \tag{6.5.5}
$$

In Figure 6.10, the results of Eq.(6.5.5) are compared to the one-loop theory. In the double logarithmic scales, Eq.(6.5.5) is a straight line, which is asymptotically close to the one-loop prediction for $\bar{\chi}_a \gtrsim 10$. The difference for $\bar{\chi}_a \lesssim 10$ is large, which implies that ROL should be used for quantitative comparison between theory and experiments.

The first quantitative comparison between the FH theory and the experimental data was made in reference\textsuperscript{100}, for a nearly symmetric ($f_A = 0.55$) PEP-PEE diblock copolymer. It was found that the FH theory has almost quantitatively described the nonlinear behavior of the scattering peak intensity in the temperature range near the order-disorder transition. In Appendix E, we re-analyzed this set of data in order to compare the FH and the ROL theories within the relevant parameter range ($\bar{N}$ and $\chi N$). In the original work, the temperature dependence of the chain’s radius of gyration is estimated using that of $q^*$ by assuming the RPA prediction is valid (thus $q^* T R_g(T)$ is a constant). They found that 6012 < $\bar{N}$ < 10978 and that the FH theory fits the experiments very well in the range 10.57 < $\chi N$ < 12.52. We find, however, using the independently determined statistical segment lengths from the homopolymer data, 3361 < $\bar{N}$ < 4325 (and a slightly different $\chi N$ range, 11.22 < $\chi N$ < 12.96\textsuperscript{101}), less than half of the original estimate. For both of these two ranges of $\bar{N}$, we find the FH and ROL theories are nearly indistinguishable for $\chi N \gtrsim 10.57$ (Appendix E). We believe the second estimate of $\bar{N}$ is more reliable. But if this is the case, the original success of the FH theory may be accidental since its $\bar{N}$ value is more than two times that of the proper one, and more careful comparisons between either theory and the experimental data seems to be desirable.
6.6 Conclusions

We presented quantitative predictions of the renormalized one-loop theory to the fluctuation effects on collective composition correlations and on single chain geometrical properties of diblock copolymers. The numerical results are based on, and the successful removal of the high-q components consistently supports, the previous analytical work.\(^{57}\)

The ROL unambiguously incorporates fluctuation effects of order \(\bar{N}^{-1/2}\) into RPA theory for the correlation function \(S(q)\) of a homogeneous melt. The results retained the Ornstein-Zernicke form and naturally breaks the inverse of \(S(q)\) into intramolecular and interactions-induced components.

The intramolecular part includes the form factors of two blocks and inter-block correlations, whose low q limit are related to the size of blocks and molecule. The deviation from the ideality is reflected in the monotonic decrease of the radius of gyration of both blocks \(R_{g,i}^2\), and the increase of the mean squared distance of center of mass of two blocks \(R_{AB}^2\), with the increasing repulsive interaction \(\chi N\), consistent with previous simulation results. For asymmetric diblock copolymers, short blocks experience stronger shrinkages and more asymmetric molecules experience stronger stretching (greater \(R_{AB}^2\)).

The theory predicts that the peak position monotonically decreases with \(\chi N\). In the non-interacting case, the peak position is greater than the RPA value, which results from the fluctuation correction to the intramolecular correlations. The effect is opposite in the large \(\chi N\) regime, where the intermolecular effects dominates. The amount of fractional change can not be accounted for by chain stretching effects, which agrees with simulation results.\(^{113}\)

Similarly, the predicted deviation of the peak intensity of \(S(q)\) from the RPA results is positive and dominated by intramolecular correlations in the small \(\chi N\) regime, and is negative and dominated by intermolecular correlations in the large \(\chi N\) regime. For diblock copolymer at the critical composition, the non-linearity of the inverse peak intensity at large \(\chi N\) is analogous to the conventional FH theory, which is shown to share the dominant \(\chi N\) dependence with ROL. For non-critical
compositions, a much stronger $\chi N$ dependence originating from the intermolecular correlation and ignored by the FH theory, may become dominant at the ODT, as shown in Figure 6.7.
CHAPTER 7

Monte Carlo Simulation of Diblock Copolymer

The cleanest way of testing the theory discussed in the previous chapter is doing computer simulations. We did Monte Carlo simulation for symmetric diblock copolymers of varying chain lengths in boxes of various sizes using an off-lattice model with a filling fraction of 0.7. The thermodynamic perturbation theory proposed recently is used to map the model parameter to the phenomenological $\chi$ parameter, which enables an unambiguous comparison of the measured correlation function with predictions of the renormalized one-loop theory. The wavevector dependence in the small interaction regime fully agrees with the theory and the $\chi$ dependence of correlation peak intensity is also qualitatively captured.

7.1 Introduction

Extensive simulation studies of diblock copolymer melts or concentrated solutions have been reported, a thorough review of which is provided in Appendix F. Historically, most of them have used lattice models. The basic questions that have been addressed include: how is the collective structure factor in the disordered states mod-
Section 7.2. Simulation Details

ified by the fluctuation effects, how are the dimensions of a single chain varying with
temperature, and what is the nature the order disorder transition (ODT). Recently,
directly exploring the (ordered) phase diagram also became possible. However, the
quantitative comparison of these studies with theories (RPA, FH theory, and SCFT)
remains elusive, largely because the unambiguous relation between the interaction
parameter in the models and the phenomenological $\chi$ parameter is absent. Further
difficulties include the appropriate choice of the order parameter needed by the accurate
determination of ODT and the effects of finite box size for any study involving
ordered phases.

Diblock copolymers in both disordered and ordered states, and the order-disorder
transition, have been studied in both lattice and continuum models. The non-ideal
single chain statistics in disordered states has been convincingly established by the
Binder’s group.\textsuperscript{113,114} Although a modified form of RPA structure factor can fit the
correlation data, a consistent theoretical description is lacking. Further, the quantitative
comparisons of the ordered phase simulation results with SCFT and the ODT
data with FH theory are largely missing become the reliable relation between the inter-
action parameters in the simulation models and the phenomenological $\chi$ parameter
in the theories is absent.

In this chapter, we use the recently proposed perturbation theory to estimate
the relation between $\chi$ and model interaction parameter, and use that to quantita-
vitively test various predictions made by the renormalized one-loop theory discussed
in Chapter 6 on the collective correlations and single-chain properties. The model
we are using is discussed in the next section and detailed comparisons are given in
Section 7.3.

7.2 Simulation Details

We choose to use a continuous model, similar to that introduced by Grest and Kremer
\textit{et al.},\textsuperscript{119} hoping that the effects of the box size and shape are smaller compared to
the lattice model, for systems still disordered but close to the ODT.

The composing beads of a diblock copolymer are connected via a harmonic bond-
Section 7.2.1. Monte Carlo Moves

The potential: \( \kappa (l - l_0)^2/2 \). \( l_0 \) and the elastic constant \( \kappa \) determine the average bond length and the chain rigidity, respectively. A contiguous block of beads are tagged by A, and the remaining, B. The same bonding potential is used for bonds in the A block, the B block and at the A-B junction. Pairs of beads interact via a symmetric and purely repulsive shifted Lennard-Jones potential with a cut-off:

\[
u_{ij} = \varepsilon_{ij} w(r) = \varepsilon_{ij} \left[ 4(r/\sigma)^{-12} - 4(r/\sigma)^{-6} + 1 \right],
\]

\[
\varepsilon_{AA} = \varepsilon_{BB}, \quad \varepsilon_{AB} = \varepsilon_{BB} + \alpha,
\]

where the range of interaction is set by \( \sigma \). The convention is adopted such that no pairing interactions for bonded beads are counted, including the pairs at junctions. Throughout this work, we use \( \sigma \) and \( k_B T \) as the length and energy units and choose \( \kappa = 400.0, \quad l_0 = 1.0 \) and \( \varepsilon_{AA} = 1.0 \). The additional strength \( \alpha \) sets the incompatibility between A and B blocks, which is directly related to the \( \chi \) parameter. The precise relation will be discussed when the comparison of the simulation to theory is being attempted.

Symmetric diblock copolymers of length \( N = 16, 32, 64 \) and 128 are simulated in the \( NVT \) ensemble. Molecules fill a cubic box of length \( L \) with density \( \rho = 0.7 \) (number of beads divided by the box volume). Periodic boundary conditions are used as usual. At least two box lengths are used for each molecular length in order to monitor the finite size effects. The details are tabulated in Table 7.1.

Each system ran at a series of \( \alpha \) values ranging from 0 to a value close to phase separation. The athermal case (\( \alpha = 0 \)) is first simulated, then \( \alpha \) is increased stepwise. Prior to any measurement, the system is allowed to relax for a period longer than the auto-correlation time determined from the Van Hove function.

### 7.2.1 Monte Carlo Moves

We implemented 4 types of molecular moves to effectively sample the configuration space, which are illustrated in Figure 7.1. The chain-flip move switches the labels of the two blocks. The reptation move displaces the chain backbone forward or backward by one step. The single rebridge move erases and re-grows a single bead
in the middle of a molecule. The double rebridge move “cuts” two molecules at the same (relative) point and re-builds them by connecting the head piece of one molecule to the tail piece of the other. To reduce the energy cost, the exchange process is accompanied by the erasing and regrowth of two beads at the cutting point, which may be thought as two single rebridge moves. In the erasing and regrowth steps of the reptation and rebriding moves, the configuration bias algorithm is used to generate several candidate positions. The details of the single and double rebridge moves are described in Appendix G.

![Typical molecular moves in Monte Carlo simulation.](image)

We augment these molecular moves with the hybrid-MC/MD move,\textsuperscript{129} in which a short period of Molecular Dynamics integration is used to generate trial configurations. The fraction of hybrid-MD move is chosen such that it consumes about half the total computation time. The length of MD integration is chosen to make the acceptance rate to be about 75%. The typical acceptance rates for the molecular moves are displayed in Figure 7.2, plotted versus $\alpha$. The chain flip moves become increasingly difficulty as $\alpha$ increases, as a result of clustering of monomers of the same
Section 7.2.1. Monte Carlo Moves

type. The rates of other moves decrease only marginally, in agreement with the expectation that the energy cost is dominated by the local arrangements of monomers. The acceptance rates for reptation (0.04 \sim 0.06), single rebridge (\approx 0.45) and double rebridge (\approx 0.03) moves are nearly independent of the system size and slightly increase with chain lengths (the reptation move shows stronger dependence).

![Diagram](image)

Figure 7.2: Typical acceptance rates of 4 molecular Monte Carlo moves in our simulations, for \( N = 32 \) and \( L = 30 \). The maximum \( \alpha \) value corresponds to \( \chi N \simeq 25 \).

For systems having large \( \alpha \) values, the replica exchange (parallel tempering)\textsuperscript{130} technique is used. An ordered sequence of systems with increasing \( \alpha \) values are simulated simultaneously and, based on the prescribed policy, they periodically attempt to exchange configurations with the neighboring ones. The acceptance rate is determined using the Metropolis rule. The \( \alpha \) values cover a broad range, and the increments are chosen to obtain (approximately) 23\% acceptance rate for each neighboring pairs as suggested in reference\textsuperscript{131}. Typically, around 20 independent replicas are needed to bridge the slowly relaxing systems to the sufficiently faster ones. As demonstrated in Figure 7.3, the acceptance rate for the replica exchange move is largely determined by the product of \( \delta \alpha \) between neighboring replicas and \( \delta \langle \theta \rangle \), regardless of chain lengths.
Section 7.2.2. Correlation Function

(and system size), where $\langle \theta \rangle$ is total “amount” of effective A-B type contacts, defined analogous to that for the intramolecular AB contacts in Eq.(I.0.2). The explicit formula in Figure 7.3 is used to design the $\alpha$ parameters for replicas in this study.

![Figure 7.3: Master curve for the dependence of acceptance rate of replica exchange move on the difference of interaction parameters between neighboring replicas and on $\langle \theta \rangle$. Data from three chain lengths are included.](image)

Figure 7.3: Master curve for the dependence of acceptance rate of replica exchange move on the difference of interaction parameters between neighboring replicas and on $\langle \theta \rangle$. Data from three chain lengths are included.

7.2.2 Correlation Function

We are primarily interested in the monomer density correlation function. The microscopic density profile at a particular simulation snapshot is defined by: $\rho_{\alpha}(r) = \sum_{i}^{M_{\alpha}} \delta(r_{i} - r)$, where the summation is taken over all $M_{\alpha}$ particles of type $\alpha$. The deviation from average is defined by $\delta\rho_{\alpha}(r) = \rho_{\alpha}(r) - M_{\alpha}/V$, based on which the correlation function (Ursell function) is defined by

$$S_{\alpha\beta}(r, r') = \langle \delta\rho_{\alpha}(r)\delta\rho_{\beta}(r') \rangle = \langle \delta\rho_{\alpha}(r - r')\delta\rho_{\beta}(0) \rangle. \quad (7.2.2)$$
Section 7.2.2. Correlation Function

Where $\langle \rangle$ means the statistical average over all sampled snapshots, which depends only on the difference $\mathbf{r} - \mathbf{r}'$ in homogeneous liquids. We define the Fourier transform of $\delta \rho_\alpha(\mathbf{r})$ by

$$
\delta \rho_\alpha(\mathbf{q}) \equiv \int d\mathbf{r} e^{i\mathbf{q} \cdot \mathbf{r}} \delta \rho_\alpha(\mathbf{r}),
$$

and that of $S(\mathbf{r}, \mathbf{r}') = S(\mathbf{r} - \mathbf{r}')$ (intensive) by

$$
S_{\alpha\beta}(\mathbf{q}) \equiv \frac{1}{V} \langle \delta \rho_\alpha(\mathbf{q}) \delta \rho_\beta(-\mathbf{q}) \rangle.
$$

Under the periodical boundary condition, the wavevector $\mathbf{q}$ must be commensurate with the simulation box: $\mathbf{q} = n_x 2\pi/L_x + n_y 2\pi/L_y + n_z 2\pi/L_z$, where $n_x$, $n_y$ and $n_z$ are integers. For a particular $\mathbf{q}$, we also average $S_{\alpha\beta}(\mathbf{q})$ over all wavevectors of the same magnitude, and denote the result by $S_{\alpha\beta}(\mathbf{q})$.

The above definition for $S$ includes the correlation of all monomers present in the system. If only those on the same molecules are counted, $S$ divided by the number of molecules represents the intramolecular correlation function, which we denote by $\Omega$ from now on.

To monitor the finite size effect, we compare the box size $L$ with the correlation length of density fluctuation $R_c$ and the lamellar domain spacing $d$ at the ODT. Leibler’s mean field theory predicts that, for symmetric diblocks, $d = 2\pi/q_0$ and $q_0 = 1.95/R_g = 1.95\sqrt{6}/(\sqrt{N}b)$. We have measured the statistical segment length $b = 1.404$. Thus $d = 1.76\sqrt{N}$. The ratios of the box lengths in our simulation and $d$ are tabulated in Table 7.1. The smallest box ($L = 21$) reported in this work holds 6272 particles.

<table>
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<th>$L$</th>
<th>$20.769976$</th>
<th>$29.955490$</th>
<th>$43.203292$</th>
<th>$62.309929$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$n$</td>
<td>6272</td>
<td>18816</td>
<td>56448</td>
<td>169344</td>
</tr>
<tr>
<td>$N=16$</td>
<td>3.0</td>
<td>4.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>32</td>
<td>2.1</td>
<td>3.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>64</td>
<td>1.5</td>
<td>2.1</td>
<td>3.0</td>
<td>4.3</td>
</tr>
<tr>
<td>128</td>
<td>1.0</td>
<td>1.5</td>
<td>2.1</td>
<td>3.0</td>
</tr>
</tbody>
</table>

Table 7.1: Ratio of box size $L$ and mean field domain spacing $d$. $n$: number of particles; $N$: chain length.

The correlation length is obtained by expanding the RPA expression for the cor-
relation function near $\chi_s N$ (mean field spinodal) and $q_0$. Thus

$$S(q) \simeq \rho N \left( \tau + F''(x^*) R_g^4 (q^2 - q_0^2 / 2)^2 \right)^{-1}, \quad (7.2.4)$$

where $\tau \equiv 2(\chi_s N - 2\chi N)$ and $F''(x^*) = 0.9624$. Its inverse Fourier transformation

$$S(r) = \left( \frac{\rho N}{4\pi q_0 R_g^4 F''(x^*)} \right) \frac{e^{-r/r_c}}{r/r_c} \sin(q_0 r). \quad (7.2.5)$$

Where the correlation length

$$R_c = \sqrt{\frac{2F''(x^*)}{\tau}} q_0 R_g^2 = \frac{2.70}{\sqrt{\tau}} R_g, \quad (7.2.6)$$

which becomes greater than $d$ in the vicinity of $\chi_s N$ while $\chi_s N - \chi N \lesssim 0.35$.

### 7.3 Results

We present simulation results for two types of quantities: correlation functions and geometric dimensions of individual molecules and composing blocks. For the former, both collective and single chain correlations are studied, at vanishing and non-vanishing $\alpha$. These results are compared to the renormalized one-loop theory predictions. To make the comparisons, we have relied on the perturbation theory proposed recently to map the $\alpha$ parameter in the simulation model to the $\chi$ parameter needed by the theory.

#### 7.3.1 Mapping $\alpha$ to $\chi$

In the literature, $\chi$ has been properly identified as a quantity proportional to $\alpha$ for small $\alpha$, the proportionality constant being $z_c$. For lattice models, $z_c$ is the average contact number at a randomly selected site. For continuum models, it is the overlap integral of the radial distribution function and the pair interaction potential. In both cases, $z_c$ is found in the $\alpha = 0$ reference state, to reflect the unperturbed liquid
Section 7.3.2. Correlation at $\alpha = 0$

This intuitive picture is hardly justified, and has two apparent flaws: first, the $z_c$ as defined depends on the chain length originating from the correlation hole effects; secondly, the potentially important nonlinear effects for large $\alpha$ can not be easily taken into account. Morse and Chung$^{73}$ have proposed a clean solution to this problem. They combined two closely related theories, a thermodynamic perturbation theory with respect to $\alpha$ and the self-consistent field theory defined using $\chi$, and applied them to a combinatorial binary blend. By assuming that the self-consistent theory becomes accurate for the system of infinitely long chains, they identified a Taylor expansion for $\chi$ in terms of $\alpha$:

$$\chi = z_c \alpha + z_2 \alpha^2 + ...$$

(7.3.1)

where $z_c$ and $z_2$ are coefficients to be determined from homopolymer blends simulations, which are addressed thoroughly in the thesis work of another PhD student, Jun Chung, of Prof. Morse’s group. The precise determination of $z_2$ is more difficult, so throughout this work, only $z_c$ is used, which is defined by

$$z_c = \lim_{N \to \infty} \rho \int dr g_{AB}(r; N) w(r).$$

(7.3.2)

Here $g_{AB}$ is the radial distribution function of B (A) monomers surrounding an arbitrary A (B) monomer in a binary A+B homopolymer blends. For our model, $z_c = 0.2965$. The $\chi$ parameter defined by $z_c \alpha$ is the same as the $\chi_e$ introduced in Chapter 5 and 6. So from now on we denote it $\chi_e$.

7.3.2 Correlation at $\alpha = 0$

We measured $S_{AB}(q)$ and $S_{AA}(q)$ for a series of waves satisfying the commensurate condition, and verified that $S_{AB}(q) = -S_{AA}(q)$, as a result of the incompressible constraint, so will focus on $S_{AB}(q)$ from now on (which is negative, so in what follows we use $S(q)$ to denote $-S_{AB}(q)$). The results for $N = 64$ and $\alpha = 0$ in boxes of length $L = 30$ and $L = 43$ are shown in Figure 7.4. Table 7.1 shows that these boxes can
Section 7.3.2. Correlation at $\alpha = 0$

hold around 2.1 and 3.0 lamellae domains, or 6.7 and 9.6 $R_g$. The fact that two sets of data seem to fall onto the same underlying smooth curve indicate that the finite size effect is small in this case.

![Fitting of RPA and RLO data](image)

Figure 7.4: Wavevector dependence of collective correlation function at $\alpha = 0$, $N = 64$, for $L = 30$ and $L = 43$. The dashed line is the RPA prediction and the solid line is the one-loop theory prediction.

We first test the RPA theory\textsuperscript{7} using this data, which needs $qR_{g,0}$ and $\chi_eN$ as input. We measured $R_g$ from independent simulations at $\alpha = 0$ for several $N$ values up to 256, and fitted $R_g(N)/N$ by a quadratic function of $N^{-1/2}$, which yields $b = 1.404$ for infinitely long chains. $R_{g,0}$ is calculated from $b$ by $(N/6)^{1/2}b$. $\chi_e = 0$ since $\alpha = 0$, and there is no ambiguity about the coordination number. The prediction is shown as dashed line in the figure, which clearly underestimates the correlation near the correlation hole peak and the peak position is also to the left of the simulated result. It has been reported that, by treating $R_g$ and $\chi_eN$ as fitting parameters (denoted by $\lambda^*$ and $\delta$ in Binder group’s work, respectively),\textsuperscript{113,116} the simulation data can be described by RPA functions. We have verified that this approach fits our own data, too, but decided not to adopt it.

We instead believe that the difference is due to fluctuation effects and attempt to
compare the data to the renormalized one-loop theory (ROL) described in Chapter 6, which has successfully built the fluctuation correction into the RPA theory. The ROL theory needs $q R_{g,0}$ and $\chi e N$ (= 0 in this case) as inputs, and the fluctuation correction scales as $\bar{N}^{-1/2}$. $\bar{N}$ value for $N = 64$ in our model is 240.2, corresponding to very short polymers of molecular weight a few hundred g/mol. The ROL prediction is shown as solid line in the figure, which captures the full $q$ dependence of $S(q)$. We find the same level of agreement for all other chains simulated.

In Figure 7.5, we show simulation results for intramolecular correlation function $\Omega_{AA}$ and $\Omega_{AB}$, for all chains studied in this work. For symmetric diblock copolymers, $\Omega_{AA} = \Omega_{BB}$, so only two independent correlations functions need to be measured, $\Omega_{AA}$ and $\Omega_{AB}$. The ROL theory predictions are also shown, which fit the $\Omega_{AB}$ data very well, even for the shortest chain ($N = 16$). The agreement between $\Omega_{AA}$ and theory is slightly worse, but is apparently improving as the chain length is increased, implying a relatively large end effects or higher order fluctuation effects. For two short chains, $\Omega_{AB}$ become negative in large $q$ region, which is well captured by one-loop theory but can not be described by any RPA type fitting.

At $\alpha = 0$, for dense polymer melts, the intermolecular contributions to $S(q)$ vanishes as we have commented in the previous chapter. The difference between RPA theory and the data or ROL theory are fully due to fluctuation corrections to Gaussian chain statistics predictions of intramolecular properties. Similar comparisons have been made for the structure factor of pure homopolymer melts.\textsuperscript{121,122} Edwards and Muthukumar’s previous justification\textsuperscript{133} of Flory’s conjecture (that the polymer chain in dense melt is essential ideal) applies to imaginary chain of infinite length. Now these earlier studies and the current one demonstrate that the intramolecular excluded volume interaction is not fully balanced by the intermolecular repulsions for any finite chain.

### 7.3.3 Correlation at $\alpha \neq 0$

For diblock copolymers, the quantities most relevant to experiments are the peak intensity and peak position of $S(q)$. In this section, we look at their $\alpha$ and $N$ de-
Section 7.3.3. Correlation at $\alpha \neq 0$

Figure 7.5: $q$ dependence of diblock intramolecular correlation functions for $N = 16$ ($L = 21$), 32 ($L = 30$), 64 ($L = 30$) and 128 ($L = 43$), at $\alpha = 0$. The solid curves represent one-loop theory predictions with no fitting parameter. The dashed curves are RPA predictions.
Section 7.3.3. Correlation at $\alpha \neq 0$

dependence prior to the ODT, and compare them to the predictions of RPA, ROL and Fredrickson-Helfand theories. We use $\chi_e = z_c\alpha$ when $\chi_e$ is needed as the input to the theory.

Collective Correlation

Since $S(q)$ is measured at discrete $q$ values, in order to get the accurate peak position ($q^*$) and peak intensity ($S(q^*)$), we fit the data points by a smooth function and find its peak values. Since ROL theory corrects the inverse of RPA prediction by a smooth function of the $q$ at fixed $\chi N$, we mimic it by using the following function:

$$S^{-1}(q, \alpha) = \tilde{S}^{-1}(q, \chi eN = 0) + [a(\alpha)q^4 + b(\alpha)q^2 + c(\alpha)]$$

(7.3.3)

where $\tilde{S}$ is the RPA prediction (evaluated at $\chi eN = 0$). Fitting parameters $a$, $b$ and $c$ depend on $\alpha$. The Levenberg-Marquardt algorithm\(^{30}\) is used in the fitting. The fitting quality is extremely good for all chain lengths and $\alpha$ values except inside the transition regime (as demonstrated in Figure 7.6), where the peak become very narrow and because of the finite box size, no good resolution can be achieved in that region, so that the fitted $S(q^*)$ only represents a lower bound.

Figure 7.7 shows the results of $NS^{-1}(q^*)/2$ for $N = 64$ in boxes of lengths $L = 30$ and $L = 43$. The fact that two sets of data nearly collapse indicate a small finite size effect for $\chi eN$ up to around 20. The straight dashed line is the RPA prediction. The deviation of simulation from it is negative for small $\chi eN$ and becomes positive for $\chi eN \gtrsim 6$. The overall shape is similar to those of previous simulation and experimental studies. The negative correction is due to the fluctuation correction to intramolecular properties, as discussed in the previous section. The positive correction is due to the increasingly important intermolecular correlations, as the molecules start to cluster locally to avoid unfavorable interactions.

The solid line shown in Figure 7.7 is the ROL prediction. It appears to capture the overall trend of simulation results nearly quantitatively, for this particular $\bar{N}$ value. However, the agreement should not be taken too seriously since we have used only linear relation between $\chi e$ and $\alpha$, and there is no guarantee that the linear relation is
Section 7.3.3. Correlation at $\alpha \neq 0$

Figure 7.6: Fitting quality for the $q$ dependence of $S(q)$ for a few representative $\chi_e$ values. The labels and curves are simulation and fitting results, respectively. The $\chi_e N$ values labeled are calculated using $\chi_e = 0.2965\alpha$. 

141
Section 7.3.3. Correlation at $\alpha \neq 0$

Figure 7.7: $\chi$ dependence of the inverse peak intensity of diblock correlation functions, for $N = 32$, $L = 30$ and $L = 43$. The diagonal dashed line is RPA prediction. The dashed curve is FH theory prediction. The solid line line is renormalized one-loop theory prediction.

sufficient for this broad range of $\alpha$. For comparison, the curved dashed line in Figure 7.7 is the prediction of the FH theory, which by construction is an asymptotic theory, and is expected to be valid only for anomalously long chains near the ODT. So it is not surprising that the prediction is quite off from the simulation results when $\chi_e N$ is small.

In Figure 7.8, analogous results are shown for all other chains, two sets of data in two different boxes included for each chain length. The data shows no finite box size effects except for very large $\chi_e N$ and for $N = 64$ and 128. The data follows similar pattern as those for $N = 64$, only that the difference between those and the RPA predictions consistently decreases as $N$ increases, indicating that the fluctuation corrections become smaller for longer chains.

The agreements between the simulation data and ROL for small $\chi_e N$ are excellent for each chain, implying that the intramolecular correlations are adequately described
Section 7.3.3. Correlation at $\alpha \neq 0$

Figure 7.8: $\chi$ dependence of the peak intensity of diblock correlation functions, for chain lengths 16, 32, 64, and 128. Data from two simulation boxes are given for each chain length. The diagonal dashed line is RPA prediction. The solid lines are renormalized one-loop theory predictions.

by this theory in this regime. In the large $\chi_e N$ regime, the theory works poorly for $N = 16$ but seems to be very good for other chains. However, since we have only used the linear term to convert $\alpha$ into $\chi_e$, at this level, we do not know whether the disagreement for short chain is due to the inadequacy of the linear relation between $\chi_e$ and $\alpha$ or is due to the failure of ROL itself.

Figure 7.9 shows the $\bar{\chi}_a N$ dependence of the measured $q^*$ (peak position) for all chains and the comparison to the one-loop theory predictions. The apparent $\chi N$ is defined using the measured peak intensity:

$$\bar{\chi}_a = 10.495 - \rho N S^{-1}(q^*)/2,$$

which, increasing with $\alpha$, avoided the use of the linear relation between $\chi_e$ and $\alpha$, and
Figure 7.9: χ dependence of the peak position of diblock correlation functions, normalized by the value of RPA results. The solid lines represent renormalized one-loop theory predictions. For each chain length, the data from two different simulation boxes are shown.
Section 7.3.3. Correlation at $\alpha \neq 0$

enables a direct comparison between simulation and theory. $q^*$ has been normalized by $q_0$, the value of $q^*$ given by the RPA theory. The monotonic decrease agrees with experimental findings. But we note that the fractional change of $q^*$ changed the sign for most chains (which occurs at around $\chi_e N = 3.5$ if linear relation between $\alpha$ and $\chi_e$ is used). The positive correction at $\chi_e = 0$ is due to the intramolecular corrections. The ROL predictions have captured properly the trend of simulation data. As the chain length is increased, the agreement is clearly improved. For $N = 64$ and 128, the theory works almost quantitatively.

Intramolecular Correlation

The $q$ dependence of intramolecular correlation functions $\Omega_{AA}$ and $\Omega_{BB}$ at $\alpha = 0$ are shown in Figure 7.5. The functional shape changes only marginally for nonzero $\alpha$, and here we are interested in the $\alpha$ dependence of the values at $q^*$. Since the functions are sampled only at discrete $q$ values, to get values at $q^*$, we choose to fit $\Omega_{ij}(q)$ by the following expression

$$\Omega_{ij}(q, \alpha) = \tilde{\Omega}_{ij}(q) + \frac{a_1(\alpha)q^2 + a_2(\alpha)q^4}{1 + b_1(\alpha)q^2 + b_2(\alpha)q^4 + b_3(\alpha)q^6}. \tag{7.3.5}$$

where $\tilde{\Omega}_{ij}$ are Gaussian chain predictions, independent of $\alpha$. The fraction is chosen to represent properly both the low and high $q$ behaviors. The order of polynomials are determined empirically. Similar to the collective correlation functions, Levenberg-Marquardt algorithm is used in the fitting.

Figure 7.10(a) shows $\Omega_{ij}(q^*)$ for all chain lengths, normalized by $N$. $\bar{\chi}_{\alpha} N$ is used for the abscissa. The dashed lines represents the RPA predictions: $\Omega_{AA}(q^*) = 0.146$ and $\Omega_{AB}(q^*) = 0.050$. The deviations from RPA predictions is caused by fluctuations, and the approaches to that as $N$ increases are apparent. It also seems that the $\Omega_{AA}$ is subjected to greater fluctuation effects, compared to $\Omega_{AB}$.

In Chapter 6, we mentioned that, for dense polymer melts, the intramolecular contribution to the inverse of collective correlation function can be summarized by a
Section 7.3.3. Correlation at \( \alpha \neq 0 \)

Figure 7.10: \( \chi \) dependence of diblock intramolecular correlation functions at \( q^* \) for different chain lengths, and that of the correction to the intramolecular contributions to the collective correlation function, \( F \equiv 2/(\Omega_{AA}(q^*) - \Omega_{AB}(q^*)) \).

Form factor (Eq. (6.2.4)):

\[
F = \frac{\Omega_{AA} + \Omega_{BB} + 2\Omega_{AB}}{\Omega_{AA}\Omega_{BB} - \Omega_{AB}^2},
\]

which equals \( 2/(\Omega_{AA} - \Omega_{AB}) \) for symmetric diblocks. In Figure 7.10(b), the deviation of \( F \) from the RPA prediction is plotted versus \( \bar{\chi}_a N \), and compared to the that of the one-loop theory prediction. The theory has predicted the correct magnitudes, but fails in capturing the shape of the curves for short chains, although it is apparent that the agreement is improved as \( N \) increases. For all chains, the theory overestimates the fluctuation effects for \( \bar{\chi}_a N \) close to 10.495. Nevertheless, \( \delta F \)'s, or the correction to intramolecular contributions to \( S^{-1} \), are negative in all cases, which, when combined with Figure 7.8, demonstrates clearly that the pre-transitional fluctuations are dominated by the intermolecular correlations, where \( \delta S^{-1} \) is positive.
The single chain dimensions have been extensively studied in the previous work. Here we focus on using our results to examine the one-loop theory prediction.

As pointed out in Chapter 6, the dimensions of diblock copolymers are characterized by the mean squared radius of gyrations of each block ($R_{g,A}$ and $R_{g,B}$) and whole molecule ($R_{g}$), and by the separation of the two block center of mass ($R_{AB}^2$). These quantities are related by (Eq.(6.4.3)):

$$R_{g} = f_A R_{g,A}^2 + f_B R_{g,B}^2 + f_A f_B R_{AB}^2.$$  (7.3.7)

The simulated results are shown in Figure 7.11, 7.12 and 7.13, respectively.

Figure 7.11: Molecular $R_g^2$, normalized by $R_{g,0}^2 = N b^2 / 6$. $\bar{\chi_a} = 10.495 - S^{-1}(q^*)/2$. The right graphs shows the fluctuation effects, rescaled by $\bar{N}^{1/2}$, and comparison to one-loop theory predictions.

In all cases, $R_{AB}^2$ increases monotonically with $\bar{\chi_a} N$, reflecting the effects of the increased repulsions. Rescaling the correction to $R_{AB,0}^2$ by $\bar{N}^{1/2}$ reasonably collapses the data (with small remaining dispersion), which also agrees roughly with the one-loop theory prediction. On the other hand, $R_{g,A}^2$ initially decreases, then increases slightly for the three longer chains. The fact that the corrections do not obey the
We have simulated disordered symmetric diblock copolymers using the continuum model and measured various single chain and collective properties, for chain length $N = 16$, 32, 64 and 128, to quantify the fluctuation correction to the mean field predictions and test the renormalized one-loop theory discussed in Chapter 6.

For the collective properties, we simulated the $q$ dependence of the monomer density correlation function, $S(q)$. The results differ from the RPA prediction already at $\alpha = 0$, and the difference can be fully accounted for by the one-loop theory. For

$\tilde{N}^{1/2}$ scaling implies a greater end/junction effects or the higher order fluctuation corrections. Thus it is not so surprising that the one-loop results greatly overestimate the shrinkage. $R^2_g$ results from the combining effects of these two quantities. It increases monotonically for two shorter chains, $N = 16$ and $N = 32$, and shows very small non-monotonic behavior for $N = 128$, which appears to approach the shape of the one-loop theory prediction.

## 7.4 Conclusions

Figure 7.12: Mean squared block center of mass separation, $R_{AB}^2$, normalized by $R_{AB,0}^2 = N b^2 / 3$. The right graphs shows the fluctuation effects, rescaled by $\tilde{N}^{1/2}$, and comparison to one loop theory predictions.
Section 7.4. Conclusions

Figure 7.13: Radius of gyration of a single block, $R_{gA}^2$, normalized by $R_{gA,0}^2 = Nb^2/12$. The right graph shows the fluctuation effects, rescaled by $\bar{N}^{1/2}$, and comparison to one-loop theory predictions.

nonzero $\alpha$, we focused on the $\alpha$ dependence of the peak intensities and peak positions. The inverse of peak intensity is smaller than the mean field (RPA) theory prediction in the small $\alpha$ region and becomes greater than that for large $\alpha$’s. The peak position at $\alpha = 0$ is higher than the RPA theory prediction and decreases monotonically as $\alpha$ increases, by up to 15% to 20%. To compare the results with theory, we rely on the recently proposed first order perturbation theory\textsuperscript{73} to map $\alpha$ to $\chi_e$. For the two longer chains, $N = 128$ and 64, the self-consistent ROL theory captures the trend of $S^{-1}(q^*)$ versus $\chi_e N$ nearly quantitatively. For the two shorter chains, $N = 32$ and 16, the agreement is still good in the small $\chi_e N$ regime, where the fluctuation effects are dominated by the single chain properties, but becomes increasingly worse in the large $\chi_e N$ regime. However, at this moment, we do not know how much the discrepancy can be attributed to the inadequacy of the first order perturbation theory in relating $\alpha$ to $\chi_e$ or to the failure of the ROL theory. To avoid the ambiguity of mapping $\alpha$ to $\chi$ in any further comparison, we used an apparent $\chi$ instead of $\chi_e$, defined using Eq.(7.3.4). Except the shortest chain, $N = 16$, the results for $q^*$ versus $\bar{\chi}_a$ agree with the ROL theory prediction in nearly the whole range of $\bar{\chi}_a$.  

149
Section 7.4. Conclusions

For the single chain properties, we investigated the intramolecular correlation functions and the dimensional characterizations of individual molecules and blocks. The results versus $\bar{\chi}_a$ are also compared to the ROL theory predictions.

For the intramolecular correlation functions, we studied two independent intramolecular correlation functions, $\Omega_{AA}(q)$ and $\Omega_{AB}(q)$. In case of $\alpha = 0$, the $q$ dependence of inter-block correlation, $\Omega_{AB}$, is adequately described by the ROL theory for all chain lengths. That of the intra-block correlation, $\Omega_{AA}$, is slightly off from the theory prediction. The convergence towards the ROL theory prediction is slower. For the dense polymer melt, the inverse of the collective correlation function can be separated into the intra- and intermolecular parts. The former can be represented by the $F$ function defined in Eq.(7.3.6). We measured this quantity at the peak wave vector. The results versus $\bar{\chi}_a$ shows large discrepancy from those of ROL theory predictions, for chain lengths 16 and 32, but the discrepancy becomes evidently smaller as chain length increases (Figure 7.10(b)).

For dimensional properties, we studied the squared radius of gyration of each block ($R_{g,A}^2$) and the mean squared center of mass separation ($R_{AB}^2$) of the two blocks, mirroring the corresponding theoretical study of the previous chapter. Since the molecular radius of gyration is the weighted summation of these two, we only summarize the results for $R_{g,A}^2$ and $R_{AB}^2$. For these quantities, our results have confirmed many conclusions in previous studies.\(^8,113\) We further tested the theory predictions by plotting the results versus $\bar{\chi}_a$. For $R_{AB}^2$, the theory gives a very good description in the full $\bar{\chi}_aN$ range. But for $R_{g,A}^2$, the theory prediction differs from the results significantly, indicating a large higher order fluctuation or end/junction effects.

In summary, predictions of the ROL theories to various equilibrium properties of the disordered diblock copolymers have been tested quantitatively using the off-lattice simulation. The theory works reasonably well for many quantities, especially the collective properties, but not for all, \textit{e.g.}, those involving the intra-block properties ($\Omega_{AA}$ and $R_{g,A}^2$). Compared to the FH theory, the ROL theory shows obvious improvements for the predictions to the collective properties and provides numerous predictions for the single chain properties which is absent in the FH theory. The $N$ in the system of the longest chain length is 480, close to the lower bound of the experimental studies,
Section 7.4. Conclusions

for which the fluctuation effects are relatively small, but not negligible, especially in the region prior to the order-disorder transition. For more realistic systems with \( \bar{N} \) values greater than this, it is expected that the ROL theory can serve as a reliable alternative (other than the FH theory) for studying pre-transitional fluctuation effects.
The renormalized one-loop theory is a coarse-grained theory for composition fluctuations in dense polymer melts. It is expected to capture the universal phenomena occurring at large length scales, which is independent of atomic details or specific simulation models, for sufficiently long chains. We have tested the theory using continuum model simulation results in Chapter 7. In this chapter, we use two lattice models to test the same theory and the idea of universality.

The comparisons require, at a minimum, two independently measured parameters: the statistical segment length and the effective coordination number. For Vassiliev and Matsen’s FCC lattice data, we re-analyzed their reported results and extracted the numerical values. For Müller’s BFM (Bond Fluctuation Model, a well studied model) data, we used his unpublished results and the parameters reported in the literature. The comparisons of their simulation results to the theory are shown in the next two sections. The possibility of mapping these results onto our continuum model is explored in the third section.
Section 8.1. Vassiliev and Matsen’s Data

8.1 Vassiliev and Matsen’s Data

Vassiliev and Matsen simulated diblock copolymers on an FCC lattice with the smallest cubic length \( d \) and the box size \( L \cdot d \). The fixed bond length is \( l = \sqrt{2}d \). The monomer occupied the volume \( V = \frac{L^3}{2} \cdot d^3 \). The filling fraction of the FCC lattice is \( \phi = \frac{nNd^3}{V} \cdot 0.8 \), so the density of the monomers is \( \rho = \frac{4}{(2d)^3} \cdot 0.8 = 0.4d^{-3} \). We estimate the statistical segment length by fitting the data of \( R_g(6/N)^{1/2}/l \) at \( \varepsilon = 0 \) versus \( \bar{N}^{-1/2} \) to a straight line. The result (for chain length 20, 30, 40) is shown in Figure 8.1(a), and can be summarized by

\[
R_g(6/N) = \left(1.237 - \frac{0.471}{N^{1/2}}\right)\sqrt{2d}. \tag{8.1.1}
\]

Figure 8.1: (a) Scaling of radius of gyration at \( \varepsilon = 0 \). (Fig.9(a) of.9) (b) Scaling of the average AB contact number at \( \varepsilon = 0 \) (Fig.7(a) of.9)

In Chapter 5, we have shown using ROL that fluctuation effects produces an \( N^{-1/2} \) correction to the \( R_g \) of a homopolymer. But a diblock copolymer in case of \( \varepsilon = 0 \) is identical to a homopolymer, so it implies the statistical segment length is just the slope of the fit, \( b = 1.237\sqrt{2}d \). This tells us that, in their model, \( \bar{N} = N\rho^2b^6 = 4.586N \). The slope to \( \bar{N}^{-1/2} \) is \( 0.471\sqrt{4.586} = 0.815 \). This should be compared to the theoretical value, 1.4. The difference may be attributed to the higher order fluctuation effects (notice the small \( N \) values used in this model) or the model specific details.

153
Section 8.1. Vassiliev and Matsen’s Data

The average AB contact number $\langle n_{AB} \rangle$ is analogous to $\theta$ we defined in Eq. (I.0.1). We plotted their athermal data for this quantity versus $\bar{N}^{-1/2}$, and found that it fits a straight line $\langle n_{AB} \rangle / V = 0.9957 + 2.0562 N^{-1/2}$, as shown in Figure 8.1(b). This quantity is related to the coordination number by ($f_A = f_B = 0.5$)

$$z(N) = \langle n_{AB} \rangle / (\phi V) / (f_A f_B) = 4.9785 \left( 1 + \frac{4.422}{\bar{N}^{1/2}} \right). \tag{8.1.2}$$

From this we can identify the effective coordination number needed to relate $\varepsilon$ and $\chi$, $z_c = 4.9785$. This is about 40% of the number (12) used in Vassiliev and Matsen’s original paper. They found $\chi N$ is around 40 at the ODT, which is much higher than the mean field theory prediction. We note that using $z_c$ brings 40 to 16.6. The quantitative comparison to the F-H theory is shown in Table F.1.

Figure 8.2: Comparison of Matsen’s correlation data to the one-loop theory.

The slope of the fit does not match the theoretical prediction, though. Eq. (I.0.4) gives 3.186, but the data fits to $2.0562 \sqrt{4.586} = 4.422$. As Figure I.2 shows, we suspect that this disagreement is caused by the fact that the intramolecular contact number approaches the asymptote slowly. Matsen and Beardsley recently measured the
Section 8.1. Vassiliev and Matsen’s Data

Figure 8.3: Diblock dimension data of Matsen’s FCC lattice model. (a) $N^{1/2} \delta R_g^2 / R_{g,0}$ versus $\chi_a N$. (b) $N^{1/2} \delta R_{AB}^2 / R_{g,0}^2$ versus $\chi_a N$. (c) $N^{1/2} \delta R_{g,A}^2 / R_{g,0}^2$ versus $\chi_a N$. 

155
inter-molecular contacts independently, which fits $z(N) = 4.9533 \left(1 + 2.41\bar{N}^{-1/2}\right)$. The slope agrees with the theory prediction 2.639 reasonably well.

The repolotted Matsen’s data using $b = 1.237\sqrt{2}d$ and $z_c = 4.9533$ are shown in Figure 8.2(a) for peak intensity and Figure 8.2(b) for peak position. The corresponding one-loop predictions using the corrected $\bar{N}$ values are also shown in the same plots. For $q^*$, the data are plotted versus $\bar{\chi}_a N$ and agree with one-loop results very well. For $S^{-1}(q^*)$, the data are plotted versus $\chi_e N$, for which the linear approximation is used. Similar to the case for our continuum model, the one-loop theory captured the behavior in the small $\chi_e N$ regime, but appears to be quite off for large $\epsilon$. We speculate that the nonlinear effects in the functional dependence of $\chi$ on $\alpha$ may be at least a partial cause.

The data of sizes of single chains and blocks are also compared to the one-loop theory, as shown in Figure 8.3, prepared in a way analogous to Figures 7.11(b), 7.12(b) and 7.13(b) for the continuum model. Two sets of data exhibit very similar behavior, and their relations to the one loop theory mirror each other closely.

### 8.2 Müller’s Data

The statistical segment length for the BFM is $b = 3.244,84$ and the effective coordination number $z_c = 2.1,82,122$ These enable a straightforward comparison between the data and theory. We merely note that since an attractive interaction is assigned for contacts of monomers of the same type, the strength being equal to that of the repulsive interaction between unlike monomers $\epsilon$, so $\chi_e = z_c(2\epsilon)$ up to the linear order.

Figures 8.4 shows the $q$ dependence of the collective correlation function for $N = 64 \ (\bar{N} = 291)$ at $\epsilon = 0$, compared to the RPA and one-loop theory predictions. The results are analogous to Figure 7.4 for our continuum model, demonstrating that the one-loop theory is able to capture the fluctuation effects associated with the intramolecular correlations.

Figure 8.5(a) and 8.5(b) show the data for the inverse peak intensities and the peak positions. The level of agreement for the peak positions is slightly better than
Section 8.2. Müller’s Data

Figure 8.4: Comparison $q$ dependence of the correlation functions in BFM model and the one-loop theory (at $\varepsilon = 0$).

Figure 8.5: Comparison of Müller’s correlation data to one-loop theory.
Matsen’s data. For the peak intensity, except in the extremely small $\chi_e$ region, the discrepancy is greater.

8.3 Test of Universality

In the previous and current chapters, we compared the predictions of the ROL theory to the $\chi_e N$ dependence of the inverse of peak intensities of correlation functions with BSM (bead-spring model, continuum), FCC lattice, and BFM lattice simulation results, respectively. The ranges of $\bar{N}$ covered are comparable for the three models: 60$\sim$480 for BSM, 92$\sim$183 for FCC, and 73$\sim$291 for BFM. But the levels of agreement between theory and data are quite different: it appears to work surprisingly good for the BSM model in a broad range of $\chi_e N$ but only works in the extremely narrow (small) $\chi_e N$ regime for the other two lattice models.

There are two possible explanations for this discrepancy. On the one hand, since the one-loop theory is the lowest order extension beyond the mean field theory, it may not capture the whole fluctuation effects for the range of $\bar{N}$ studied. But this could not explain the fact that the same theory works for the BSM model, but not for the two lattices models. So even if this is one of the reasons, there must exist other factors that can explain the apparent difference among different models. On the other hand, we have noted in previous chapter (Eq.(7.3.1)) that $\chi_e$ is generally cast into a Taylor expansion in $\alpha$, but for all three models, we have used only the linear relation to calculate $\chi_e$ from $\alpha^1$, which may well be insufficient. Before we found any reliable method to estimate the higher order coefficients, $z_2, z_3$ and so on, and obtain a reliable correspondence between $\chi_e$ and $\alpha$, we can not separate the effects of these two factors.

However, we may assume that the long range correlations in polymer liquids is universal for sufficiently long chains and that irrespective of the microscopic models (lattice type and interaction type), a $\chi$ parameter can be identified and be used to quantify the universal behavior. In particular, for the inverse peak intensity, as suggested by the systematic loop expansions for the fluctuating field theory developed

\footnote{We used $\alpha$ rather generically, which is $\varepsilon$ for the FCC model and is $2\varepsilon$ for the BFM model.}
Section 8.3. Test of Universality

in Ref.\textsuperscript{56}, the universal function could be written as

\[ \rho NS^{-1}(q^*; \alpha, N) = \tilde{h}(\bar{\chi}_e(\alpha)N, \bar{N}) \equiv \tilde{h}(\bar{\chi}_e, \bar{N}) \equiv h(\bar{\chi}_e, \bar{N}), \quad (8.3.1) \]

where \( \bar{\chi}_e(\alpha) \equiv \chi_e(\alpha) \cdot (N/\bar{N}) = \chi_e(\alpha)/(\rho^2 b^6) \). The re-parametrization enables us to avoid referring to both \( N \) and \( \bar{N} \) when comparing different models. Evidently \( \bar{\chi}_e \) can also be cast into a Taylor series of \( \alpha \), whose coefficients are specific to models but are independent of \( N \). In general, the function \( h \) includes fluctuation effects up to any order. The one-loop theory represents merely the lowest order approximation to it. For any specific model, if we know how to map \( \alpha \) precisely to \( \bar{\chi}_e \) and the functional form of \( h \), we would be able to predict the behavior of \( \rho NS^{-1}(q^*) \). In other words, the universality assumption states that, if the system’s behavior is universal, for each possible microscopic model, a function \( \bar{\chi}_e(\alpha) \) can be found, such that a single function \( h(\bar{\chi}_e, \bar{N}) \) describes correctly the behavior of \( \rho NS^{-1}(q^*) \).

![Figure 8.6: Map Matsen’s BFM data onto BSM model. \( \chi_e = 0.2965\alpha \) is used for BSM model data. \( \chi_e = 4.9533\varepsilon + 15.0\varepsilon^2 + 650.0\varepsilon^3 \) is used for FCC lattice data. For clarity, the lattice data points are connected with straight lines.](image)

We now show that, the data collected from three different models are in harmony
with this assumption, even without knowing the precise functional form of $\bar{\chi}_e(\alpha)$ for each model. Consider two models having interaction parameters $a$ and $b$ respectively, for which functions $\bar{\chi}_e(a) \equiv A(a)$ and $\bar{\chi}_e(b) \equiv B(b)$ can be found such that $\rho N S^{-1}(q^*; a, \bar{N}) = h(A(a), \bar{N})$ and $\rho N S^{-1}(q^*; b, N) = h(B(b), \bar{N})$. Notice further that $h(B(b), \bar{N})$ may be re-written as $h(A \circ A^{-1} \circ B(b), \bar{N}) \equiv h(A(a_b), \bar{N})$, where $\circ$ represents the functional composite, $A^{-1}$ is the inverse of $A$, and $a_b \equiv A^{-1} \circ B(b)$. This means that if $h$ is truly universal, a mapping $A^{-1} \circ B$ can be used to evaluate $a_b$ from $b$, such that in the model $A$, an interaction $a_b$ will yield the same results as an interaction $b$ in model $B$, provided that they use the same $\bar{N}$. Moreover, if the mapping $A^{-1} \circ B$ has been found to match the data using a single $\bar{N}$ value, it should work for all other $\bar{N}$ values. This last statement thus provides a strong test for the idea of universality.

We have collected results from two lattice models and one off-lattice model, and is thus in a position to test the idea of universality. Since the exact $\bar{N}$ values do
Section 8.3. Test of Universality

Figure 8.8: Direct comparisons of $q^*$ for FCC and BSM models. The data of FCC model are connected with straight lines. Notice that $q_0 \propto R^{-1}_{g,0}$, so plotting the ratio is the same as plotting $q^* R_{g,0}$.

not match, we re-designed the chain lengths in our BSM model, and measured the inverse peak intensity for the correlation function with $\bar{N}$ ($N$) values agreeing with those of both FCC and BFM model results. The mapping results between the FCC and BSM model, between the BFM and BSM model are shown in Figures (8.6) and (8.7) respectively. In both figures, we have used the linear relation between $\chi_e$ and $\alpha$ for the BSM model data set. So if the universality assumption is correct, what are plotted are the functions $h(\bar{\chi}_e, \bar{N})$ versus $z_c A^{-1}_{BSM} (\bar{\chi}_e) \bar{N}$, $z_c$ being the effective coordination number in the BSM model, 0.2965, for three different $\bar{N}$ values. For the two lattice models, the nonlinear terms are allowed when evaluating the $x$-axis – which may represent an composite operation, $z_c A^{-1}_{BSM} \circ B_{lattice}$, to the $\alpha$ values. The nonlinear coefficients come from those of $A^{-1}_{BSM}$ (or $A_{BSM}$) and $B_{lattice}$, which we do not know at this stage. We have to manually adjust those numbers to obtain the best collapse of data from on- and off- lattice models. We found that for the pairs of either FCC and BSM models or BFM and BSM models, a single mapping function $(A^{-1} \circ B)$ can be devised to nearly collapse the data for three different $\bar{N}$ values. The
agreements for the BFM and BSM pair are particularly good. The small discrepancy for $\bar{N} = 92$ in the FCC and BSM comparison may be attributed to model specific contributions associated with chain ends or junctions.

A cleaner test of the idea of universality can be made by noticing that, for each model, two quantities can be measured simultaneously: peak position ($q^*$) and peak intensity ($S(q^*)$) of the collective correlation function. If there exist universal descriptions to both $q^* R_{g,0}$ and $S(q^*)$ which are independent of models and are controlled by $\bar{N}$, when these two quantities are plotted versus each other, one for $x$-axis and another for $y$-axis, the results should be independent of models, provided that the same $\bar{N}$ values are used. This provides us with another test, and furthermore, the test will be more reliable, since no assumptions for the functional forms of $\chi_e(\alpha)$ are needed. For the model pairs of FCC/BSM and BFM/BSM, the comparison results are shown in Figures 8.8 and 8.9 respectively. As a reminder, we note here that the $x$-axis $\bar{\chi}_a \bar{N} \equiv 10.495 - v N S^{-1}(q^*)/2$ is uniquely determined by $S^{-1}(q^*)$. For the FCC/BSM pair, as $\bar{N}$ values are increased from 92 to 183, the agreements between
models are clearly increased, until for $\bar{N} = 183$, they falls nearly on top of each other. For the BFM/BSM pair and for $\bar{N} = 73, 146$ and 291, results from two models nearly fall on top of each other. This type of data collapse strongly supports the idea of universality, and implies that the idea becomes asymptotically correct as the $\bar{N}$ value is increased (based on FCC/BSM pair). The small difference for the FCC/BSM pairs and for the two smaller $\bar{N}$ values may be attributed to the facts that the chain lengths are not sufficiently long ($N = 20$ and 30), for which the model specific effects may become non-negligible.

8.4 Conclusions

We collected two sets of lattice model simulation results and compared them to the predictions of the one-loop theory. The level of agreements for each comparison set is comparable to that of the off-lattice set, except the results for $S^{-1}(q^\star)$ using large $\alpha$ or $\varepsilon$ values. The exception is in contrast to what we found in the previous chapter, where the agreements are good up to very large $\alpha$ values. This raises the question of the importance of nonlinear effects in the $\chi_e-\alpha$ relations and the doubt over the idea of universality. To at least partially resolve the conundrum, we attempted the possible mapping between models, using available data sets.

Two types of mapping between two lattice results and our continuum model results are attempted. On the one hand, we mapped the inverse of peak intensity of the lattice data sets to our model, by allowing implicitly the presence of nonlinear terms in the $\chi_e-\alpha$ relations. This map suggests that the three data sets are compatible with the idea of universality, although the question of how to assess the importance of the nonlinear effects is still illusive. On the other hand, we compared directly the relationship $q^\star-S^{-1}(q^\star)$ between lattice models and the BSM models. The unambiguous universal behavior is clearly seen for the longest chain in the FCC model for the two chain lengths in BFM model.
I summarize the key results for various topics touched in this thesis and give my own perspective of questions or problems which may be worth answering in the future.

**Numeric SCFT and Triblock Copolymer Phase Behavior**

The symmetry-adaptive pseudo-spectral versions of the solution to the modified diffusion equations and of the stress calculation were implemented; A hybrid Broyden-Newton-Raphson iteration method was implemented to solve SCFT equation; The $F^0$ triblock copolymer phase behaviors were explored systematically, which was accompanied with the weak segregation theory analysis; The symmetry-adaptive perturbation were incorporated and were used to study the spinodal stability limit of gyroid (as the continuation of Ranjan’s thesis work) and $Fddd$ (Appendix J) phases in diblock copolymers.

The phase behavior of non-frustrated ($\chi_{AC} \gg \chi_{AB} \cong \chi_{BC}$) triblock copolymers have been thoroughly explored. The composition dependence, chain length dependence (up to a relatively high segregation regime), and the dependence on the ratio $k = \chi_{AC}/\chi_{AB}$, of the topology of the phase diagrams are explored. The discrep-
ancy among three earlier studies (Matsen’s, Erukhimovich, and ours) is removed. The analogous study on a model system representing poly(isoprene-styrene-ethylene oxide) triblock copolymer matches with experimental results very well.\textsuperscript{43,44} In particular, the phase window of the $F_{dddd}$ network phase agrees with the experimental discovery.

The current codes in Prof. Morse’s group is highly efficient for phases with known symmetry and in regimes of intermediate segregations. The potential improvements may address the following questions:

(1) Memory problem: The explicitly stored Jacobian matrix and chain contour discretizations consume the majority of the computer memory. The later one can only be relieved by parallelizing the code and distribute the burden. In case that the Jacobian dominates, \textit{e.g.}, for less symmetric phase, both the storage and the initial inversion may be problematic. The alternative is to use the Jacobian free iteration, such as the GMRES,\textsuperscript{31} or to use a certain mixing rule.

(2) Symmetry constraints: The current code is based on the symmetry of the phase, which is best used when augmented with less accurate but more flexible real space method. To explore the potentially more complicated $F^1$ and $F^2$ triblock copolymers, the combination of the two seems to be a better strategy.

(3) Generalization: The code now can handle linear polymers with Flory-Huggins type interactions. It may be generalized to be able to also carry out computations for molecules of complex architecture (which needs a proper abstraction of the molecular “structure”) and for systems involving hydrogen bonding or electrostatic interactions in poly-electrolytes.

Since SCFT has evolved into a reliable theoretical tool for understanding the phase behavior of polymeric materials, the scope of its application could be greatly expanded into, \textit{e.g.}, periodic structures in polymer solutions, non-periodic polymer brushes and micelles, and multi-block copolymers with more complicated architectures. Since systems having large polydisperse is attracting increasing interests nowadays, the question such as the effects of the polydispersity on the spinodal spectra in diblock copolymer ordered phase may be worth looking at. Another interesting question may be to look at the geometric properties such as the curvature distribution of the $F_{dddd}$
phase (The other classical phases have been analyzed).

**Renormalized One-Loop Theory**

Fluctuation effects in binary homopolymer blends and diblock copolymers have been studied using the renormalized one-loop theory. In both cases, the collective correlation functions in the disordered states, as well as the single chain (block) properties were studied separately. The fluctuations effects were found to be significant for intra-molecular properties for small $\chi$ and become dominated by inter-molecular correlation for large $\chi$.

In the blend case, the theory’s obvious success is its ability to nearly quantitatively capture the single chain properties when $\chi$ is small, as demonstrated in the comparison with the simulation studies of Beckrich et al. for pure homopolymers. The theory also provides a quantitative treatment of the $N$-dependent depth of the correlation hole in the melt. For large $\chi N$, in the blend case, the theory predicts a shift in the critical $\chi$ values by an amount proportional to $\bar{N}^{-1/2}$.

In the diblock case, the theory nearly quantitatively captures the $q$-dependence of the intra-molecular correlation for small $\chi N$. It predicts that fluctuation correction to the peak intensity of the correlation function is positive in the small $\chi N$ regime and becomes negative for large $\chi N$. It also predicts a decrease in the peak position with $\chi N$ and that, close the ODT, the shift in $q^*$ is dominated by the inter-molecular correlations. Regarding the relation of this theory to the conventional one, we showed that its behavior is asymptotically equivalent to the Fredrickson-Helfand theory for extremely large $\chi N$. Many of the theoretical predictions have been confirmed in the direct simulation studies.

Theoretical development: On the homopolymer blends side, the theory fails to capture the critical behavior characteristic of the Ising universality class. The predicted shift in critical $\chi N$ appears to be too big. A natural next step would be to combine the current theory with the method of renormalization group to study the critical behavior. On the diblock side, the biggest problem seems to be constructing a properly renormalized theory for the ODT, which will be very useful for comparison with experiments and simulations. In a long term and from a purely theoretical
viewpoint, it seems to be worth generalizing the renormalization at one-loop level to the (linear) multi-block copolymers in order to solidify the idea: the generalization of renormalizing the statistical segment lengths and the effects of the junctions and chain ends may be obvious, but that of the renormalization of several $\chi$ parameters may be not. Before the theory has been thoroughly examined with simulations and experiments, it may be premature to generalize (beyond the formal level) the theory to two-loop or high order approximations.

Further examination of the theory: Besides making comparison with simulation studies, it will be invaluable to systematically re-analyze existing experiments for measuring the temperature, composition and $N$ dependence of $\chi$ parameters, from both homopolymer blends and diblock copolymers, by comparing the fluctuation corrected correlation functions to those measured.

**Simulations**

A continuum model for symmetric diblock copolymers of various lengths were simulated in NVT ensemble with several box sizes. Various Monte Carlo moves were implemented to improve the sampling efficiency, including configuration biased chain flip, reptation, single and double chain re-bridging, which were combined with occasional MD integrations and the parallel tempering (replica exchange) algorithm. The collective correlation functions of the homogeneous phase were measured and compared to the one-loop theory prediction. Quantitative agreements were found in the small $\chi N$ regime. In the large $\chi N$ regime, the agreement is less satisfying but is still better than that of the Fredrickson-Helfand theory. At this stage, we have used a linear correspondence between the microscopic interaction parameter in the simulation model and $\chi$, which may well be insufficient and may cause the failure of the theory for large $\chi N$’s. By collecting simulation data from two lattice models, and using the mapping procedures described in Section 8.3 to compare different models, we have shown that certain forms of the non-linear relation can be used to demonstrate that there exists a universal description for the fluctuation phenomena, irrespective of the model details.

The next step would be to simulate ordered phases. Based on the reports of
previous simulation works: reducing the elastic constant in the model and allowing the unphysical bond crossing may be a better strategy to equilibrate ordered phases and obtain large $\bar{N}$ values (Of course, given the fact that the ordered phase is more susceptible to the boundary condition, the box size may also need to be increased to accommodate greater $R_g$). Another important modification is to use the NPT ensemble, so that the size and shape of the simulation boxes may be adjusted automatically. After successfully simulating the ordered phase, the location of ODT may be examined carefully and compared with the available theory.

Long term perspective: The successful simulation of gyroid phase using an off-lattice model by the Escobedo’s group suggests that directly simulating more complicated ordered phases now becomes possible. Later on, direct and realistic simulations of molecules with complicated architectures may become an alternative routine to probe the phase behavior other than SCFT, which is a better strategy since the fluctuation effect is naturally built in.


BIBLIOGRAPHY


BIBLIOGRAPHY


BIBLIOGRAPHY


BIBLIOGRAPHY


BIBLIOGRAPHY


178


BIBLIOGRAPHY


181


We discuss the $k$-dependence ($k \equiv \chi_{AC}/\chi_{AB}$) of the spinodal surfaces and critical lines for symmetric ABC triblocks at both the symmetric and asymmetric compositions, calculated using the method explained in Chapter 3.

A.1 Spinodal Surface

In Chapter 3 we have discussed the $k$-dependence of the spinodal lines in the AC-isopleth. The results can be summarized in a more compact way which will also reveal the dependence on the chain length and the composition. We have noted that the AC-modulated and B-modulated spinodals intersect for $k < 2$. The locus of the intersection points (DSP) are now plotted in the $\chi_{AC}-\chi_{AB}$ plane, Figure(A.1). Each point on this orbit is accompanied by a distinct value of $f_B$, and we have labeled the points for which $f_B = 0.1, 0.2, ..., 0.8$ with circles. The points with smaller value of $\chi_{AC}N$ has smaller value of $f_B$. Here and hereafter, we shall call this locus of DSP’s the “degenerate” curve.

The tangent line with slope 0 (the slope of Eq.(3.2.9)) of the degenerate curve
Section A.1. Spinodal Surface

approaches $\chi_{AC}N = 10.5$ and $f_B = 0$ to the lower right limit, which is the spinodal value (also the critical value) for symmetric diblock copolymer. The tangent line of the degenerate curve with slope 4 (the slope of Eq.(3.2.10)) cuts the $\chi_{AB}N$ axis at the value of around 18, which is the lowest value of $\chi_{AB}N$ of the spinodal curve in the $A_1A_2$-isopleth for an $A_1BA_2$ triblock copolymer, and touched the degenerate curve at $f_B \approx 0.47$, which is the composition of the minimum on the spinodal in $A_1BA_2$ triblocks in the AC-isopleth (Figure 7 of reference.\textsuperscript{137}) The projective line from the origin to this point has slope $k \approx 0.9$.

From Figure A.1, we can read off the information of the spinodal along the AC isopleth of all symmetric triblock copolymers with specific values of $\chi_{AC}N$ and $\chi_{AB}N$: the type of modulation and the composition at the spinodal. Each symmetric triblock copolymer is represented by a single point in the $\chi_{AC}N$-$\chi_{AB}N$ plane, and the nature of the spinodal is classified into 4 distinct classes.

(1) In the blank region: the homogeneous mixture remains stable to both AC- and B-modulated instabilities. No spinodal exists.

(2) In the AC-modulation region: the spinodal instability is AC modulated. The composition of the spinodal point is found from the intersection of a horizontal curve passing though the point $(\chi_{AB}N, \chi_{AC}N)$ and the degenerate curve. The major portions of $k = 4$ and $k = 2$ belong to this category.

(3) In the B-modulation region: the spinodal instability is B-modulated. If the point lies in the B-modulation region below $\chi_{AC}N = 10.5$, there are two spinodal compositions (Note the shape of B-spinodal in Figure 3.1). A straight line passing through the point $(\chi_{AB}N, \chi_{AC}N)$ with slope 4 will intersect the degenerate curve at two points. The values of $f_B$ at these two points are the spinodal compositions. If the point lies in another B-modulation region, only the larger composition is the valid spinodal composition, since the other one is preceded by the AC-modulated spinodal.

(4) In the “AC+B”-modulation region, there exist two B-modulated spinodal points and one AC-modulated spinodal point. The spinodal compositions are found by the same methods as described above.
Section A.2. Critical Lines

A.2 Critical Lines

The critical behavior of various systems are analyzed numerically by using Eq.(3.2.6). For each composition, one first finds the parameters defining the spinodal, $(\chi_{ij}N)^*$ and $q^*$, then calculates the scalar value $\gamma_3$ by contracting the third order vertex with the corresponding eigenvector. The points at which $\gamma_3$ vanishes yields 3-dimensional critical curves on the spinodal surface.

The number and the topology of the critical curves intimately depends on the relative magnitudes of the interaction parameters, which is quantified by the ratio $k = \chi_{AC}/\chi_{AB}$ for symmetric triblocks. Our numerical examination has yield 4 distinct critical behaviors. The representative results are projected onto the composition triangle and shown in FigureA.2.

(a) $k \geq 2$: Two critical lines. The solid yellow line connects the AC diblock critical point (C.P.) and B point. The critical chain length increases as B point is approached, and goes to infinity eventually. The solid cyan line connects the AB diblock C.P. and BC diblock C.P. The critical chain length increases from both diblock C.P.'s to the AC isopleth. The two critical lines intersect with each other. The value of $f_B$ at the intersection point decreases as the value of $k$ decreases.

(b) $0.9 \leq k < 2$: Two critical lines. The situation is similar to that for $k \geq 2$ except that, the solid yellow line now does not extends all the way to B point and will ends at the singular cusp where AC and B modulated spinodals intersects, which is circled in the figure. The value of $f_B$ at the cusp decreases as $k$ decreases.

(c) $0.4 \leq k \leq 0.9$: Three critical lines exist. The solid cyan one connecting AB diblock C.P. and BC diblock C.P. persists but the middle of the curve is curved towards AC isopleth. The solid yellow line which ends at the singular cusp persists. A new heart-shaped loop is developed in the center of the triangle. For any value of $k$ in this category, this third curve will pass through the point labeled with star, at which $f_B \approx 0.49$, and ends at the singular cusp. As the value of $k$ decreases, the heart-shaped loop enlarges and moves closer to the critical line connecting AB diblock C.P. and BC diblock C.P.

(d) $k \leq 0.4$: Three critical lines. A solid cyan one connects the AB diblock C.P.
Section A.2. Critical Lines

and BC diblock C.P. and always passes the B-modulated critical point labeled with star as in the cases of $0.4 \lesssim k \lesssim 0.9$. As $k$ decreases, the shape of this line does not change much and the limiting curve is the critical line identified in ABA triblocks by Mayes and de la Cruz$^{137}$ (Figure 1 of reference$^{38}$ and Figure 3 of reference$^{137}$). Near the AC diblock edge, the solid yellow line starting from AC diblock C.P. and ending at the singular cusp is the same one as in previous situations. The emergent loop near AC diblock edge starts from the singular cusp and intersects with the solid yellow line. The value of $f_B$ at the intersection points decreases as $k$ decreases.

A closer look at the results for $k$ values in the intermediate of the case (c) and case (d) reveals that a separatrix line exists for a critical value of $k$ (around 0.4), at which the heart-shaped critical curve (case (c)) intersects with the critical curve connecting AB diblock edge and BC diblock edge. Right after that point, the two curves “interchange” their segments, which results in the topology in case (d). Furthermore, it is curious to note that both the heart-shaped loop in case (c) and the loop near AC diblock edge in case (d) are not closed. They both approaches the singular cusp, but will not close there.
Figure A.1: The locus of the DSP’s for symmetric triblock copolymers at different values of $k$. Each triblock copolymer with certain chain length is represented by a point in the plane. The shaded regions indicate different spinodal behavior along the AC isopleth. The circles indicate the values of $f_B$ at the DSP’s. From lower to higher values of $\chi_{AC}N$, $f_B = 0.1, 0.2, ..., 0.8$, respectively.
Section A.2. Critical Lines

Figure A.2: The projection of critical lines in symmetric triblocks onto the composition triangle at different values of $k$. The solid yellow line lying on the AC isopleth is the AC-modulation critical line. The cusp point where the AC modulated spinodal intersects with B modulated spinodal is labeled with circle. The B modulation critical point is labeled with star.
B.1 Radius of Gyration

The $k$-dependence of the correction to the intramolecular correlation function of a homopolymer, Eq.(5.5.2), comes from that of $\psi_i^{(4)}(k, -k, q, -q)$. A straightforward Taylor expansion of $\psi_i^{(4)}$ shows that in the low $k$ regime, to second order in an expansion in powers of $|k|$, 

$$\psi_i^{(4)} \simeq N_i^4 f(q^2 R_{g0,i}^2) k^2 R_{g0,i}^2 \cos^2 \theta \quad (B.1.1)$$

where $\theta$ is the angle between vectors $k$ and $q$, and

$$f(x) \equiv \frac{2}{3} \left( \frac{1}{x^2} - \frac{24}{x^4} - \frac{96}{x^5} - \frac{120}{x^6} \right) e^{-x}$$

$$+ \frac{8}{3} \left( \frac{1}{x^3} - \frac{3}{x^4} - \frac{6}{x^5} + \frac{30}{x^6} \right) \quad (B.1.2)$$
This expansion has been obtained previously in studies of chain sizes in semi-dilute solutions and in melts. Using the fact that \( \omega(k) \simeq N_i^2(1 - k^2R_{g,i}^2/3) \) in the low-\( k \) region and Eq.(5.5.2), one finds:

\[
\frac{\delta R_{g,i}^2}{R_{g0,i}^2} = \frac{3N_i^2}{2} \int \frac{f(q^2R_{g0,i}^2)\cos^2 \theta G_{ii}(q)}{q} .
\]  

This is the general expression used to calculate the fractional change of the radius of gyration.

Consider the variation of \( R_g^2 \) for a tracer amount of polymer species 1 in a matrix of chains of species 2. In the relevant limit \( \phi_1 \to 0 \), the screened interaction \( G_{11}(q) \) reduces to:

\[
G_{11}(q) = \frac{v}{N_2} \left( \frac{1}{g(q^2R_{g0,2}^2)} - 2\chi_e N_2 \right),
\]  

where \( g(x) = 2(e^{-x} - 1 + x)/x^2 \) is the Debye function and \( R_{g0,2} = N_2b_2^2/6 \). Substituting this expression into Eq.(B.1.3), and hereafter taking \( b_1 = b_2 = b \), we find:

\[
\sqrt{N_1} \frac{\delta R_{g,1}^2}{R_{g0,1}^2} = \frac{F(p)}{p} - 2F(0) \cdot \chi_e N_1
\]  

where

\[
F(p) \equiv \frac{6^{3/2}}{4\pi^2} \int \frac{dy}{g(py^2)} \frac{f(y^2)y^2}{g(py^2)}
\]  

where \( p \equiv N_2/N_1 \), and where \( y \equiv q^2R_{g0,1}^2 \). \( F(p) \) is convergent when \( p = 0 \) and is UV-divergent for any non-vanishing \( p \). In the latter case, a constant \( 4/3 \) has to be subtracted from the integrand to account for the renormalization of the statistical segment length.

Three special cases of this result are noted in the main text: The fractional shrinkage of \( R_g^2 \) in a homopolymer melt, which is discussed in subsection 5.5.1, is obtained by setting \( \chi_e = 0 \) and \( p = 1 \). This yields \( \sqrt{N} \delta R_g^2/R_{g,0} = F(1) = -1.42 \). In section 5.5.2, the curve shown in Figure 5.6 is given by \( F(p)/p \). Its asymptotic behavior in the limit of a small molecule solvent, \( p \to 0 \), is given by \( F(0)/p = 0.31/p \). In section 5.5.3, the \( \chi_e N \) dependence of the fractional change of \( R_g^2 \) in the limit of \( \phi_1 \to 0 \) is
given by $\partial(\sqrt{N}dR^2_g/R^2_{g,0})/\partial(\chi_e N) = -2F(0) = -0.62$.

## B.2 Mean-squared End-to-End Distance

We calculate the one-loop correction to the mean-squared end-to-end distance $R^2$ using the method described in reference\(^ {22} \). There, the same quantity was calculated for a finite segment of an infinitely long chain in a semi-dilute solution, using a Lorentzian approximation for the screened interaction. The analogous result for a chain of species 1 in an incompressible binary blend is obtained by using the appropriate screened interaction $G_{ij}$. The final result for a symmetric blend ($N_1 = N_2$ and $b_1 = b_2$) is

$$\frac{\delta R^2_1}{R^2_0} = \frac{\sqrt{24}}{\pi^2 \sqrt{N}} \int dy h(y^2) \frac{y^4}{g(y^2)} \left(1 - 2\phi_{2} \chi_e N g(y^2)\right) \left(1 - 2\phi_{2} \chi_e N g(y^2)\right)$$

(B.2.1)

where $y \equiv q^2 R^2_{g,0}$, and

$$h(x) \equiv \left(\frac{1}{x^2} + \frac{4}{x^3} + \frac{6}{x^4}\right) e^{-x} + \frac{2}{x^3} - \frac{6}{x^4}.$$  

(B.2.2)

This expression reduces to Eq. (15) of reference\(^ {68} \) for a one-component melt ($\phi_2 = 0$).

The integral is divergent in the high-$q$ region, and the dangerous term in the integrand is “1”. This is precisely the divergent term identified by Edwards, which he identified as a renormalization of the statistical segment length.\(^ {22} \) We subtract this term from the integrand in order to obtain a UV convergent prediction for $\delta R^2$, which is the deviation of $R^2$ from the value $R^2_0(N)$ predicted by a Gaussian model with a statistical segment length equal to that obtained for infinitely long chains. For a pure homopolymer melt, by numerically completing the convergent integral, we recovered the result reported in reference:\(^ {68} \) $\delta R^2 / R^2_0 = -1.40 / \sqrt{N}$. 

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191
In Section 6.4.5 of Chapter 6, we presented results for the sizes of individual diblock copolymers and the composing blocks. Here we show how those quantities are related to the intra-molecular correlation functions ($\Omega_{ij}$).

The size of a single diblock molecule is characterized by the radius of gyration of the whole molecule ($R_g^2$) and of the two blocks ($R_{g,i}^2$), and by the mean squared center of mass distance of two blocks ($R_{AB}^2$). Define the center of the mass of each block by $r_{0}^{(i)}$, then that of the whole molecule is $r_0 = f_AR_0^{(A)} + f_BR_0^{(B)}$. By definition:

$$R_g^2 \equiv \frac{1}{N} \sum_{i}^{A} (r_i - r_0)^2 + \frac{1}{N} \sum_{j}^{B} (r_j - r_0)^2.$$  \hspace{1cm} (C.0.1)
To express this in terms of $R_{g,A}$ and $R_{g,B}$, we insert $r_0^{(A)}$ and $r_0^{(B)}$, and get

$$R_g^2 = \frac{1}{N} \sum_i^A \left( r_i - r_0^{(A)} + r_0^{(A)} - r_0 \right)^2 + \frac{1}{N} \sum_j^B \left( r_j - r_0^{(B)} + r_0^{(B)} - r_0 \right)^2$$

$$= \frac{1}{N} \left[ \sum_i^A \left( r_i - r_0^{(A)} \right)^2 + \sum_i^A \left( r_0^{(A)} - r_0 \right)^2 + 0 \right] + [...] . \quad (C.0.2)$$

Substituting the definition of $R_{g,A}$ and $R_{g,B}$, $f_A = N_A/N$ and $f_B = N_B/N$, we have

$$R_g^2 = f_A R_{g,A}^2 + f_A \left( r_0^{(A)} - r_0 \right)^2 + f_B R_{g,B}^2 + f_B \left( r_0^{(B)} - r_0 \right)^2$$

$$= f_A R_{g,A}^2 + f_A f_B^2 \left( r_0^{(A)} - r_0^{(B)} \right)^2 + f_B R_{g,B}^2 + f_B f_A R_{g,AB}^2 . \quad (C.0.3)$$

The last line shows the connection of the three geometric quantities. This last line is easily generalized to multi-block copolymers.

$$R_g^2 = \sum_{i,j}^{\text{block}} f_i R_{g,i}^2 + \sum_{i}^{\text{block}} f_i (r_0^{(i)} - r_0)^2 . \quad (C.0.4)$$

$R_{g,i}$ are related to $\Omega_{ii}$ through the Guinier law:

$$\Omega_{ii}(q) = \frac{1}{vN} \sum_{i,j}^A \langle e^{iq \vec{r}_{ij}} \rangle$$

$$= \frac{1}{vN} \sum_{i,j}^A \left( 1 + i q |r_i - r_j| \cos \theta_{ij} - \frac{q^2}{2} |r_i - r_j|^2 \cos^2 \theta_{ij} + [...] \right)$$

$$\approx \frac{N_A^2}{vN} \left( 1 - \frac{q^2}{3} \frac{1}{2N_A} \sum_{i,j}^A \langle (r_i - r_j)^2 \rangle \right)$$

$$= \frac{N f_i^2}{v} \left( 1 - \frac{1}{3} q^2 R_{g,i}^2 \right) . \quad (C.0.5)$$

193
For inter-block correlation function

\[ \Omega_{AB}(q) \simeq \frac{N f_A f_B}{v} \left( 1 - \frac{1}{3} q^2 \frac{1}{N_A N_B} \sum_i \sum_j \langle (r_i - r_j)^2 \rangle \right). \]  \hspace{1cm} (C.0.6)

This implies that

\[ \Omega_{AA}(q) + \Omega_{BB}(q) + 2\Omega_{AB}(q) \]
\[ \simeq \frac{1}{vN} \left( \sum_i^A \sum_j^A + \sum_i^B \sum_j^B + \sum_i^A \sum_j^B + \sum_i^B \sum_j^A \right) \left( 1 - \frac{q^2}{6} \langle (r_i - r_j)^2 \rangle \right) \]
\[ = \frac{N}{v} \left( 1 - \frac{q^2}{3} \frac{1}{2N^2} \sum_{i,j}^{A+B} \langle (r_i - r_j)^2 \rangle \right) \]
\[ = \frac{N}{v} \left( 1 - \frac{1}{3} q^2 R_g^2 \right). \]  \hspace{1cm} (C.0.7)

Using the established relation among these three quantities, it is evident that

\[ (\Omega_{AA}(q) + \Omega_{BB}(q) + 2\Omega_{AB}(q)) - \frac{1}{f_A} \Omega_{AA} - \frac{1}{f_B} \Omega_{BB} \]
\[ \simeq N \left[ (1 - f_A - f_B) - \frac{q^2}{3} \left( R_g^2 - f_A R_{g,A} - f_B R_{g,B} \right) \right] \]
\[ = - N f_A f_B \frac{q^2}{3} R_{AB}^2. \]  \hspace{1cm} (C.0.8)

Using this expansion to represent \( \Omega_{AB}(q) \) in terms of the other quantities. The above two equations also implies that

\[ \Omega_{AA}(q) \Omega_{BB}(q) - \Omega_{AB}^2(q) \simeq \left( \frac{N f_A f_B}{v} \right)^2 \frac{q^2}{3} R_{AB}^2. \]  \hspace{1cm} (C.0.9)
We analyze IR (infra-red) asymptotic behavior of the one-loop prediction to the intra- and inter-molecular correlation functions, Eq.(6.3.1) and (6.3.11) in Chapter 6. We first look at the IR behavior of the screened interaction (Eq. (6.3.3)), \( \tilde{G}(q) \). By eliminating the \( \chi \)-dependent terms in the numerator, \( \tilde{G}(q) \) can be written as

\[
\tilde{G} = \tilde{\Omega}^{-1} - \frac{s_0}{\tilde{\Omega}} = \tilde{\Omega}^{-1} - \tilde{\Omega}^{-1} s_0 \tilde{\Omega}^{-1},
\]  

(D.0.1)

where

\[
s_0 \equiv \varepsilon \varepsilon^T \frac{\Delta}{\tilde{\Omega} + |\tilde{\Omega}| - 2v \chi_0}.
\]  

(D.0.2)

Here \( \varepsilon^T = (1, -1) \). \( S_0 \) is the mean field expression for the correlation function \( S \). Only the second term depends on \( \chi \) and it controls the IR asymptotic behavior of Eq.(6.3.1) and (6.3.11). Expand the denominator of \( S_0 \) around \( \chi_s N \) and \( q_0 \), up to the linear order in \( \tau \equiv 2(\chi_s N - \chi N) \) and \( (q^2 - q_0^2)^2 \). We find:

\[
S_0(q) \simeq \frac{\varepsilon \varepsilon^T / v}{\tau + \xi_0^4 (q^2 - q_0^2)^2}.
\]  

(D.0.3)

195
where $\xi_0 \equiv R_g^2 \tilde{F}''(q_0^2 R_g^2, f) / 2$ and $F''$ is the curvature of $\tilde{\Omega}_+/|\tilde{\Omega}|/v$ at the the minimum.

Figure D.1: IR asymptotics of the Brazovskii propagator, for single (left) and double kernel (right) cases. The shaded are regions contributing significantly to the integration over $k$.

For the intra-molecular contribution (Eq.(6.3.1)), the integrals are dominated by the volume of the shell around $q_0(f)$ with thickness proportional to $\tau^{1/2}$ (Figure D.1, left). Its contribution to the integral scales as $\tau^{-1}(q_0^2 \tau^{1/2}) \propto \tau^{-1/2}$, as seen more explicitly from the following representative (single kernel) integral ($\alpha \equiv \xi_0^4 / \tau \propto \tau^{-1/4} \gg 1$):

$$\frac{1}{\tau} \int_0^\infty \frac{dk}{1 + \alpha^4 (k^2 - q_0^2)^2} \lesssim \frac{1}{\tau} \int_0^\infty \frac{dk}{1 + 4q_0^2 \alpha^4 (k - q_0)^2} \lesssim \frac{1}{2q_0 \tau \alpha^2} \int_{-\infty}^{\infty} \frac{dk}{1 + k^2} = \frac{\pi}{2q_0 \tau \alpha^2} \propto \tau^{-1/2} \quad (D.0.4)$$

For the inter-molecular part, in place of any $\tilde{G}$ term in Eq.(6.3.11) and Eq.(6.3.12), either $\tilde{\Omega}^{-1}$ or $\tilde{\Omega}^{-1} S_0 \tilde{\Omega}^{-1}$ can be substituted. Eq.(6.3.12) can be decomposed into:

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196
\[
\Sigma_{ij}(q) = \frac{1}{2} \int \tilde{\Omega}_{ikm}^{(3)}(q, k_-, -k_+) \tilde{\Omega}_{kl}^{(3)}(k_+) \tilde{\Omega}_{jnl}^{(3)}(-q, -k_-, k_+) \tilde{\Omega}_{mn}^{(3)}(k_-) \quad (D.0.5)
\]

\[+
\int \tilde{\Omega}_{imk}^{(3)}(q, k_-, -k_+) \tilde{\Omega}_{kl}^{(3)}(k_+).
\]

\[\tilde{\Omega}_{jnl}^{(3)}(-q, -k_-, k_+) \tilde{\Omega}_{mn}^{(3)}(k_-) (D.0.5)
\]

\[+
\int \tilde{\Omega}_{imk}^{(3)}(q, k_-, -k_+) \tilde{\Omega}_{kl}^{(3)}(k_+ \cdot \tilde{\Omega}_{jnl}^{(3)}(-q, -k_-, k_+) \tilde{\Omega}_{mn}^{(3)}(k_-)
\]

\[\tilde{\Omega}_{jnl}^{(3)}(-q, -k_-, k_+) \tilde{\Omega}_{mn}^{(3)}(k_-) (D.0.6)
\]

The substitution with no \(S_0\) term (Eq.(D.0.5)) results in no \(\chi\) dependence. The ones with one \(S_0\) term (Eq.(D.0.6) results in \(\tau^{-1/2}\) divergence close to \(\chi_s\), of the type represented by Eq.(D.0.4). The one with two \(S_0\) terms (Eq.(D.0.7) results in \(\tau^{-1/2}\) plus a stronger \(\tau^{-1}\) divergence (Figure D.1, right): since two kernels can diverge simultaneously \(\tau^{-2}\) in the circular band in \(k\) domain satisfying \(|k - q/2| = |k + q/2| = q_0\), whose volume scales as \(\tau\). This may be seen more clearly by analyzing the dominant asymptotics of the (double kernel) integral:

\[I = \frac{1}{\tau^2} \int_0^\infty dk \frac{1}{1 + \alpha^4(k_+^2 - q_0^2)^2} \frac{1}{1 + \alpha^4(k_-^2 - q_0^2)^2}
\]

\[= \frac{\pi q_0^2}{4\tau^2\alpha^2 ((2a^2 \cos^2 \theta - q_0^2)^2 + \alpha^{-4} a^2 \cos^2 \theta / (q_0^2 - a^2 \cos^2 \theta))} \cdot (4\alpha^4(q_0^2 - a^2 \cos^2 \theta) a^2 \cos^2 \theta + 1).
\]

(D.0.8)

Where \(k_+ \equiv |k + q/2|, k_- \equiv |k - q/2|, \cos \theta \equiv k \cdot (q/2)/(ka)\), and \(q_0 > a \equiv q/2\). The behavior of Eq.(D.0.8) in the limit of large \(\alpha\) and at \(a = q_0/2\) is particularly interesting to us (the other cases can be analyzed similarly and may be slightly more subtle\(^1\), but \(a = q_0/2\) is the most important one). Two results are possible, depending on the values of \(\theta\):

\(^1\)For instance, when \(q_0/\sqrt{2} < a < q_0\).
1. $\theta$ in the vicinity of $\pi/2$

$$I_1 = \frac{\pi}{4\tau^2 \alpha^2 q_0}$$  \hspace{1cm} (D.0.9)

2. otherwise ($a = q_0/2$ has been substituted)

$$I_2 = \frac{2\pi}{\tau^2 \alpha^6 q_0^5 |\cos \theta|^7}$$  \hspace{1cm} (D.0.10)

The width of the $\theta$ range for $I_1$ to be important is inferred from the denominator of the last line in Eq.(D.0.8): $\alpha^4 \cos^2 \theta \simeq 1$, which implies that $\delta(\cos \theta) \simeq \alpha^{-2}$. Thus when the angular integration over $\theta$ is performed, we have $I_1 \cdot \delta(\cos \theta) \propto \tau^{-1}$. The width of $\theta$ range for $I_2$ to be important is of order 1, so $I_2 \cdot 1 \propto \tau^{-1/2}$.

Therefore the strongest divergence in Eq.(D.0.7) for the correction to the intermolecular correlation is $\tau^{-1}$. We now show that, at the critical composition, this term vanishes when $\delta C_{ij}(q_0)$ is used to construct $\delta \chi_a(q_0)$ through $\delta \chi_a = \varepsilon_i \varepsilon_j \delta C_{ij} / (2\nu)$. A close look of this equation, Eq.(D.0.7) and (6.3.11) suggests that, the $\varepsilon$ and $\tilde{\Omega}^{-1}$ terms can be absorbed into $\tilde{\Omega}^{(3)}$. We thus define

$$\epsilon_i \epsilon_j \epsilon_k \tilde{\Omega}_{\alpha \beta \gamma}^{-1}(q) \tilde{\Omega}_{\alpha \beta \gamma}^{-1}(k_-) \tilde{\Omega}_{\alpha \beta \gamma}^{-1}(k_+) \tilde{\Omega}_{\alpha \beta \gamma}^{(3)}(q, k_-, -k_+) = \gamma_3(q, k_-, -k_+)$$  \hspace{1cm} (D.0.11)

Here $\gamma_3(q, k_-, -k_+)$ is recognized as the third order coefficient in Leibler’s free energy expression,\textsuperscript{7} which vanishes at the critical composition when the three arguments complete an equilateral triangle of length $q_0$ – a condition necessary for the strongest divergence to occur (In the right portion of Figure D.1, the points at $-q/2$, at $q/2$ and those at the intersections of the two spheres complete such triangles). This result is analogous to the one for blends, for which the strongest divergences vanishes at the critical composition.\textsuperscript{122}
We test the renormalized one-loop theory using Bates and Rosedale’s measured temperature dependence of the SANS profile for nearly symmetric PEE-PEP diblock copolymers.\textsuperscript{100} The scattering profile $I(q)$ is proportional to the correlation function $S(q)$: $\tilde{I}(q) = (a_A - a_B)^2 v^{-1} S(q)$, where $a_A$ and $a_B$ are segmental scattering lengths. Although the theory yield direct prediction to $S(q)$, we can not compare it directly with the experiments because of the instrument smearing effects (wavelength spread, finite collimation and detector resolution). But since the data has been compared to the FH theory (Figure E.1(a)), we can compare the prediction of our theory to that of the FH theory. To achieve that, we have to find the temperature dependence of $\bar{N}$ and $\chi N$.

We tried two different ways to estimate $\bar{N}$ and $\chi N$: the one used in Bates et al.’s original analysis and another one based on data collected in their later (1995) publication.\textsuperscript{101}
Figure E.1: (a) Bates-Rosedale-Fredrickson’s data. Fig.11 of reference.\textsuperscript{100} (b) The comparison of FH (dashed) and ROL (solid) theories for $\bar{N} = 5000 & 10000$. The straight dashed (green) line near the lower left corner are RPA results – (not in the same sense as in (a)).
E.1 Analysis in the 1990 Paper

The paper\textsuperscript{100} includes the first quantitative comparison between the FH theory and experimental results. Their original analysis is explained in the appendix and summarized below.

- The statistical segments are defined based on a common reference monomer weight, $m_0 = 56$ g/mol, based on which they found $N_{PEP} = 564$, $N_{PEE} = 462$, and $f_{PEP} = 0.55$.

- The temperature dependence of the average statistical segment length $b$ is found from that of the peak position $q^*$, by assuming that the RPA prediction for the peak position is correct and that the shift is fully caused by the temperature dependence of $b$. Using $(q^*(T)N b^2/6) = 3.800$ (RPA prediction), it was found that (Eq. A9, in Å):

$$\ln b^2 = -2.21 \times 10^{-3} T + 4.84 \quad (E.1.1)$$

- The temperature dependence of the reference volume is determined using the typical liquid polymer thermal expansivity (Eq. A10, in Å$^3$):

$$\ln v = 6.5 \times 10^{-4} T + 4.489 \quad (E.1.2)$$

- The temperature dependence of the $\chi$ parameter is determined by fitting the order-disorder transition temperatures of three diblock copolymers to those of the FH theory prediction. It was found (Eq. A12):

$$\chi = \frac{4.69}{T} + 4.44 \times 10^{-4} \quad (E.1.3)$$

The temperature range in Figure E.1(a) is $2.1 < 10^3 T^{-1} < 2.5$, which implies that

$$5.86 < b^6/v^2 < 10.70 \quad \rightarrow \quad 6012 < \bar{N} < 10978 \quad (E.1.4)$$

$$0.0103 < \chi < 0.0122 \quad \rightarrow \quad 10.57 < \chi \bar{N} < 12.52 \quad (E.1.5)$$
For this range of $N$ and $\chi N$, the FH theory and ROL theory are nearly indistinguishable, as shown in Figure E.1(b).

### Section E.2. Analysis Using Parameters in the 1995 Paper

The paper collects and analyzed results for several symmetric PEP-PEE, PEP-PE, PEE-PE diblocks, including the 1990 sample (PEP-PEE-5H of Table 1). The scattering profiles are plotted versus inverse temperature near the ODT, but not compared to the FH theory. However, they offered independently measured statistical segment lengths (from homopolymers,\textsuperscript{139}) and obtained slightly different expressions for $\chi(T)$.

- The statistical segments are defined based on a common reference monomer weight, $m_0 = 56$ g/mol, based on which they found $N_n = 978$, and $f_{PEP} = 0.55$.

- The temperature dependence of the reference volume is estimated “based on a typical polyolefin thermal expansivity” (no citation; and is slightly different from that in the 1990 paper) in Å$^3$:

\[
V = 81.527 \exp(0.685 \times T), \quad [T] = 10^3 K \tag{E.2.1}
\]

- The statistical segment lengths are also corrected by “thermal expansivities” (based on Fetters’ 1994 paper, in Å):

\[
b_{PEP} = 8.559 \exp(-0.58 \times T), \quad [T] = 10^3 K \tag{E.2.2}
\]
\[
b_{PEE} = 4.711 \exp(+0.2 \times T), \quad [T] = 10^3 K. \tag{E.2.3}
\]

The average ($f_{PEP} = 0.55$):

\[
b^2 = f_{PEP}b_{PEP}^2 + f_{PEE}b_{PEE}^2 \tag{E.2.4}
\]
\[
= 40.291 \exp(-1.16 \times T) + 9.987 \exp(+0.4 \times T), \quad [T] = 10^3 K. \tag{E.2.5}
\]
Section E.3. Summary

The relevant ratio needed to connect \( N \) to \( \bar{N} \):

\[
\frac{b^2}{v^{2/3}} = 2.143 \exp(-1.617 \times T) + 0.531 \exp(-0.057 \times T), \quad [T] = 10^3 K. \tag{E.2.6}
\]

- Similarly, \( \chi(T) \) are obtained by fitting the ODT data of diblock copolymers to the FH theory prediction (the result is slightly different from that of the 1990 paper).

\[
\chi = (4.46 \times T^{-1} + 2.1) \times 10^{-3} \quad [T] = 10^3 K \tag{E.2.7}
\]

Within the temperature range \( 2.1 < T^{-1} < 2.5([T] = 10^3 K) \) and \( 127 < T < 203^\circ C \) in Figure E.1(a),

\[
3.436 < \frac{b^6}{v^2} < 4.419 \quad \Rightarrow \quad 3361 < \bar{N} < 4325 \tag{E.2.8}
\]

\[
0.01147 < \chi < 0.01325 \quad \Rightarrow \quad 11.22 < \chi \bar{N} < 12.96 \tag{E.2.9}
\]

For this range of \( \bar{N} \) and \( \chi \bar{N} \), the relation between the FH theory and ROL theory are shown in Figure E.2(a) and E.2(b), versus \( \chi \) and \( T \) respectively. The range of \( \chi \bar{N} \) has not changed much, but the \( \bar{N} \) value we obtained is about the half that obtained from the estimate in the 1990 paper.

### E.3 Summary

The biggest difference between these two estimates are the estimates of the statistical segment lengths, which results in a factor of 2 difference in the \( \bar{N} \) values. The 1995 estimate using independently measured \( b \)'s is more appropriate. The agreement between the FH theory and the experimental data may thus be accidental. Within both ranges of the \( \bar{N} \) values, the FH and renormalized one-loop theories are hardly distinguishable. When compared to experiments, these two theories should behaves similarly.
Figure E.2: Analysis of Bates-Rosedale-Fredrickson’s data using the parameters of the 1995 paper, plotted versus (a) $\chi_eN$ and (b) $T^{-1}$, for $\bar{N} = 3361$ & 4325.
We give a thorough review of previous simulation study of diblock copolymers, including both lattice and off-lattice models. For the work from each individual group, the model, the basic quantities studied, and the conclusions related to the structure of disordered diblocks and the order-disorder transition are summarized.

F.1 Lattice Models

Binder Group

Binder and Fried studied symmetric\textsuperscript{113,114} and asymmetric\textsuperscript{115} ($f = 3/4$) diblock copolymer. They simulated polymers of lengths ranging from 16 to 60 on simple cubic lattice with filling fraction 0.2, and used a majority of snake-slithering move combined with some chain-flip moves to equilibrate the system. The interaction strength $\varepsilon$ is assigned for AB contacts (nearest neighbor) and non interaction for others. They studied both the single chain dimensions and the collective correlation function in the disordered states, and established clearly: the $\varepsilon$ dependence of chain dimensions and
Section F.1. Lattice Models

peak position of the correlation function. By comparing the temperature dependence of the chain size and the inverse of the peak position, which they identified as a “collective” length scale $\lambda^*$, they concluded that the pre-transitional fluctuation and the shift in $q^*$ is dominated by the collective behavior. The ODT was crudely estimated by measuring the relaxation time of the slowest mode of the principle direction of the moment of the inertia. They also pointed out that when $\epsilon = 0$, the correction of Fredrickson-Helfand theory to RPA theory on the peak intensity has an opposite sign than the simulation results.

Binder and Micka studied the finite size effects \cite{Binder1987} for asymmetric diblock copolymers. They identified the correlation length $\xi$ from the width of the correlation peak and concluded that because of the existence of two competing length scales, $\xi$ and $\lambda^*$, a standard finite size scaling technique does not work. They also verified the oscillation with distance of the correlation function (see Eq.(7.2.5)).

Larson\cite{Larson1996, Larson1998, Larson2006} also used a model on simple cubic lattice. The form of interaction is similar to Binder’s but has a large range coordination number $z = 26 \langle\langle 100\rangle\rangle, \langle\langle 110\rangle\rangle, \langle\langle 111\rangle\rangle$ directions). He included two types of solvents (one good for A and the other for B), with varying compositions (typically 40%). He simulated chains of lengths $N = 6 \sim 48$ \cite{Larson1996} and $N = 48 \sim 192$ \cite{Larson1998} with varying compositions. He found the spontaneously formed lamella phase after stepwise quenching and found hexagonal, BCC packed spheres and gyroid phase in some short molecular surfactant simulations.

Larson has focused on the disorder-lamella transition. To estimate $\chi$ parameter, the dilution effects by solvent molecules has been included and the number of self-contacts removed: $z_{\text{eff}} = z - 4 = 22$ and $\chi = \phi_{\text{diblock}} z_{\text{eff}} w$, where $w$ is the interaction strength between unlike contacting units. He studied the finite size effects size by conducting the same simulations in varying box sizes, and found that: chain lengths $N < 50$, box including $2 \times 2 \times 2$ lamella phase should be sufficient to locate the ODT; for chain length greater than 50, the correlation length of the composition fluctuations seems to be greater than the lamellar domain spacing, and much bigger boxes are
needed. He used the disordering (from lamella) transition temperature as ODT and the estimated $\chi_{ODT}N$ are in gross agreement with the FH prediction.

**Matsen Group**

Vassiliev and Matsen\textsuperscript{8} studied symmetric diblock copolymer and compared the simulation results with mean-field theory constructed on lattice. To have a larger coordination number ($z = 12$), they used an FCC lattice with molecule filling fraction 0.8. The contact interaction $\epsilon_{ij} = \epsilon$ for AB pair and 0 otherwise. They used slithering snake, chain reversal, crankshaft, block exchange moves to equilibrate the system, and simulated chain lengths 20, 30 and 40 in boxes of lengths 24, 32, 40, 48 respectively. They studied both the structure factor of the disordered phase and the ODT. We will re-analyze their disordered state data in the later section.

Matsen \textit{et al.} also studied the asymmetric cases in a later publication:\textsuperscript{9} the case of $f = 0.3$ was studied thoroughly for chain lengths 20, 30 and 40, analogous to the work for symmetric case. The $N = 30$ case 30 was examined for the composition range $0.2 \leq f \leq 0.8$ and a partial phase diagram given including the ODT for the $L$, $HPL$ and $C$ phases. They found very weak $N$ dependence in the ODT at $f = 0.5$ and $f = 0.3$.

**Molina & Freire**

Molina and Freire did Monte Carlo simulation for symmetric diblock copolymers on a simple cubic lattice of symmetric diblock copolymers with both non-selective\textsuperscript{118} and selective\textsuperscript{144} solvents. Monomers of the same type attract each other, and those of different types (include solvent or vacant sites) do not interact. Chains of length 36 and 60 were simulated. They studied the chain dimension and structure factor in the disordered phase.

**Pakula & Vilgis Group**

Pakula \textit{et al.}\textsuperscript{145–147} did simulations using CMA (cooperative motion algorithm) lattice model with filling density 1. Typically, FCC lattice with coordination number $z = 12$
Section F.1. Lattice Models

were used. Both disordered states and the ODT were studied. Chains of lengths \( N = 20, 32, 40, \) and 50 were simulated. They measured the temperature dependence of the heat capacity and used the apparent maxima to define the ODT. In the ordered region, both symmetric and asymmetric \( (f = 0.25) \) molecules have been simulated, and lamellae and cylindrical phases were identified.

**Dotera & Hatano**

Dotera and Hatano\(^{148}\) introduced the diagonal bond model and examined various systems. They studied diblock copolymer of 16 beads in the \( 40^3 \) box with filling fraction 0.8, and focused on the ODT and the formation of ordered phase diagram. They commented that by allowing the crossing of bonds of chains, the system can be equilibrated relatively fast. They obtained a lamella phase directly after quenching the system from the high temperature disordered state. They also noted that the boundary condition has a strong effect on the formation of ordered phase, and that lamellae are able to align themselves to the favorable directions. They bracket the order-disorder transition temperature by monitoring the jump in the average energy. Both the melting temperature and the solidification temperature were found. They also collected the histogram for the average energy, which has very clear double peak, indicating the transition is of first order. The chain dimensions have also been studied and chain stretching effects is verified.

**Hoffmann, Sommer & Blumen**

Hoffmann *et al.* have studied both symmetric\(^{116}\) and asymmetric\(^{149}\) cases, and have looked at both the high temperature properties and ODT. They used bond fluctuating model (BFM) with \( z = 54 \) and fill factor 0.6. For the symmetric diblocks: Chain length of 16, 24, 32 & 48 and box size of \( 50 \times 50 \times 135, 200, 270 \) & 410 were used. Periodic boundary condition was used along \( x \) and \( y \) directions and repulsive wall along \( z \) direction. For the asymmetric diblocks: chain length of 24 & box size of \( 50 \times 50 \times 200 \), and chain length of 32 & box size of \( 50 \times 50 \times 270 \) were used. Block fractions \( f = 0.5, 0.66, 0.83, 0.92 \) were used for \( N = 24 \) and \( f = 0.5, 0.63, 0.75, 0.875 \).
for $N = 32$.

They measured the correlation function and use the emergence of the Bragg peak to estimate ODT: $9 \leq \epsilon N \leq 12$ (for $N = 24$ and $N = 32$). They used box counting to estimate the range of monomer clustering, the temperature dependence of this size is consistent with that inferred from the peak position of the scattering function. In the asymmetric case, energy distribution along the chain is also examined and results with different chain length and block fractions given (Fig. 6) at $\varepsilon = 0.1$. The results are consistent with what we got for diblocks. Energy and its variation also examined.

**Wang & Pablo**

Wang, Nealey and Pablo$^{150}$ studied the lamella structure formed in symmetric diblock copolymer and quantitatively compared the density profile with that of with SCFT predictions. The simulation were conducted on a simple cubic lattice, and non-zero contact interactions are used for AB pairs. Configuration biased reptation, kink-jump and crank-shaft moves are used equilibrate the system. They simulated chains of lengths 24, 48 and 96. The box sizes were chosen to accommodate 2 lamellar domain spacing (along [001] direction). Relation between $\chi$ parameter and Monte Carlo interaction parameter is extracted by measuring the chemical potential and map that to the one given by SCFT.

**Francisco & Escobedo**

Francisco and Escobedo$^{151}$ simulated chains length 20 on simple cubic lattice with 25% voids. Each lattice site was assigned 26 interacting neighboring sites. $\chi$ was estimated using $(26 - 2)(1 - 0.25)\epsilon = 18\epsilon$. Displacement, reptation and chain flip moves were used to equilibrate system (with ratio 100:10:1). They focused on phase diagram, and found all classical phases: lamella, cylinder, sphere and gyroid. PL phase was also found but verified to be meta-stable by comparing free energies. A co-continuous phase bearing similarity to the $Fddd$ phase were also found, but has not been justified. By simulating two model bi-disperse systems, they also verified that the stability of gyroid phase can be improved by introducing appropriate poly-
dispersity.

Others

Chakrabarti \textit{et al.} \cite{152} did two dimensional lattice simulation to test the chain length dependence of lamellar domain spacings at the scaling level and the wave vector dependence of the correlation functions. Chains of lengths 10, 20, 30, 40 are simulated in the box of size 128 with the filling factor 0.6. An attractive interaction of strength $-J$ is assigned to monomer pairs of the same type. A single interaction strength was used for all chains, corresponding the weak segregation regime. No clear lamella ordering were given, and domain spacing were inferred from the first zero of the pair correlation function.

Yang \textit{et al.} \cite{153} simulated chains of length 21 ($N_A = 10$ and $N_B = 11$) in a two dimensional 41 $\times$ 41 domain with high filling factor 0.9545. The nature of the non-random mixing is quantitative assessed, and compared with the random mixing approximation, which highlighted the inefficiency of the later.

Besold \textit{et al.} \cite{154} did lattice simulation with a coarse grained Hamiltonian. Vacancies were introduced to facilitate the monomer movements. Standard local displacement moves were used. For chains of 30 beads, they get lamella for $N_A : N_B = 15 : 15$ and hexagonal phase for $N_A : N_B = 7 : 23$.

Ko and Mattice \cite{155} simulated symmetric diblock copolymer of 20 sites in a selective solvent (of the same type of one of the block), on a simple cubic lattice. Reptation and kink-jump bond motions were used to equilibrate the system. Sites of different types repel each other when they are in contact. By varying the fraction of the diblock copolymer from 0.45 to 0.85 at intervals of 0.05, a progression of ordered morphologies were identified: spherical, cylindrical, mono-continuous catenoid-lamellar (mesh) and lamellar.
F.2 Continuum Models

Grest & Kremer

Grest and Kremer et al. proposed an isobaric continuum model with short ranged ($r_c = 2^{1/6}$) and purely repulsive shifted L-J pairing potential with cut-off and an anharmonic bonding potential, $U_{ch}(r) = -\frac{1}{2}kR_0^2\ln\left(1 - \frac{r}{R_0}\right)^2$ for $r \leq R_0$ and $\infty$ otherwise. They choose $k = 30\epsilon/\sigma^2$ and $R_0 = 1.5\sigma$, where $\epsilon$ and $\sigma$ are parameters in L-J potential. (This particular choice prevents the chains from cutting each other.) They found that the external pressure $5\epsilon\sigma^{-3}$ is needed to achieve a density $\rho = 0.85$. They combined the damped MD simulation (with thermal bath) and the chain flip algorithm to study the static properties of diblocks and homopolymer blends.

For symmetric diblock copolymers, they studied both the correlation function in the disordered phase and the ODT. In reference$^{119}$: they studied the disordering transition of lamellae in systems of $N = 40$ and $M = 800$ ($M$: number of molecules), of $N = 100$ and $M = 200$, and of $N = 100$ and $M = 400$; they also studied the ordering transition for systems of $N = 20$ and $M = 800$, of $N = 40$ and $M = 800$, and of $N = 100$ and $M = 400$. In reference$^{117}$: the systems starting from disordered state is similar to that in reference$^{119}$; for disordering transition, they also included results for $N = 400$ and $M = 200$.

For runs starting from lamellae, they estimate ODT by monitoring density profile and found: $\tilde{\epsilon}_{ODT}(N = 40) = 0.85 \pm 0.05 = 9.9\tilde{\epsilon}_{c, \text{blend}}$,$^{119} \tilde{\epsilon}_{ODT}(N = 100) = 0.28 \pm 0.03 = 8.2\tilde{\epsilon}_{c, \text{blend}}$,$^{119} \tilde{\epsilon}_{ODT}(N = 200) < 0.2$,$^{117}$ (they were not able to determine ODT along this direction). For runs starting from disorder, they were not able to grow lamella phase out of disorder and estimated ODT by looking at the relaxation time of the slowest mode, similar to that, introduced by Binder group$^{113}$ and found: $\tilde{\epsilon}_{ODT}(N = 20) \geq 2.9$, $\tilde{\epsilon}_{ODT}(N = 40) \geq 0.80$, $\tilde{\epsilon}_{ODT}(N = 100) \geq 0.28$.

They propose to map the $\epsilon$ values to the $\chi$ parameter by estimating the effective coordination number for large $N$ using the one-fluid approximation and find that $z_c \approx 0.76$. By approximating their anharmonic potential with a harmonic one near the minimum of pair potential using a spring constant $\kappa = 518.4$, we find the chain length dependence of the inter-molecular contacts number in their model is fitted by
Section F.2. Continuum Models

is fitted well by \( \frac{0.172 + 0.198}{\sqrt{\bar{N}}} + 0.776/\bar{N} \), where \( \bar{N} \) is calculated using \( \rho = 0.85 \) and \( b = 1.28 \), which suggests that \( z_c(\infty) = \frac{0.172}{(x_A x_B)} = 0.687 \). Thus one \( \chi_c = 0.687 \varepsilon \). For blend, this coordination number implies \( \chi_c \bar{N} = 2.32 \). For diblock, the ODT data are tabulated in Table F.1.

<table>
<thead>
<tr>
<th>( N )</th>
<th>( \bar{N} )</th>
<th>F-H</th>
<th>( \chi_{ODT} \bar{N} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>92</td>
<td>19.59</td>
<td>( 16.4-18.1 ) (a)(^8)</td>
</tr>
<tr>
<td>30</td>
<td>138</td>
<td>18.44</td>
<td>( 16.4-18.3 ) (a)(^8)</td>
</tr>
<tr>
<td>40</td>
<td>183</td>
<td>17.71</td>
<td>( 16.0-18.1 ) (a)(^8)</td>
</tr>
<tr>
<td>20</td>
<td>64</td>
<td>20.75</td>
<td>( \gtrsim 39.7 ) (b)(^119)</td>
</tr>
<tr>
<td>40</td>
<td>127</td>
<td>18.66</td>
<td>( \gtrsim 22.0 ) (b) &amp; = 23.2 \pm 1.4 (c)(^119)</td>
</tr>
<tr>
<td>100</td>
<td>318</td>
<td>16.50</td>
<td>( \gtrsim 19.2 ) (b) &amp; = 19.1 \pm 2.1 (c)(^119)</td>
</tr>
</tbody>
</table>

Table F.1: Collected ODT data. (a) using the order parameter \( \psi \equiv \sum_{i \neq j} G_{ij}^2 / V^2 \), where \( G_{ij} \equiv \langle \delta \sigma_i \delta \sigma_j \rangle \). (b) using the relaxation time \( \tau_s \) of \( \phi_s \equiv \langle |e_1(t) \cdot e_1(0)| \rangle - 1/2 \), where \( e_1 \) is the director corresponding to the smallest principal moment of inertia. (c) using the order parameter \( \psi(z) \equiv (L_x L_y)^{-1} \int \psi(r) dx dy \).

Groot & Madden

Groot and Madden\(^{156}\) did simulations using dissipative particle dynamics (DPD) for diblocks of 10 beads long. They simulated systems with fixed (but large) incompatibility and focused on the ordered phases. By varying the composition they obtained a progression of micellar, hexagonal, HPL, and lamellar phases. The DPS seems to be very efficient for quickly equilibrating the system.

Schultz, Hall & Genzer

Schultz, Hall and Genzer\(^{157}\) did discontinuous molecular dynamics (DMD) simulation of diblock copolymer, in which the molecules are modeled as hard sphere chains. They simulated systems with chains of length 10 and 20, with packing fraction 0.35, 0.40, and 0.45, and with block fractions 0.1, 0.2, 0.3, 0.4, and 0.5. They also used adjust the box dimensions periodically when simulating the disordered phase (different from the isobaric simulations), which seems to be more efficient if only the correct box size and
not the equilibration dynamics is needed. The box size is increased stepwise, along with the adjusting algorithm turned on. Then at a large enough box size, no box size variation is allowed and the simulation in NVT ensemble is performed. They also used the EVALENCH algorithm\textsuperscript{158} to estimate free energy and determine whether or not a particular ordered phase is meta-stable.

They focused on the ordered phases. First the simulation in a smaller box is simulated, with the box adjusting algorithm turned on; then duplicated to create a larger box, also with the box adjusting algorithm turned on; eventually, the adjusting algorithm is turned off and a purely NVT simulation is performed. The ordered morphologies emerges spontaneously from this recipe. lamellar, cylindrical, BCC spheres were obtained in the appropriate composition window. Perforated lamellae is obtained in the gyroid composition window, but no gyroid phase is obtained.

The ODT is identified as the disordering transition temperature of the ordered phase. When the simulation results are compared to theory, $\chi$ is related to the model parameter by $\chi = z(\epsilon_{AB} - \frac{1}{2}(\epsilon_{AA} + \epsilon_{BB}))$, $z$ being the average number of non-bonded neighbors within the interaction range and $\epsilon$ being the interaction strength of different particle pairs. $z$ is determined from the simulation. The estimated OD-$\chi$ seems to agree with FH predictions.

**Horsch & Glotzer et al.**

Horsch and Glotzer et al.\textsuperscript{159} mapped out a phase diagram for diblock copolymers of 8 and 10 beads using Brownian dynamics simulations with 2 types of soft conservative interacting potentials, in both fixed and variable boxes with filling fraction 0.85. The number of beads simulated ranges from 8000 to 27000. Lamella, perforated lamella, hexagonally packed cylinders, disordered spherical micelles were obtained. The existence of PL and H phase shows that the hydrodynamics is not required for simulating phases ordering along 2 or 3 dimensions. The companying MD and DPD simulations are also carried out and the results are consistent with those obtained from BD simulations.

The quantitative comparison between simulations and SCF results were also attempted. Relation between $\chi$ and the interaction parameter were established by
Section F.2. Continuum Models

simulating the interface of the monomeric liquids with 50% A beads and compare the mutual solvation concentration to that of the Flory-Huggins prediction. This is analogous to Wang and Pablo’s later approach in which $\chi$ is related to model parameter by requiring the SCFT to produce the same chemical potential as that of simulation.

Francisco and Escobedo

Francisco and Escobedo\textsuperscript{160} successfully simulated the gyroid phase (for the first time) using off-lattice simulations with dissipative particle dynamics model. The free energies are compared when multiple ordered phases emerges under the same condition. Throughout the work, they simulated diblock copolymer of 20 beads. Two types of potentials were used and compared: Groot’s soft potential model and Soddemann’s shifted L-J potential model with a very small elastic constant, which is very similar to Grest and Kremer’s model. The author noted that by allowing for the crossing of molecules, the dynamics of phase separation becomes faster. The direct free energy comparison indicates that the varying box sizes is crucial for identifying the truly stable phase. A phase diagram including lamella, gyroid, cylinders are prepared, in which Groot’s original method was used to estimate $\chi$: $a_{ij} = a_{ii} + 3.27\chi$, where $a_{ij}$ were the interaction parameters built into the model.
Configuration Biased Trimer Rebridge MC Move

In the simulation study of diblock copolymers discussed in Chapter 7, we have used various moves to update the molecular configurations, including the single-chain rebridge and double-chain rebridge moves. Each of these involves regrowing a bead linked to two other beads. Here we explain the implementation of this trimer rebridging move. As shown in Figure G.1, given two beads (2 and 0), if we want to re-grow the middle one (1) connecting the two, with preferred bond length $l_0$ and elastic constant $\kappa$, we first generate new trial configurations using the following recipe:

1. Choose bond length $l_{21}$ with probability:

$$P(l_{21}) \sim e^{-\kappa(l_{21}-l_0)^2/2}.$$

2. Compute the preferred orientation ($\theta_0$) of vector $\mathbf{r}_{21}$ which points from bead 2 to bead 1 using the preferred bond length. Then compute the associated elastic constant $\kappa_\theta$ using the procedure explained in Sec. G.1, which will be needed to bias the bonding orientation, the bias function being $e^{-\kappa_\theta(\theta-\theta_0)^2/2}$. 

215
3. Choose a certain number (predefined) of trial orientations using the orientation bias function, the probability of generating particular sets of trial configuration is equal to

\[
\prod_i \frac{e^{-\kappa_\theta (\theta - \theta_0)^2/2}}{N(\theta_0)} \equiv \prod_i \frac{P(\theta_i)}{N(\theta_0)}
\]

4. Select one (labeled \(n, \text{new}\)) out of those trials by assigning each one a weight

\[ B_i = e^{-\varepsilon_{10} - \varepsilon_{ex}}, \]

where \(\varepsilon_{10}\) is the bonding energy between particles indexed as 1 (at trial positions) and 0 and \(\varepsilon_{ex}\) is the pairing interaction between particle 1 and the other particles (non-bonded). For convenience, we define \(W_n \equiv \sum_i B_i\). Thus the chance that one particular candidate is selected is proportional to \(B_i/W_n\).

After a new trial configuration has been selected, we impose the super-detailed balance condition to calculate the acceptance rate, which in the current context, reads

---

Figure G.1: Illustration of monomer labels, bond labels and orientations in a trimer rebridging move.

The values of \(\theta_0, \kappa_\theta\) and normalization constant \(N(\theta_0) = \int e^{-\kappa_\theta (\theta - \theta_0)^2/2} d\theta\) may be pre-computed before the simulation is started.
(o: old; n: new):

$$E_o P(l_{21}^n) G(o \rightarrow n) \frac{B_n}{W_n} P_J(n', o') A(o \rightarrow n)$$

$$= E_n P(l_{21}^o) G(n \rightarrow o) \frac{B_o}{W_o} P_J(o', n') A(n \rightarrow o). \tag{G.0.1}$$

Where $E_o$ and $E_n$ is the expected statistical weight for the old (“n”) and new (“n”) states. $G(o \rightarrow n)$ refers to the probability of generating the $n$-th orientation

$$G(o \rightarrow n) = \frac{e^{-\kappa(\theta_n - \theta_0^n)^2/2}}{N(\theta_0^n)} \tag{G.0.2}$$

and $G(n \rightarrow o)$ is the reverse probability. $P_J(n', o') = P_J(o', n')$ is the joint probability of generating the particular pair of “old” and “new” companying orientations:

$$P_J = \prod_{i \neq n} \frac{P(\theta_i)}{N(\theta_0^n)} \cdot \prod_{j \neq o} \frac{P(\theta_j)}{N(\theta_0^o)} \tag{G.0.3}$$

$A(o \rightarrow n)$ and $A(n \rightarrow o)$ are the acceptance rate of the forward and backward moves, respectively. The ratio of them is calculated by:

$$\frac{A(n \rightarrow o)}{A(o \rightarrow n)} = \frac{E_n P(l_{21}^o) B_o W_n G(n \rightarrow o)}{E_o P(l_{21}^n) B_n W_o G(o \rightarrow n)}$$

$$= \frac{W_n G(n \rightarrow o)}{W_o G(o \rightarrow n)} \tag{G.0.4}$$

Here $W_n/G(o \rightarrow n)$ contributes to the forward Rosenbluth factor and $W_o/G(n \rightarrow o)$ contributes to the reverse one. The last expression is used in our code to generating or rejecting a trial configuration.
G.1 Effective Elastic Constant for Orientation

The values of $\kappa_\theta$ are obtained by perturbing

$$\varepsilon = \varepsilon(\theta) = \frac{\kappa}{2}(l_{10} - l_0)^2$$

around the equilibrium. Note that $\theta$ and $l_{10}$ are related by

$$l_{10} = (l_{20}^2 + l_{21}^2 - 2l_{21}l_{20}\cos \theta)^{1/2},$$

so we have

$$\varepsilon' = \kappa(l_{10} - l_0)'_{10} = \kappa(l_{10} - l_0)\frac{l_{20}l_{21}}{l_{10}} \sin \theta$$

At the equilibrium, either $l_{10} = l_0$ or $\sin \theta = 0$. The second derivative of the total energy with respect to $\theta$, evaluated around the equilibrium are

- $l_{10} = l_0$ and $\sin \theta \neq 0$

$$\varepsilon''(\theta_0) = \kappa(l'_{10})^2 = \kappa\left(\frac{l_{20}l_{21}}{l_0}\sin \theta_0\right)^2$$

- $l_{10} \neq l_0$ and $\sin \theta = 0$

$$\varepsilon''(0) = \kappa(l_{10} - l_0)\frac{l_{20}l_{21}}{l_{10}} \cos \theta_0 = \kappa\frac{(l_{20} - l_{21} - l_0)}{l_{20} - l_{21}}l_{20}l_{21} \cos \theta_0$$

In the general cases, these two results are used in our code to compute $\kappa_\theta$. But for some extreme cases, the values have been computed and stored before the simulation starts.

- $l_{21} = l_0$ and $l_{20} \to 0$: $\theta_0 = \pi/2$

$$\kappa_\theta = \kappa\left(\frac{l_{20}l_{21}}{l_0}\sin \theta_0\right)^2 \to 0$$

$$\mathcal{N}(\theta_0) = \int_0^\pi e^{-\kappa_\theta(\theta - \theta_0)^2/2} \sin \theta d\theta = 2 \quad \text{(G.1.1)}$$
Section G.1. Effective Elastic Constant for Orientation

- $l_{20} \geq l_{21} + l_0$: $\theta_0 = 0$
  \[ \kappa_\theta = \kappa \frac{l_{20} - l_{21} - l_0}{l_{20} - l_{21}} l_{20} l_{21} \]  
  $\kappa_\theta$ approaches $\kappa l_{20} l_{21}$ as $l_{20} \gg l_{21} + l_0$.

- $l_{20} < l_{21} - l_0$: $\theta_0 = 0$
  \[ \kappa_\theta = \kappa \frac{l_{21} - l_{20} - l_0}{l_{21} - l_{20}} l_{21} l_{20} \]  

- $l_{20} < l_0 - l_{21}$: $\theta_0 = \pi$
  \[ \kappa_\theta = \kappa \frac{l_0 - l_{21} - l_{20}}{l_{21} + l_{20}} l_{21} l_{20} \]
The monomer density correlation function for homogeneous liquids is normally calculated in $q$ space because of the translational invariance. Here we shall derive the real space behavior (at the long distance) of this quantity using the RPA expression for diblock copolymers near the mean field spinodal. The results is used to estimate the correlation length and is used in Chapter 7 to assess the finite size effects. Consider the inverse Fourier transform of

$$g(q) = 1/(\alpha^2 + (q^2 - q_0^2)^2) \quad (\alpha \propto \chi_s N - \chi N > 0),$$

which is the expansion of the RPA expression for the collective correlation function near the spinodal, up to linear order in $\chi_s N - \chi N$ and $(q^2 - q_0^2)^2$. 


\[
g(r) = \int \frac{dq}{(2\pi)^3} g(q)e^{iqr}
\]
\[
= \frac{2\pi}{(2\pi)^3} \int_0^\infty \frac{q^2}{\alpha^2 + (q^2 - q_0^2)^2} dq \int_{-1}^1 e^{iqr\cos \theta} d(\cos \theta)
\]
\[
= \frac{1}{(2\pi)^2r} \int_0^\infty \frac{2q\sin(qr)}{\alpha^2 + (q^2 - q_0^2)^2} dq
\]
\[
= \frac{1}{(2\pi)^2r} \int_{-\infty}^\infty \frac{q\sin(qr)}{\alpha^2 + (q^2 - q_0^2)^2} dq
\]
\[
= \frac{1}{(2\pi)^2r} \text{Im} \left\{ \int_{-\infty}^\infty \frac{qe^{iqr}}{\alpha^2 + (q^2 - q_0^2)^2} dq \right\}
\]

(H.0.1)

To use the residue theorem, the poles of the denominator are explicitly computed:

\[
q^2 - q_0^2 = \pm i\alpha \longrightarrow q^2 = q_0^2 \pm i\alpha
\]

(H.0.2)

The poles \((\pm p_1, \pm p_2)\) are all of first order, such that

\[
\alpha^2 + (q^2 - q_0^2)^2 = (q + p_1)(q - p_1)(q + p_2)(q - p_2).
\]

(H.0.3)

Where \(p_1 = \rho e^{i\theta}\) and \(p_2 = -\rho e^{-i\theta}\), and \(\rho = (q_0^4 + \alpha^2)^{1/4}\) and \(\theta = \frac{1}{2} \arctan (\alpha/q_0^2)\). Note that \(\pm p_1\) and \(\pm p_2\) are solutions to \(q^2 = q_0^2 + i\alpha\) and \(q^2 = q_0^2 - i\alpha\), respectively. \(\alpha \ll q_0^2\) is relevant, which implies that \(p_1\) and \(p_2\) are in the upper plane. So use the contour in the upper plane, one finds:
\[ g(r) = \frac{1}{(2\pi)^2 r} \text{Im} \left\{ 2\pi i \left[ \frac{p_1 e^{ip_1 r}}{2p_1(p_1^2 - p_2^2)} + \frac{p_2 e^{ip_2 r}}{2p_2(p_2^2 - p_1^2)} \right] \right\} \]

\[ = \frac{1}{4\pi^2 r} \text{Im} \left\{ \pi i e^{ip_1 r} - e^{ip_2 r} \right\} \frac{p_1}{p_1^2 - p_2^2} \]

\[ = \frac{1}{4\pi^2 r} \text{Im} \left\{ \pi i e^{ip_1 r} - e^{ip_2 r} \right\} \frac{2i\alpha}{2i\alpha} \]

\[ = \frac{1}{4\pi^2 r} \text{Im} \left\{ \pi e^{-\rho r \sin \theta} \left( e^{i\rho r \cos \theta} - e^{-i\rho r \cos \theta} \right) \right\} \]

\[ = \frac{1}{4\pi^2 r} \pi e^{-\rho r \sin \theta} \sin(\rho r \cos \theta) \]

\[ = \frac{e^{-\rho r \sin \theta}}{4\pi \alpha r} \sin(\rho r \cos \theta) \quad (H.0.4) \]

The correlation length

\[ R_c = \frac{1}{\rho \sin \theta}. \quad (H.0.5) \]

Since \( \theta \) vanishes with \( \alpha \), \( R_c \) diverges as \( 1/\alpha \). In this limit, \( \sin \theta \simeq \alpha/(2q_0^2) \), \( \cos \theta \simeq 1 \), \( \rho \simeq q_0 \), and

\[ g(r) = \frac{1}{8\pi q_0} \frac{(2q_0/\alpha)e^{-r/(2q_0/\alpha)}}{r} \sin(q_0 r). \quad (H.0.6) \]

Here \( R_c = 2q_0/\alpha \), which may have been guessed by approximating the original \( S(q) \) as \( \alpha^{-2}(1 + 4q_0^2/\alpha^2(q - q_0)^2) = \alpha^{-2}(1 + R_c^2(q - q_0)^2) \).
Statistics of Intramolecular Contacts in Diblock Copolymer

In Chapter 7, we presented simulation results for various collective and single chain properties. Here we present results on the analysis of intramolecular contacts at $\alpha = 0$, for chains of length 16, 32, 64, 128 and 256, in order to understand the local packing effects of the model. We quantify this by measuring the number of interacting neighbors surrounding a typical monomer, and are interested in only the additional interaction between A-B monomer pairs. As $\alpha = 0$, for symmetric diblocks, A and B monomers are indifferent except labeling. For a typical A (or B) monomer, the number of B (or A) monomers surrounding it on a different molecule can be deduced from the study of symmetric binary homopolymer blends, using the same model\textsuperscript{73}. Since the two systems contain the same amount of A and B monomers, the number of inter-molecular A-B contacts in a diblock melts is identical to that of homopolymer melts. So we need only to study the intramolecular A-B contacts.

We denote the numbers of A and B monomers on a molecule by $N_A$ and $N_B$, the fractions by $f_A$ and $f_B$, and label the monomers along a chain contour by $s$ which ranges from 1 to $N_A$ for A block and from $N_A + 1$ to $N$ for B block. Then we define
the number of the intramolecular AB contacts for an A monomer labeled \( s \):

\[
\theta(s) \equiv \sum_{s'=N_A+1}^{N} \langle w(|\mathbf{r}(s) - \mathbf{r}(s')|) \rangle
\]  

(I.0.1)

where \( s' \) runs over all B monomers on the same chain, \( \mathbf{r}(s) \) is the position of monomer \( s \), and \( w(r) \) is the interaction function defined in Eq.(7.2.1). The average is taken over all molecules and sampling snapshots. For \( s = N_A \), the above summation does not include \( s' = N_A + 1 \) term, since it is bonded to \( s \) monomer. Qualitatively, we expect higher \( \theta(s) \) values for monomers closer to the junction. The results are shown in Figure I.1, the normalization chosen to collapse data for different chain lengths (see below).

Figure I.1: The amount of intramolecular contacts for each monomer along the contour, for chain lengths 16, 32, 64, 128, and 256. The data from different chains collapse when normalized by \( \bar{N}^{1/2} \). The solid line represents random walk model prediction, given by Eq.(I.0.2).

The \( s \) and \( N \) dependence of \( \theta(s) \) may be analyzed using random walk statistics\(^{73}\). Consider a monomer \( s \), the random walk model predicts that the probability
that another monomer $s'$ wanders back to the vicinity of the $s$ monomer is $\beta|s' - s|^{-3/2}/(8\rho b^3)$, where $\beta = (6/\pi)^{3/2}$. For long chain molecule, the local liquid structures of typical $s$ monomers are similar and the contour separation $|s' - s|$ is large for typical $s'$, then when $s'$ monomer wanders back to $s$ monomer, it gives approximately a constant contribution to the summation in Eq. (I.0.1), because $w(r)$ is short ranged. We call this constant the effective coordination number and denote it by $z_c$. $z_c$ reflects the local liquid structure and does not depend on whether or not $s$ and $s'$ monomers are on the same chain. It can be measured accurately through independent homopolymer simulations. For our model, $z_c = 0.2965$. Therefore, we arrive at

$$\theta_{\text{intra}}(s) = \frac{z_c\beta}{8\rho b^3} \int_{N_A}^{N} (s' - s)^{-3/2} ds'$$

$$= \frac{z_c\beta}{4N^{1/2}} \left( \frac{1}{\sqrt{f_A - \hat{s}}} - \frac{1}{\sqrt{1 - \hat{s}}} \right).$$

(I.0.2)

Where the summation over $s'$ has been replaced with an integral, $\hat{s} \equiv s/N$, and $\bar{N} = N\rho^2 b^6$. The divergence near $s = f_A$ reflects the failure of random walk statistics for small $s' - s$. When expressed in terms of $\hat{s}$, $\theta(s)$ depends on $N$ through the simple factor $\bar{N}^{-1/2}$, which motivates the normalization in Figure I.1. Clearly, the behavior of $\theta(s)$ for different chains are very well captured by the random walk model, in which the independently measured $z_c$ has been used. The visible deviation occurs close to the junction ($\hat{s} = 0.5$), where the exceptional drops for monomers at $s = N_A$ is due to the treatment of the A-B interaction at the junction. Near the other defect, chain end at $\hat{s} = 0$, $\theta(s)$ increases with decreasing $s$ (slightly). The monomers there are more open to contacts, because they are crowded bonded only at one side, similar to the situation in homopolymers. Similar results have been reported by Hoffmann et al. The average intramolecular A-B contact number per monomer is given by:

$$\theta_{\text{intra}} = \frac{1}{\bar{N}} \int_{0}^{N_A} \theta_{\text{intra}}(s) ds$$

$$= \frac{z_c\beta}{2\bar{N}^{1/2}} \left( \sqrt{f_A} - 1 + \sqrt{f_B} \right).$$

(I.0.3)
For symmetric diblock copolymer in our model, \( \theta_{\text{intra}} = 0.5466z_cN^{-1/2} = 0.1605N^{-1/2} \). For \( f_A = 0 \) or \( f_B = 0 \), \( \theta_{\text{intra}} \) vanishes. The simulated results and this prediction are shown in Figure I.2. The simulation results clearly approach the prediction asymptotically as the chain length increases.

![Figure I.2: Average intramolecular AB contacts for diblock copolymers of lengths 16, 32, 64, 128 and 256. The solid line is the prediction of random walk model, given by Eq.(I.0.3).](image)

In \(^73\), it has been shown that the number of inter-molecular A-B contacts per monomer is given by \( \theta_{\text{inter}}(N) = z_c \left(1 + \beta N^{-1/2}\right) \). Thus total number of A-B contacts per monomer is

\[
\theta = \theta_{\text{inter}} + \theta_{\text{intra}} = z_c \left(1 + \frac{\beta}{N^{1/2}} \sqrt{f_A} + \frac{\beta}{N^{1/2}} \sqrt{f_B}\right). \tag{I.0.4}
\]

For symmetric diblocks, \( \theta = z_c \left(1 + 3.186N^{-1/2}\right) \).
Epitaxial Relation Between \textit{Fddd} And Hex

\textit{Fddd} phase (space group \# 70; the density profile is shown in Figure J.1) was first discovered in ISO triblocks in 2002, by Bates \textit{et al.}, which is perhaps the first example of self-assembled orthorhombic structure in soft matter.\textsuperscript{43} Its stability over the other classical phases in diblocks in terms of SCFT free energy was demonstrated in 2007, by Tyler and Morse.\textsuperscript{161} Recently, it was found experimentally in IS (poly isoprene-styrene) diblock.\textsuperscript{162}

In the following parts, I summarize the study of the stability limit of \textit{Fddd} phase, and based on these results to deduce the possible (crystalline) epitaxial relation between \textit{Fddd} and Hex phases.

Denote the lengths of the orthorhombic unit cell of \textit{Fddd} phase by \(a\), \(b\) and \(c\) respectively. It was found that the ratios \(a : b : c\) are very closely to \(1 : 2 : 2\sqrt{3}\): experimentally, this is inferred from the fact that the first three scattering peaks [004], [022] and [111] nearly overlap; theoretically, this particular set of ratios minimize the SCFT free energy with respect to the variation in domain spacings.\textsuperscript{163} We will show that these particular ratios are compatible with a particular epitaxial relationship between \textit{Fddd} and Hex phase, by studying the thermodynamic stability limit of
Figure J.1: Unperturbed Fddd morphology at $\chi N = 12$ and $f^c_A = 0.42$. The projection along the [110] direction is also shown.

**Fddd** phase using the method described in reference$^{135}$. We use the linear response theory (perturbation theory to SCFT) described in reference$^{163}$ to study the stability limit. The method is based on the Taylor expansion of the SCF free energy with respect to the inhomogeneous composition fluctuations:

$$f(\phi) = f(\phi_0) + \frac{1}{2} f^{(2)}(\phi_0)(\phi - \phi_0)^2 + ...$$

(J.0.1)

Here $\phi_0$ denotes the equilibrium compositions, and $\phi - \phi_0$ measures the deviation from it. Linear response theorem states that $f^{(2)}$ is inverse to the monomer density correlation function, $S(\mathbf{r}, \mathbf{r}')$. $S(\mathbf{r}, \mathbf{r}')$ can be evaluated by first finding the SCFT solution (the equilibrium $\phi$ and $\omega$ fields), then calculate the change in density fields caused by a small perturbation in the potential fields. In practice, it is more convenient to work in reciprocal space for systems having translational symmetry: For the homogeneous phase, $S$ is diagonalized in $\mathbf{k}$ space. For periodical phase, the Bloch theorem says that $S$ is block diagonalized, namely, the entries $S(\mathbf{k}, \mathbf{k}')$ are non-zero only for $\mathbf{k}$ and $\mathbf{k}'$ differing by multiples of the reciprocal lattice basis vectors (see Section 2.4 for introduction). Therefore the entries can be grouped into blocks, $S_{\mathbf{k}}(\mathbf{G}, \mathbf{G}')$, each of which being labeled by a unique wave vector inside the first Brillouin zone (FBZ),
Figure J.2: The first Brillouin zone for face centered orthorhombic structure, with cell parameter: $a : b : c = 1 : 2 : 2\sqrt{3}$. The coordinates for the conventional critical points are: $\Gamma(0,0,0)$, $N\left(\frac{2\pi}{3a},0,0\right)$, $Y\left(0,\frac{\pi}{b},0\right)$, $Z\left(0,0,\frac{\pi}{c}\right)$, and $P\left(\frac{\pi}{2a},\frac{\pi}{2b},\frac{\pi}{2c}\right)$, respectively.

$k$. Here $G$ and $G'$ represent arbitrary reciprocal lattice vectors. The perturbation code we developed allows us to evaluate $S_k(G, G')$ for any given $k$ in the FBZ using symmetry adapted basis functions as explained in reference 135.

If the SCFT solution to a particular phase is stable, all eigenvalues of $S_k^{-1}(G, G')$ are positive except the three trivial modes at $k = 0$ which correspond to the macroscopic displacements. The condition that any of the other eigenvalues become 0 defines the stability limit. The natural of the corresponding eigenvectors tells us how the phase loses its stability. The stability limit of all classical phases in diblock copolymers135,164 have been studied using shi method and have found the epitaxial relationship between Lam and Hex (cylinders are aligned parallel to the lamellar plane), BCC and Hex (cylinders are parallel to the [111] direction of the cubic unit cell), and gyroid and Hex (cylinders are parallel to the [111] direction of the cubic unit cell). Since its discovery, nobody has reported the corresponding study for $Fddd$ phase.

The $Fddd$ phase has a face centered orthorhombic unit cell, to which the reciprocal lattice is a body centered orthorhombic. Depending on the relative lengths of $a$,
Figure J.3: *Fddd* morphology perturbed by 5% (a) and 20% (b) of the unstable mode at $\chi N = 12$ and $f_A = 0.42$. The [110] projection shows the trend of the variation and the epitaxial relationship between *Fddd* and Hexagonal phase.
$b$ and $c$, the FBZ may be one of the 4 types discussed in reference\textsuperscript{165}. For the ratios $1 : 2 : 2\sqrt{3}$, the FBZ is shown in (belong to the type shown in Fig. 3 of reference \textsuperscript{165}) Figure J.2. We first calculated $S_k(G, G')$ $k$ vectors along several representative directions ($\Gamma - Y$, $\Gamma - Z$, $\Gamma - N$, $\Gamma - P$); then evaluate the eigenvalues and check their signs.

![Diagram](image)

Figure J.4: Epitaxial instability limit of $Fddd$ phase in symmetric diblock copolymer.

We used the grid discretization $12 \times 24 \times 40$. For compositions and $\chi N$ inside the $Fddd$ phase window, all eigenvalues are positive (except the translational modes at $\Gamma$ point). For particular compositions inside the window of the Hexagonal phase, we find an unstable mode (its eigenvalue becoming zero) at the $\Gamma$ point. The mode is non-degenerate and has an inversion center, so we can use the even basis functions to expand the mode and speed up the calculations.

To understand the nature of this mode, we add a small density fluctuation represented by the eigenvector of the unstable mode to the non-perturbed $Fddd$ Morphology for $\chi N = 12$ and $f_A = 0.42$ (as an example) shown in Figure J.1. The resulting density profile and the projection along the [011] direction for 5\% and 20\% addition are shown respectively in Figure J.3(a) and J.3(b). As the perturbation fraction is increased, the distortion in the unperturbed morphology results in clearly a hexagonally

231
packed cylindrical array along the [011] direction, which suggests that the discovered unstable mode leads to an epitaxial transition into the Hexagonal phase. Similarly, subtracting the “dangerous” mode leads cylinders packed along [011] direction.

On the other hand, if we start from the hexagonal phase and pack the cylinders in the way suggested by Figure J.3(b), it is straightforward to show that the ratios of the unit cell parameters of the orthorhombic phases are $1 : 2 : 2\sqrt{3}$ and that $a = d_{01}$ being equal to the nearest cylinder pair’s distance. The $q^*$ values are also equal for the two phases.

The completed (epitaxial) instability limit for the $Fddd$ phase in symmetric di-block copolymers for $\chi N$ upto 13.5 is shown as the dashed line in Figure J.4. To right side of the phase window, we did not find any unstable mode other than the mechanical ones, similar to the case for gyroid phase.$^{135}$