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DENSITY FUNCTIONAL THEORY OF MICROPHASE SEPARATION IN BLOCK COPOLYMERS
AND
MONTE CARLO SIMULATIONS OF POLYELECTROLYTE ELECTROPHORESIS

A Dissertation Presented
by
JAMES M MELENKEVITZ

Submitted to the Graduate School of the University of Massachusetts in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY
May 1992
Department of Polymer Science and Engineering
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ABSTRACT

DENSITY FUNCTIONAL THEORY OF MICROPHASE SEPARATION IN BLOCK COPOLYMERS

AND

MONTE CARLO SIMULATIONS OF POLYELECTROLYTE ELECTROPHORESIS

MAY 1992

JAMES M MELENKEVITZ, B.S., RUTGERS UNIVERSITY

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Directed by: Professor Murugappan Muthukumar

In the first half of this dissertation, density functional theory of first order transitions was used to describe the ordering phenomena of amorphous diblock copolymers. The resulting formalism was then applied to the ordering of symmetric diblock copolymers to the lamellar morphology for values of $\chi N$ above the microphase separation transition. $\chi$ refers to the Flory interaction parameter and $N$ is the number of statistical segments comprising the copolymer. Three distinct regimes for the $N$ dependence of the domain space, $D$, were identified. For $10.495 < \chi N < 12.5$, the weak segregation limit is realized where $D$ is proportional to $N^{0.5}$. For $\chi N > 105$, the strong segregation limit is achieved where $D$ is proportional to $N^{0.67}$. Between these limits, for $15 < \chi N < 95$, a new regime with characteristics distinctly different from those of the weak and strong segregation regimes was found. Within this "intermediate" regime, $D$ is proportional to $N^{0.72}$ and the domain boundaries support substantial fluctuations. The distinct features of the microscopic density profiles in the various regimes are discussed.
In addition, density functional theory was employed to investigated the phase behavior of non-symmetric diblock copolymers. In the second half of this dissertation, Monte Carlo simulations were performed in order to study the dynamics of a polyelectrolyte chain in three-dimensional random porous media with an applied electric field. It was found that the dependence of the chain mobility, \( \mu \), on the number of segments comprising the polymer, \( N \), is in qualitative agreement with actual gel electrophoresis experiments. Further, three regions for the \( N \) dependence of the mobility were identified and determined to be a function of the average size of the polyelectrolyte in relation to the average pore size in the random medium. In the region of small \( N \), the mobility is influenced primarily by collisions with the random media. As the average size of the polymer becomes comparable to the average pore size, the existence of entropic barriers has the effect of introducing a strong dependence of the mobility on \( N \). In the high \( N \) regime, the polymer chains become significantly entangled with the random medium, further impeding the motion of the chains. However, in this high \( N \) regime, the chain dynamics cannot be explained by reptation. Lastly, it was demonstrated that the chain dynamics of a polyelectrolyte in the presence of a regular array of obstacles with an applied electric field defers from the dynamics of a chain in a random medium. Indeed, it was demonstrated that the presence of random medium gave rise to a much more efficient separation of polyelectrolytes of different \( N \).
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CHAPTER 1

INTRODUCTION TO DENSITY FUNCTIONAL THEORY
OF
BLOCK COPOLYMERS

1.1 Microphase Separation in Block Copolymers

Block copolymers are formed by the chemical linkage to two or more chemically dissimilar homopolymers (denoted by A,B,C, etc.). Variations in the chemical coupling of the constituent homopolymers lead to the formation of a number of different architectures. For example linking together two homopolymers, A and B, yields an A-B diblock copolymer, while the chemical coupling of the ends of more than two A-B diblock copolymers produces a star block copolymer[1].

At sufficiently low temperatures, such systems frequently exhibit two phase morphology. Unlike incompatible polymer blends which undergo macrophase separation, the presence of the intersegment linkage between the homopolymers constituting the block copolymer restricts phase segregation to micro-dimensional scales. Further, the major component comprising the block copolymer will normally exist as a continuous matrix with the minor component forming discrete domains. These domains are not randomly arranged, however, but tend to form ordered arrays
depending on the composition of the block copolymer[2]. The variation of morphology for an A-B diblock copolymer as a function of block copolymer composition is depicted in Figure 1.1. For the volume fraction of the minor component, \( f \), in the range 0 to 0.2 the minor component exists as spheres arranged on a body-centered-cubic lattice. When \( 0.2 < f \leq 0.34 \), the minor component occurs as cylinders organized on a hexagonal lattice. For \( 0.37 < f \leq 0.5 \), the minor component exists as alternating lamellae.

In addition to the three morphologies discussed above, a new morphology, ordered-bicontinuous double diamond (OBDD), has recently been discovered for polystyrene-polyisoprene block copolymers[3,4] with the composition of polystyrene in the range 0.62 to 0.66. The basic structural unit, a tetrahedron of polyisoprene rods imbedded in a polystyrene matrix, is shown in Figure 1.2 along with the arrangement the tetrahedral units within the unit cell. The resulting structure exhibits the symmetry of the \( \text{Pn3m} \) space group[4].

As a result of the microphase separation, block copolymers have many properties different from those of their constituent homopolymers. For example, the mechanical properties depend strongly on the morphology as well as the component forming the continuous matrix.

The unique properties of block copolymers provides for a wide range of industrial applications[5]. Block copolymers may be used as solubilizing agents to increase the compatibility between its corresponding homopolymers. Also, blending a block copolymer with one of the constituent homopolymers can produce a fine
Figure 1.1 (from reference 2) Morphology of an A-B diblock copolymer as a function of composition. $f$ refers to the volume fraction of the minor component comprising the copolymer.
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dispersion of "foreign" segments within a homopolymer matrix. In fact, this is the technology exploited in the production of impact-modified thermoplastics. In view of the practical importance of block copolymers, understanding the phase separation process from a theoretical perspective would be of great utility.

When a homogeneous block copolymer is cooled, it undergoes a transition to one of the ordered microphases discussed earlier. By drawing an analogy between the microphase separation transition of diblock copolymers and the freezing of simple liquids, one could apply concepts from the theories of freezing to study block copolymer ordering. In recent years, density functional theory[6-15] has been developed to describe the freezing of simple liquids with remarkable success. One of the advantages of applying density functional theory to study freezing, over other theoretical methods[16], is that it easily incorporates a volume change which ordinarily accompanies first order phase transitions like freezing.

In the first half of this dissertation, density functional theory will be implemented to describe the microphase separation of non-crystalline A-B diblock copolymers. Section 1.2 discusses previous theories for the microphase separation of diblock copolymers. These theories have considered two limits of the microphase separation of diblock copolymers. For temperatures near the order-disorder transition, weak segregation theories, discussed in Section 1.2.1, determine the onset of microphase separation along with the prevailing morphology. In Section 1.2.2, strong segregation theories, which determine the relative stability of the various ordered morphologies as a function of block copolymer composition.
at temperatures well below the microphase transition temperature, will be examined. Next, density functional theory of freezing for monatomic systems will be reviewed in Section 1.3 with the application to the freezing of a hard sphere fluid in Section 1.3.1. In Chapter 2, density functional theory will be applied to block copolymers. Section 2.2 develops the formalism for the density functional theory of block copolymers. In Section 2.3 the theory constructed in Section 2.2 will be applied to the ordering of a symmetric diblock copolymer to the lamellar morphology. In Section 2.4, the theory developed is used to determine the phase diagram for a diblock copolymer. The first part of this dissertation concludes with Chapter 3, where some suggestions for future studies are made.

1.2 Previous Theories for the Microphase Separation of Diblock Copolymers

Flexible noncrystalline diblock copolymers in the bulk form various distinct morphologies[1-5,17-25] as either the temperature is lowered or the molecular weight is increased. The boundaries of the stability of the various ordered morphologies are experimentally found to depend on the composition of the diblock copolymer, the temperature and the molecular weight of the copolymer. For diblock copolymers containing an A-type chain of degree of polymerization \( N_A \) and a B-type chain of degree of polymerization
The pertinent variables are the total degree of polymerization $N = N_A + N_B$, the composition of the A-type segments $f = N_A / N$ and the Flory-Huggins interaction parameter, $\chi$, which expresses the selectivity of A-B contacts. In general, the temperature dependence of $\chi$ for diblock copolymers[21-24] is given by, $\chi = \alpha + \gamma / T$, where $\alpha$ and $\gamma$ are constants specific to a given copolymer system. For a given block copolymer composition $f$, as the value of $\chi N$ is increased either by increasing $N$ or reducing the temperature the disordered diblock copolymer melt undergoes a transition at $(\chi N)_t$ to an ordered state. For $\chi N > (\chi N)_t$, the variation of the domain spacing, and the interfacial thickness of the ordered state with molecular weight and temperature has been an area active experimental pursuit[3,17-36] over the past two decades.

Numerous theoretical investigations have had, as an objective, the understanding of the phase diagram of diblock copolymers. These theories may be broadly classified into two groups. The first group, referred to as strong segregation theories[27-36] was pioneered by Meier[27] and Helfand[28-31] and focuses on the microscopic details of block copolymers in the phase-separated state at temperatures well below the microphase separation temperature appropriate for a particular morphology. The strong segregation regime is characterized by the strong spatial variation of composition for the two constituents composing the diblock copolymer, along with a very narrow interface separating the domains of the two components. The second class[37-39] of theories deals with the weak segregation limit. Within the weak segregation limit the microscopic density profile of the components
of the diblock copolymer is considered to vary weakly and approximately sinusoidally in space. The two chains comprising the diblock are highly interpenetrating and the period $D$ of the sinusoidal density profile scales as $N^{0.5}$. Further details of the two classes of theories for the microphase separation of diblock copolymers will be given in Section 1.2.1 and Section 1.2.2.

1.2.1 Weak Segregation Limit

The common feature of weak segregation theories is the predicted small variation of the volume fraction of the components comprising the block copolymer in space. For example consider the lamellar morphology:

\[
\phi_A(r) = \text{volume fraction of } A \text{ segments}
\]

The first investigation into the weak segregation regime was performed by Leibler[37] who used a Landau analysis, which is
strictly valid only for weak first order transitions, to determine the onset of microphase separation and the existing morphology. The free energy density of the ordered phase is determined by expanding in powers of $\phi_A(r)$:

$$
\Delta F = \frac{1}{2} \int_q G_2(q,-q) \ a(q) \ a(-q)
$$

$$
+ \frac{1}{3!} \int_{q_1} \int_{q_2} G_3(q_1,q_2,-q_1-q_2) \ a(q_1) \ a(q_2) \ a(-q_1-q_2)
$$

$$
+ \frac{1}{4!} \int_{q_1} \int_{q_2} \int_{q_3} G_4(q_1,q_2,q_3,-q_1-q_2-q_3) \ a(q_1) \ a(q_2) \ a(q_3) \ a(-q_1-q_2-q_3)
$$

(1.1)

where \{a(q)\} are the Fourier components of the order parameter, $\Psi'(r) = < \phi_A(r) - f >$, $f$ is the fraction of A units in comprising the A-B diblock copolymer, $\phi_A(r)$ is the volume fraction of A segments at space point $r$ and $<$ > denotes the thermal average. The vertex functions ($\Gamma_2, \Gamma_3, \Gamma_4$) were calculated using the Random Phase Approximation (RPA). In general, the second order vertex function, $\Gamma_2$, is related to the structure factor of the homogeneous disorder phase, $S(q)$, by

$$
N \Gamma_2(q,q) = \frac{N}{S(q)}
$$

(1.2)
Within RPA, the structure factor determined by Leibler is

\[ \frac{N}{S(q)} = F(x,f) - 2\chi N, \]

(1.3)

where \( F(x,f) \) is given by,

\[ F(x,f) = \frac{g(1,x)}{\left\{ g(f,x) g(1-f,x) - \frac{1}{4} [g(1,x) - g(f,x) - g(1-f,x)]^2 \right\}} \]

\[ g(f,x) = \frac{2}{x^2} \left[ e^{-fx} - 1 + fx \right] \]

with \( x = k^2 R_g^2 \) and \( R_g^2 \) is the square of the radius of gyration of the unperturbed copolymer, which is assumed to be proportional to molecular weight, \( N \). \( \chi \) is the Flory-Huggins interaction parameter defined earlier. Leibler assumed that if the microphase transition is sufficiently close to the spinodal (i.e. thermodynamic stability limit), defined as the point where the minimum of \( \Gamma_2 \) is zero, then the important contributions to the free energy are those with a single wave vector \( q^* \). For the higher order vertex functions, \( \Gamma_3 \) and \( \Gamma_4 \), Ohta and Kawasaki[33] found that the full angular dependence of \( \Gamma_3(q_1,q_2,q_3) \) and \( \Gamma_4(q_1,q_2,q_3,q_4) \) may be replaced by \( \Gamma_3(1) \) and \( \Gamma_4(0,0) \). \( \Gamma_3(1) \) and \( \Gamma_4(0,0) \) are coefficients defined by
Leibler[37]. With these approximations, Leibler’s theory for the free energy change upon microphase separation, $\Delta F = \Phi$, becomes

$$
\Phi = n \tau a_n^2 - \frac{2}{3} n \theta_n a_n^3 + \frac{1}{2} n a_n^4 (\eta_n + n \lambda)
$$

$$
\tau = \frac{2}{c^2} [(\chi N)_s - \chi N]
$$

$$
c = \left[ \frac{1}{3} x \frac{\partial^2 F(x, f)}{\partial x^2} \right]_{x=x^*}^{1/2}
$$

(1.4)

where $x^*$ is the value of $x$ at the minimum of $F(x, f)$ and $\chi N_s$ is the value of $\chi N$ at the spinodial, defined above. $\theta_n$ and $\eta_n$ depend on the morphology being studied,

- **lamellae**
  - $\theta_1 = 0$
  - $\eta_1 = -\lambda/2$

- **cylinders**
  - $\theta_3 = -\mu$
  - $\eta_3 = -\lambda/2$

- **BCC spheres**
  - $\theta_6 = -2\mu$
  - $\eta_6 = 3\lambda/2$

where $\mu = N \Gamma_3(1)/c^3$ and $\lambda = N \Gamma_4(0,0)/c^3$. The values of $x^*$, $\chi N_s$, $c$, $\mu$ and $\lambda$ at various $f$ pertinent for this dissertation are given in Table A.1 of Appendix A.
Within the single wave vector approximation made by Leibler the order parameter becomes

\[
\Psi(r) = a_n \sum_{i=1}^{n} \left[ e^{iQ \cdot r} + e^{-iQ \cdot r} \right]
\]

(1.5)

For the lamellar phase, \( n=1 \), the vectors with magnitude \( q^* \) are:

\[ Q_1 = q^*(1,0,0). \]

For the hexagonal cylinders, \( n=3 \), the vectors are:

\[ Q_1 = q^*(1,0,0), \]
\[ Q_2 = (q^*/2) (-1, 3, 0), \]
\[ Q_3 = (q^*/2) (-1, -3, 0). \]

Lastly, the vectors for the body-centered-cubic spheres, \( n=6 \), are:

\[ Q_1 = (q^*/2) (1,1,0), \]
\[ Q_2 = (q^*/2) (-1,1,0), \]
\[ Q_3 = (q^*/2) (0,1,1), \]
\[ Q_4 = (q^*/2) (0,1,-1), \]
\[ Q_5 = (q^*/2) (1,0,1), \]
\[ Q_6 = (q^*/2) (1,0,-1). \]

The phase diagram for a diblock copolymer calculated using Leibler's theory is presented in Figure 1.3. The order parameters, \( \{a_n\} \) at the order-disorder transition to body-centered-cubic spheres that will be compared to the results of the density
Figure 1.3 (from reference 37) Phase diagram for an A-B diblock copolymer calculated from the mean field theory of Leibler. The regions marked DIS (disordered phase), BCC (body-centered-cubic spheres), HEX (hexagonal cylinders), and LAM (lamellae) refer to the thermodynamically stable phase in that region. \( \chi \) is the Flory interaction parameter, \( N \) is the number of statistical segments, and \( f \) is the fraction of A segments contained in the A-B diblock copolymer.
functional theory developed in Chapter 2 are given in Appendix A. The order parameters for the transitions to the cylindrical and lamellar morphologies necessary for comparison to the predictions of density functional theory also appear in Appendix A. The theory predicts a first order transition to BCC spheres for all compositions excluding f=0.5. The transition at f=0.5 is predicted to be continuous and the ordering is directly to the lamellar morphology. Due to the assumption that the transition be in the vicinity of the spinodal, Leibler's theory would be expected to work best only near f=0.5.

Intrinsic in Leibler's development was the homogeneous state used in the expansion for the free energy of the ordered phase, has a uniform density (i.e. fluctuations are absent). The weak segregation theory of Fredrickson and Helfand[39] attempted to add fluctuations into the theory of Leibler in a self-consistent manner, with the assumption of a dominant wave vector, q*, being retained. The resulting expression for the free energy of the ordered state ends up being very similar to the liquid crystal system modeled by Brazovskii[40]. The inclusion of fluctuations into the disordered phase gives rise to the phase diagram being a function of the number of statistical segments, N. Figure 1.4 gives the phase diagram for two values of N. The important features of this model are: (1) the N dependence of the phase diagram gives rise to a fluctuation induced first order for f=0.5, (2) there exists composition ranges for which it is possible to pass directly to any of the ordered mesophases and (3) Leibler's phase diagram is recovered in the limit N→∞. As with Leibler's theory, because of the
Figure 1.4 (from reference 39) Phase diagram for a diblock copolymer with $N=10^9$ and $N=10^4$ calculated using the theory of Fredrickson and Helfand. The regions denoted by DIS (disordered phase), BCC (body-centered-cubic spheres), HEX (hexagonal cylinders), and LAM (lamellae) refer to the thermodynamically stable phase in that region. $\chi$ is the Flory interaction parameter, $N$ is the number of statistical segments, and $f$ is the composition of the diblock copolymer.
presumed single wave vector dominance, the theory of Fredrickson and Helfand can be expected to hold only near f=0.5. Further, the model is restricted to polymers with a very large number of statistical segments (N>10⁴). The phase diagram in Figure 1.4 demonstrates that the body-centered-cubic spheres have completely disappeared for N=10⁴, however; experimental results provided in reference 30 show that the spherical morphology has indeed been observed in a number of block copolymer systems with N<10⁴.

In both of the weak segregation theories presented above it was assumed that the order phase could be described by a single dominant wave vector, q*. Neither theory attempted to determine the extent of the weak segregation regime, nor do they provide a prescription for determining the cross over to the strong segregation limit. The density functional theory constructed in Chapter 2 will address these important questions.

1.2.2 Strong Segregation Limit

Strong segregation theories[27-36] focus on the morphology of block copolymers at temperatures well below the microphase separation temperature. The strong segregation regime is characterized by the very strong spatial variation of composition for the two components contained in the diblock copolymer.
Consider the lamellar morphology:

\[ \phi_A(r) \]

\( \phi_A(r) \) = volume fraction of A units

The total free energy of the system in the strong segregation limit is considered to consist of two contributions, (1) the interfacial energy and (2) the stretching of the polymer chains which is a consequence of the increased incompatibility of the two constituents forming the block copolymer at lower temperatures. The competition between these two effects gives rise to the N dependence of the domain spacing to be given by \( D \sim N^{\alpha} \), where \( \alpha \) is close to 2/3. The 2/3 scaling exponent for the domain spacing has been observed experimentally for some systems[3,20-22], however; other investigators[24,25] obtained a power of 0.8. In addition, the compositional dependence of the morphology predicted within the strong segregation theory of Ohta and Kawasaki[33] is in fairly good agreement with experimental findings[3,21,22].

Given the deficiencies of the weak segregation theories discussed earlier and since strong segregation theories should only be valid at very low temperatures (i.e. \( \chi N \gg (\chi N)_T \), there is a
critical need for a comprehensive theory for the microphase separation of noncrystalline diblock copolymers. It would be advantageous if a single theory could predict not only the onset of microphase separation and the prevailing morphology, but also determine the morphology at temperatures below the transition approaching the strong segregation limit. The goal of the first half of this dissertation is to apply density functional theory to describe the microphase separation of block copolymers to satisfy these challenges. Prior to applying density functional theory to block copolymers, a review of density functional theory of freezing of simple liquids will be undertaken in the next section.

1.3 Density Functional Theory of Freezing

Density functional theory was first developed to study the freezing of simple liquids[6-15] and later applied to a wide variety of other problems[41-44] including glass formation, surface tension of mixtures of monatomic liquids,and liquid crystals. Commonly, density functional theory employs the Grand Canonical ensemble (constant T,V and \(\mu\)) to predict the thermodynamic properties of a system with a microscopically varying density profile (ordered state) by expanding the free energy of the ordered state about a uniform disordered state. Within the Grand Canonical ensemble, the minimization of the Grand Potential, \(\Omega(=PV)\), determines the equilibrium state of the system.
As a specific example, consider the freezing of a single component monatomic substance. The change in $\Omega$ upon freezing is given by,

$$\Delta \Omega = \Delta A - \Delta G,$$

(1.6)

where $\Delta A$ and $\Delta G$ are respectively, the change in the Helmholtz free energy and Gibbs free energy upon freezing. When the Grand Potential is implemented to study freezing, the chemical potential, $\mu$, is equivalent in the solid and liquid phases. Therefore, $\Delta G$ is

$$\Delta G = \mu \int [\rho(r) - \rho_l] \, dr.$$

(1.7)

Here, $\rho(r)$ is the density profile of ordered solid phase and $\rho_l$ is the density of the homogeneous liquid. The change in the Helmholtz free energy upon freezing is,

$$\Delta A = A[\rho(r)] - A[\rho_l],$$

(1.8)

where the free energy of the ordered phase is a functional of the microscopic density $\rho(r)$. Next, the customary procedure in density functional theory is to divide the total Helmholtz free energy of the solid into an "ideal" contribution, $A_{\text{id}}[\rho(r)]$, and an excess part, $A_{\text{ex}}[\rho(r)]$. The ideal contribution being,

$$A_{\text{id}}[\rho(r)] = kT \int \rho(r) \left[ \ln \rho(r) - 1 \right] \, dr,$$

(1.9)
which accounts for the entropy loss associated with creating a non-
uniform density profile in the absence of interparticle interactions.

The crucial approximation in density functional theory involves expanding the excess Helmholtz free energy, $A_{\text{ex}}[\rho(r)]$, in a
functional Taylor series about the disordered liquid state with the same chemical potential as the solid.

$$A_{\text{ex}}[\rho(r)] = A_{\text{ex}}[\rho_1] + \int \frac{\delta A_{\text{ex}}}{\delta \rho(r)} \bigg|_{\rho_1} [\rho(r) - \rho_1] \, dr$$

$$+ \frac{1}{2} \int \int \frac{\delta^2 A_{\text{ex}}}{\delta \rho(r) \delta \rho(r')} \bigg|_{\rho_1} [\rho(r) - \rho_1] [\rho(r') - \rho_1] \, dr \, dr' + \ldots$$

(1.10)

The derivatives, $\frac{\delta^n A_{\text{ex}}}{\delta \rho(r_n) \ldots \delta \rho(r_1)} \bigg|_{\rho_1}$, are related to the $n$th order
direct correlation functions of the liquid, $C^{(n)}(r_1, r_2, \ldots, r_n)$, by

$$C^{(n)}(r_1, r_2, r_3, \ldots, r_n) = -\frac{1}{kT} \frac{\delta^n A_{\text{ex}}}{\delta \rho(r_n) \ldots \delta \rho(r_2) \delta \rho(r_1)} \bigg|_{\rho_1}$$

(1.11)

Using the fact that $C(r_1) = -\mu/kT + \ln \rho_1$ and combining equations (1.6) through (1.11) yields:

$$\frac{\Delta \Omega}{kT} = \rho_1 V + \int dr \, \rho(r) [\ln \rho(r) - 1]$$

$$- \frac{1}{2} \int \int C^{(n)}(r_1, r_2) [\rho(r_1) - \rho_1] [\rho(r_2) - \rho_1] \, dr_1 \, dr_2 + \ldots$$

(1.12)
In practice, the series in equation (1.12) is usually truncated after the second order term without any aprior justification. Recent work\[12,13,45\] has focused on the inclusion of higher order correlation functions into the description of freezing, with the predicted freezing transition being found to vary slightly with the addition of the higher order correlation functions.

The advantage of truncating the series after the second order term follows from the relation\[46\]

\[
S(k) = \frac{1}{1 - \rho_1 C^{(2)}(k)},
\]

(1.13)

where \(S(k)\) and \(C^{(2)}(k)\) are the Fourier transforms of the static structure factor and second-order direct correlation function of the liquid, respectively. The second-order direct correlation function is synonymous with the Ornstein-Zernike direct correlation function from the theory of simple liquids. Clearly, density functional theory may be used to predict the freezing of liquids even in the absence of a theoretical model for the liquid state, if experimental data or a computer simulation results for the static structure are available.

The minimization of \(\Delta \Omega\) with respect to the density profile provides the equilibrium state of the system for a given \(\rho_1\). For the minimum of \(\Delta \Omega > 0\), the disordered phase is the thermodynamically stable phase. When the minimum of \(\Delta \Omega < 0\) the solid is the stable phase. The point where the minimum of \(\Delta \Omega\) is zero signifies the equilibrium freezing point.
To determine $\Delta \Omega$ in equation (1.12), the density profile for the solid is expanded in a Fourier series specific to the crystal structure being studied

$$\rho(r) = \rho_s + \sum_{q \neq 0} A_q e^{i q \cdot r},$$

(1.14)

where $\{A_q\}$ are the reciprocal lattice vectors of the crystal habit being studied and $\rho_s$ is the average density of the solid phase.

Commonly two approaches have been utilized to determine the freezing transition. The first method[13-15], a conjectured functional form for the density profile with a small number of variational parameters is specified and the grand potential difference for freezing is minimized with respect to the variational parameters. The other method[8-10], attempts to solve for the global minimum of $\Delta \Omega$ and $\{A_q\}$ directly. In the next section these methods will be applied to the freezing of a hard sphere liquid.

1.3.1 Hard Sphere Freezing

The application of density functional theory to predict the freezing of a hard sphere liquid has been undertaken by a number of investigators[7-10,12-15]. As a demonstration of the solution methods typically applied in density functional theory and also to
identify possible difficulties that may arise when determining a phase transition, hard sphere freezing will be examined here.

The series in equation (1.12) will be truncated after second order and $C^{(2)}(r_1, r_2)$ was obtained by applying the Percus-Yevick approximation to the closure of the Ornstein-Zernike equation[46].

Method I[13-15]:
Here the density profile takes a presumed functional form

$$\rho(r) = \left(\frac{\alpha}{\pi}\right)^{\frac{3}{2}} \sum_{R} \exp[-\alpha (r-R)^2]$$

(1.15)

where $\{R\}$ are the lattice vectors of crystal type being studied and $\alpha$ is a variational parameter. Assuming the Gaussian functions are sharply peaked on the lattice sites, $\{R\}$, the coefficients in equation (1.14) are:

$$A_q = \rho_s \exp[-|q|^2/4\alpha].$$

(1.16)

Then for a given a liquid density $\rho_1$:

(A) Set the value of $\rho_s$ and vary $\alpha$ to minimize $\Delta\Omega$.

(B) Vary $\rho_s$ until the global minimum of $\Delta\Omega$ is found.

A flow chart for the computer program that applies Method I is provided in Appendix B. The equilibrium transition occurs at the point where the global minimum of $\Delta\Omega$ is zero. Figure 1.5 gives $\Delta\Omega$ as a function of $\rho_s$ for $\rho_1=0.95$. The global minimum occurs at $\rho_s=1.11$ with $\Delta\Omega/VkT=0.213$. Therefore, the disordered liquid is
Figure 1.5 Dimensionless grand potential difference per unit volume, $\Delta \Omega/VkT$, as a function of the solid phase density, $\rho_s$, for the freezing of a hard sphere liquid calculated using density functional theory. The density of the liquid phase, $\rho_l$, is 0.95.
the thermodynamically stable phase at $\rho_l=0.95$. Applying this procedure gives $\rho_1=0.967$ and $\rho_S=1.148$ ($\alpha=483.08$) for the equilibrium freezing transition which is in good agreement with previous predictions[13,15]. In addition, the predicted transition via density functional theory is in fairly good agreement with the Monte Carlo simulation of Hoover and Ree[47] which yielded, $\rho_1=0.948$ and $\rho_S=1.045$ for the transition.

Method II[8-10]:
For a given liquid density $\rho_1$:

(A) Solve for the local extremum (i.e. $\delta \Delta \Omega / \delta \rho(r)=0$) of equation (1.12) given by,

$$\ln \frac{\rho(r)}{\rho_1} = \int C^{(2)}(r_1,r_2) [\rho(r_2) - \rho_1] \, dr_2$$

Which is combined with equation (1.14) to determine the coefficients $\{Aq\}$ and $\rho_S$ at the local extremum.

(B) Determine the value of $\Delta \Omega$ at the local extremum from equation (1.12).

A flow chart of the computer program used to implement Method II is given in Appendix B. Application of Method II for $\rho_1=0.95$ gave $\rho_S=0.97$ with $\Delta \Omega/\rho_1 \sqrt{kT}=0.30$. Recall the result obtained by way of Method I at $\rho_1=0.95$ was $\rho_S=1.11$ with $\Delta \Omega/\rho_1 \sqrt{kT}=0.224$. The origin of the discrepancy between the two results may arise from the possibility of convergence to saddle points[15] which is sometimes a consequence of employing
Method II. One possible way to avoid the convergence to saddle points is to work directly with equations (1.12) and (1.14) in a manner similar to Method I.

Modified Method II:

For a given liquid density \( \rho_1 \):

(A) Find the values of \( \{A_q\} \) which minimize \( \Delta \Omega \) at fixed \( \rho_S \).

(B) Vary \( \rho_S \) until the global minimum of \( \Delta \Omega \) is found. Again the equilibrium transition occurs for the value of \( \rho_1 \) where \( \Delta \Omega \) at the global minimum is zero. The flow chart for the computer program that invokes the Modified Method II is given in Appendix B. The results for the equilibrium transition obtained using this method are in very good agreement with the predictions of Method I.

Given the success of density functional theory at predicting the freezing transition for simple monatomic substances, such as the hard sphere fluid, it should be possible to apply the density functional formalism to study the microphase separation in diblock copolymers.

1.4 Conclusions

Diblock copolymers are well known to undergo an order-disorder transition to a microphase separated state as the temperature is decreased. Previous theories were concern with two limits of the
microphase separation. Weak segregation theories[37-39] consider the determination of the onset of the microphase separation transition and the prediction of the thermodynamically stable phase near the order-disorder transition. The weak segregation theories assumed that the microscopic density profile of the constituent segments varies sinusoidally in space. Neither the validity of this assumption, nor the temperature range of the weak segregation regime were determined by the weak segregation theories. The other class of theories address the strong segregation limit. Strong segregation theories[27-36] establish the microscopic details of the phase separated diblock copolymer at temperatures well below the microphase separation temperature. The result of strong segregation theories is the domain spacing, D, scales as the molecular weight of the copolymer to the two-thirds power. Also, the extent in temperature where the strong segregation theories should be valid was not obtained. By exploiting the analogy between the freezing of a simple liquid and the microphase separation of block copolymers, it should be possible to apply density functional theory to diblock copolymers. The resulting theory should be able to determine not only the extent of the weak and strong segregation regimes, but also the cross over between these limits.
References of Chapter 1

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CHAPTER 2

DENSITY FUNCTIONAL THEORY OF DIBLOCK COPOLYMERS

2.1 Introduction

The microscopic details of the ordered phase-separated states in diblock copolymers have been an area of active experimental pursuit over the past two decades[1-16]. These investigations have focused on the determination of the stability of the different ordered phases[2-6] as a function of block copolymer composition as well as the variation of the domain spacing and the interfacial thickness[10-16] with temperature and molecular weight of the copolymer. In order to compare the experimental findings to the predictions of the numerous theories[17-29], it is necessary to determine whether the experiments correspond to the weak or strong segregation limits. However, the theories for the weak segregation limit[27-29] have neglected to address the range of temperatures and molecular weights where weak segregation behavior should be observed. In addition, the strong segregation theories[17-26] fail to provide a clear criterion for the onset of this segregation regime and none of the existing theories discusses the nature of the crossover between the two limits. In this chapter a density functional theory is constructed to describe the order-disorder transition of diblock copolymers to one of the three
morphologies, body-centered-cubic (BCC) spheres, hexagonal cylinders, and lamellae. Also, density functional theory will be used to determine the thermodynamically stable morphology at temperatures below the microphase transition, approaching the strong segregation limit. The chapter is organized as follows. In Section 2.2 the density functional formalism will be developed for diblock copolymers. Section 2.3 applies the resulting formalism to the lamellar ordering of symmetric diblock copolymers. Here the extent of the weak segregation limit is determined along with the onset of the strong segregation limit. In addition, a new regime, intermediate in temperature with respect to the weak and strong segregation limits is discovered. In Section 2.4 density functional theory is used to determine the phase diagram of an A-B diblock copolymer. Lastly, in Section 2.5 conclusions regarding the utility of density functional theory for describing the microphase separation of block copolymers are made.

2.2 Application of Density Functional Theory to Describe the Ordering of Diblock Copolymers

Consider an A-B diblock copolymer system with chemical potential $\mu$ contained in a volume $V$ at temperature $T$. Within the grand canonical description, the system is open to the number of diblock copolymer chains, $n$. Each copolymer chain consists of $N$ segments with the fraction of A segments in a chain being given by
Throughout this chapter, it will be assumed that the segments comprising both the A and the B blocks have the same Kuhn length, $l$. Although the system considered here is a one component system in the thermodynamic sense, there are two microscopic density variables at any space point $r$, namely, $\rho_A(r)$ and $\rho_B(r)$ corresponding respectively to the local monomer densities of type A and B. Instead of describing the system in terms of $\rho_A(r)$ and $\rho_B(r)$, the total microscopic monomer density $\rho(r)$ and either $\rho_A(r)$ or $\rho_B(r)$ could equivalently be used since $\rho(r) = \rho_A(r) + \rho_B(r)$. Here, the A-B diblock copolymer system will be described by $\rho(r)$ and $\rho_A(r)$. The grand potential $\Omega[\rho_A(r), \rho(r)]$ ($\Omega = -PV$, where $P$ is pressure) and Helmholtz free energy $F[\rho_A(r), \rho(r)]$ are unique functionals of the two microscopic density variables $\rho(r)$ and $\rho_A(r)$:

$$
\Omega[\rho(r), \rho_A(r)] = F[\rho(r), \rho_A(r)] - \frac{\mu}{N} \int \mathrm{d}r \, \rho(r).
$$

(2.1)

Note that the chain density $\rho(r)/N$ is the conjugate variable to the chemical potential, $\mu$. The equilibrium density profiles $\rho_{A0}(r)$ and $\rho_0(r)$ for the system are determined by minimizing the grand potential functional with respect to variations in $\rho_A(r)$ and $\rho(r)$:

$$
\frac{\delta \Omega}{\delta \rho_A(r)} \bigg|_{\rho_{A0}(r), \rho_0(r)} = 0,
$$

$$
\frac{\delta \Omega}{\delta \rho(r)} \bigg|_{\rho_{A0}(r), \rho_0(r)} = 0.
$$

(2.2)
Evaluated at the equilibrium densities, $\Omega[\rho_0(r),\rho_{A0}(r)]$ and $F[\rho_0(r),\rho_{A0}(r)]$ are respectively, the grand potential and Helmholtz free energy for the system.

The total Helmholtz free energy functional, $F$, can be conveniently divided into two parts, an ideal contribution, $F_{id}$, which neglects potential interactions between segments but takes into account the polymer chain connectivity, and an excess part, $F_{ex}$, containing the effects of the potential interactions.

$$F = F_{id} + F_{ex}$$

(2.3)

Substitution of the functional forms of $F_{id}[\rho(r),\rho_A(r)]$ and $F_{ex}[\rho(r),\rho_A(r)]$ into equation (2.1) and (2.2) yields a set of two coupled self-consistent equations for the equilibrium densities $\rho_0(r)$ and $\rho_{A0}(r)$:

$$\frac{\delta F_{ex}}{\delta \rho(r)} \bigg|_{\rho_{A0}(r), \rho_0(r)} = - \frac{\delta F_{id}}{\delta \rho(r)} \bigg|_{\rho_{A0}(r), \rho_0(r)} + \frac{\mu}{N},$$

$$\frac{\delta F_{ex}}{\delta \rho_A(r)} \bigg|_{\rho_{A0}(r), \rho_0(r)} = - \frac{\delta F_{id}}{\delta \rho_A(r)} \bigg|_{\rho_{A0}(r), \rho_0(r)}.$$

(2.4)

The existence of one of the various ordered morphologies in the microphase separated state of diblock copolymers corresponds to a solution of this coupled set of equations for which $\rho_0(r)$ and $\rho_{A0}(r)$ are periodic in space. In practice, the equilibrium ordered states are found by parameterizing $\rho(r)$ and $\rho_A(r)$ with the presumed
symmetries of the ordered states and minimizing $\Omega$ with respect to the period and amplitude of $p_A(r)$ and $\rho(r)$. The coexistence between the disordered phase and the ordered state occurs when $T$, $\mu$, and $\Omega$ in the two phases are equal.

The key approximation for density functional theory\[30-40\] of order-disorder transitions is to expand the excess Helmholtz free energy $F_{ex}$ of the ordered state in a functional Taylor series about a disordered phase with the same chemical potential, $\mu$, as the ordered phase. For diblock copolymers the homogeneous disordered phase is characterized by densities $\rho_d=<\rho_d(r)>_0$ and $\rho_A=<\rho_A(r)>_0$, where $< >_0$ denotes the average over all density profiles in the homogeneous state. This leads to the functional expansion for $F_{ex}[\rho(r),p_A(r)]$ in powers of $[\rho(r) - \rho_d]$ and $[\rho_A(r) - \rho_{Ad}]$ to be given by,

$$F_{ex}[\rho_A(r),\rho(r)] = F_{ex}[\rho_{Ad},\rho_d] + \int dr \frac{\delta F_{ex}}{\delta \rho(r)} \bigg|_{\rho_{Ad},\rho_d} [\rho(r) - \rho_d]$$

$$+ \int dr \frac{\delta F_{ex}}{\delta \rho_A(r)} \bigg|_{\rho_{Ad},\rho_d} [\rho_A(r) - \rho_{Ad}]$$

$$+ \frac{1}{2} \int dr' dr \frac{\delta^2 F_{ex}}{\delta \rho(r) \delta \rho(r')} \bigg|_{\rho_{Ad},\rho_d} [\rho(r) - \rho_d] [\rho(r') - \rho_d]$$

$$+ \int dr' dr \frac{\delta^2 F_{ex}}{\delta \rho(r) \delta \rho_A(r')} \bigg|_{\rho_{Ad},\rho_d} [\rho(r) - \rho_d] [\rho_A(r') - \rho_{Ad}]$$

$$+ \frac{1}{2} \int dr' dr \frac{\delta^2 F_{ex}}{\delta \rho_A(r) \delta \rho_A(r')} \bigg|_{\rho_{Ad},\rho_d} [\rho_A(r') - \rho_{Ad}] [\rho_A(r) - \rho_{Ad}]$$

$$+ \ldots \ldots .$$

(2.5)
The Helmholtz free energy of the diblock copolymer system studied here is obtained directly from the coarse grained microscopic Hamiltonian, which is taken to be the generalized Edwards Hamiltonian,

$$\beta H = \sum_{\alpha=1}^{n} \sum_{i=1}^{N} \frac{p_{\alpha,i}^2}{2m} + \frac{3}{2l^2} \sum_{\alpha=1}^{n} \sum_{i=1}^{N-1} (R_{\alpha,i+1} - R_{\alpha,i})^2$$

$$+ \frac{1}{2} \sum_{\alpha,\beta=1}^{n} \sum_{i,j=1}^{N} v(R_{\alpha,i} - R_{\beta,j}),$$

(2.6)

where all segments are assumed to have the same mass $m$ and the Kuhn length, $l$, is identical for both blocks. $R_{\alpha,i}$ and $p_{\alpha,i}$ are respectively the position and momentum of the $i^{th}$ segment on chain $\alpha$. $v(R_{\alpha,i} - R_{\beta,j})$ is the short-ranged pairwise interaction and is different for different types of segment pairs such as A-A, A-B, and B-B. $\beta^{-1}$ is the Boltzmann constant times the temperature $T$.

The explicit functional form for $F_{ex}[\rho(r),\rho_A(r)]$ employed in this dissertation was determined by Leibler[27] using the random phase approximation and the result is merely quoted below. The ideal contribution $F_{id}[\rho(r),\rho_A(r)]$ can readily be obtained by considering the canonical ensemble and taking the interaction term $v(R_{\alpha,i} - R_{\beta,j})$ in the Hamiltonian above to be zero. It is given by,

$$F_{id} = -\frac{1}{\beta} \ln Z_{id},$$

(2.7)
where

\[ Z_{id} = \frac{1}{n!} \hbar^{3nN} \left[ \int \prod_{i=1}^{N} d\mathbf{p}_i \prod_{j=1}^{N} d\mathbf{R}_j \ e^{-\beta \frac{\hbar}{2m} \sum_{i=1}^{N} p_i^2 - \frac{3}{2} \sum_{j=1}^{N-1} (R_{j+1} - R_j)^2} \right]^n. \]

Integrating over position and momentum yields,

\[ Z_{id} = \frac{V^n}{n!} \left( \frac{2\pi l^2}{3} \right)^{\frac{3n}{2}(N-1)} \lambda_T^{-3Nn}, \tag{2.8} \]

where \( \lambda_T = \left( \frac{\beta \hbar^2}{2\pi m} \right)^{1/2} \) with \( \hbar \) being the Planck constant. Defining \( \rho = Nn/V \) as the total segment density and substituting equation (2.8) into equation (2.7) gives,

\[ F_{id}(\rho) = \frac{V}{\beta N} \rho (\ln \rho - \theta_N), \tag{2.9} \]

where,

\[ \theta_N = 1 + \ln N + \frac{3}{2} (N-1) \ln \left( \frac{2\pi l^2}{3} \right) - 3N \ln \lambda_T. \]

If \( \rho \) is not a constant as assumed here but a spatially varying quantity, \( \rho(\mathbf{r}) \), \( F_{id} \) becomes

\[ F_{id}[\rho(\mathbf{r})] = \frac{1}{\beta N} \int d\mathbf{r} \ \rho(\mathbf{r}) [\ln \rho(\mathbf{r}) - \theta_N]. \tag{2.10} \]
It is to be noted that this result is the direct generalization of \( F_{id} \) for monatomic systems, now accounting for the polymer chain connectivity. Therefore, \( F_{id} \) for monatomic systems can be recovered by taking the limit \( N=1 \) in equation (2.10). Also, different choices for \( F_{id} \) of polymers, other than the one used here, have been made previously by other investigators[41-43]. McCoy et al.[39] applied the reference interaction site method (RISM) [41] to polyatomic systems. The ideal contribution to the total Helmholtz free energy, \( F_{id} \), was determined to be,

\[
F_{id} = \sum_{\alpha,M} \int dr \left< \rho_{\alpha M}(r) \right> \left[ \ln \left< \rho_{\alpha M}(r) \right> \chi^3 - 1 \right] + F[\left< \rho_{\alpha M}(r) \right>]
\]

(2.11)

where \( F[\left< \rho_{\alpha M}(r) \right>] \) refers to the density at \( r \) of site \( \alpha \) on the molecule of type \( M \). The first term in equation (2.11) is just the entropy functional for an ideal gas of sites, while the second term, \( F[\left< \rho_{\alpha M}(r) \right>] \), provides the effects of the intramolecular bonding for the polyatomic molecule. McCoy et al. expanded \( F[\left< \rho_{\alpha M}(r) \right>] \) in a functional Taylor series about a uniform liquid state. Then, to lowest order \( F_{id} \) is just that for a monatomic liquid mixture composed of all the sites contained in the polyatomic molecule. The major deficiency of the approach taken by these workers is that in order to properly account for the chain connectivity of polymers, the series expression for \( F[\left< \rho_{\alpha M}(r) \right>] \) would have to be carried out to many orders, making applications to polymers difficult.

Similarly, McMullen and Freed[43] relegated all the intramolecular
interactions to the excess free energy, $F_{ex}$. Note, the expression for $F_{id}$ derived here (equation 2.10) includes the effects of intramolecular bonding for flexible polymers in a simple expression.

By combining equations (2.1), (2.3), (2.5), and (2.10) the expression for the difference in grand potential between an ordered state with densities $\rho(r)$ and $\rho_A(r)$, and a disordered state with densities $\rho_d$ and $\rho_{Ad}$ is:

$$\Omega[\rho_A(r), \rho(r)] - \Omega[\rho_{Ad}, \rho_d] =$$

$$= \frac{1}{\beta N} \int dr \rho(r) \ln \frac{\rho(r)}{\rho_d} - \frac{1}{\beta N} \int dr [\rho(r) - \rho_d]$$

$$+ \frac{1}{2} \int dr dr' \frac{\delta^2 F_{ex}}{\delta \rho(r) \delta \rho(r')} \bigg|_{\rho_{Ad}, \rho_d} [\rho(r) - \rho_d] [\rho(r') - \rho_d]$$

$$+ \int dr dr' \frac{\delta^2 F_{ex}}{\delta \rho(r) \delta \rho_A(r')} \bigg|_{\rho_{Ad}, \rho_d} [\rho(r) - \rho_d] [\rho_A(r') - \rho_{Ad}]$$

$$+ \frac{1}{2} \int dr dr' \frac{\delta^2 F_{ex}}{\delta \rho_A(r) \delta \rho_A(r')} \bigg|_{\rho_{Ad}, \rho_d} [\rho_A(r') - \rho_{Ad}] [\rho_A(r) - \rho_{Ad}]$$

$$+ \ldots$$

(2.12)

In obtaining the expression for $F_{ex}$ using the random phase approximation, Leibler[27] employed the incompressibility constraint,

$$\rho_A(r) + \rho_B(r) = \rho.$$
Note that the total density, \( \rho \), is independent of \( r \). Although this constraint need not be imposed in the calculational scheme outlined above, it will be adhered to in the present investigation. Therefore, \( F_{\text{ex}} \) remains a functional of \( \rho_A(r) \) but now is only a function of \( \rho \).

The explicit form of \( F_{\text{ex}} \) obtained by Leibler is,

\[
F_{\text{ex}}[\rho_A(r), \rho] = \frac{1}{2\beta \rho V} \sum_k \rho_A(k) \rho_A(-k) \left[ \frac{F(x,f)}{N} - 2\chi \right] + \frac{1}{6\beta \rho^2 V^2} \sum_k \sum_{k'} \Gamma_3(k, k', -k-k') \rho_A(k) \rho_A(k') \rho_A(-k-k') \\
+ \frac{1}{24\beta \rho^3 V^3} \sum_{k_1} \sum_{k_2} \sum_{k_3} \Gamma_4(k_1, k_2, k_3, -k_1-k_2-k_3) \rho_A(k_1) \rho_A(k_2) \rho_A(k_3) \rho_A(-k_1-k_2-k_3) \\
+ \ldots \ldots
\]

(2.13)

where \( \rho_A(k) \) is the Fourier transform of \( \rho_A(r) \),

\[
\rho_A(k) = \int \! d\mathbf{r} \ e^{i \mathbf{k} \cdot \mathbf{r}} \rho_A(r)
\]

(2.14)

and the sums are over all wave vectors \( k \) excluding \( k=0 \). \( \chi \) is the Flory interaction parameter for the A and B segments comprising
the diblock copolymer. \( F(x,f) \) is given by,

\[
F(x,f) = \frac{g(1,x)}{\left\{ g(f,x) g(1-f,x) - \frac{1}{4} \left[ g(1,x) - g(f,x) - g(1-f,x) \right]^2 \right\}}
\]

\[
g(f,x) = \frac{2}{x^2} \left[ e^{-fx} - 1 + fx \right],
\]

(2.15)

where \( x = k^2 R_g^2 \) with \( R_g^2 = \frac{Nl^2}{6} \). As was employed in the past by other workers[23,29] on diblock copolymers, the study here will make use of the local approximation for \( \Gamma_3(k_1,k_2,k_3) \) and \( \Gamma_4(k_1,k_2,k_3,k_4) \) which amounts to taking \( \Gamma_3(k_1,k_2,k_3) = \Gamma_3(1) \) and \( \Gamma_4(k_1,k_2,k_3,k_4) = \Gamma_4(0,0) \), where \( \Gamma_3(1) \) and \( \Gamma_4(0,0) \) are coefficients defined by Leibler[28].

To accomplish the minimization condition of (2.2), the customary procedure in density functional theory of expressing the periodic density, \( \rho_A(r) \), in terms of a Fourier series specific to the particular morphology being investigated will be employed:

\[
\rho_A(r) = \rho f_A(r) = \rho f + \sum_{k_n} \rho \left[ a_n \cos(k_n \cdot r) + b_n \sin(k_n \cdot r) \right].
\]

(2.16)

Here \( f_A(r) = \rho A(r) / \rho \) is the reduced density profile and \( \{k_n\} \) are the reciprocal lattice vectors of the morphology being studied. The prime on the summation indicates that the sum is over \( k_n \) but not
\(-k_n\) and excludes \(k_n = 0\). The coefficients \(\{a_n\}\) and \(\{b_n\}\) are the order parameters of the theory and are determined by the minimization procedure. In general, the phase with the lowest grand potential is taken as the stable phase.

Combining equations (2.12), (2.13), and (2.16), the difference in the dimensionless grand potential per chain between an ordered state with densities \(\rho\) and \(\rho_A(r)\) and a disordered phase with densities \(\rho_d\) and \(\rho_{Ad}\) is,

\[
\frac{\beta N (\Omega_0 - \Omega_d)}{\rho_d V} = (1+\eta) \ln(1+\eta) - \eta - f^3 \eta^3 \left[ \frac{\eta G_3(1)}{6} (2\eta - 1) - \frac{\eta G_4(0,0)}{24} \eta f \right]
\]

\[
-\frac{1}{4} (1+\eta)^2 (1-\eta+\eta^2) \sum_{k_n} (a_n^2 + b_n^2) [2\chi N - F(x,f)]
\]

\[
-\eta (1+\eta)^2 f \sum_{k_n} (a_n^2 + b_n^2) \left[ \frac{\eta G_3(1)}{4} (2\eta - 1) - \frac{\eta G_4(0,0)}{8} \eta f \right]
\]

\[
-\frac{1}{8} (1+\eta)^3 [\eta G_3(1) (2\eta - 1) - \eta G_4(0,0) \eta f]
\]

\[
\sum_{k_n} \sum_{k_m} (a_n a_m a_{n+m} + 2a_n b_m b_{n+m} - b_n b_m b_{n+m})
\]

\[
+ \frac{\eta G_4(0,0)}{192} (1+\eta)^4 \sum_{k_n} \sum_{k_m} \sum_{k_l} (4a_n a_m a_{1+n+m+1} + 3a_n a_m a_{1+n+1-m}
\]

\[-4b_n b_m b_{1+n+m+1} + 3b_n b_m b_{1+n+1-m} - 12b_n b_m a_{1+n+m+1}
\]

\[+12a_n a_m b_l b_{n+m+l} + 12a_n a_m b_l b_{n+l-m} - 6a_n a_m b_l b_{n+m-1})
\]

\(2.17\)
where \( \eta = (\rho - \rho_d)/\rho_d \) is the reduced density difference between an ordered state with total segment density \( \rho \) and a disordered state with the same chemical potential as the ordered state and density \( \rho_d \).

Equation (2.17) provides a complete description of the ordering of A-B diblock copolymers. The morphology to be examined is specified through the set of reciprocal lattice vectors, \( \{k_n\} \), chosen. Equation (2.17) must then be minimized with respect to \( \eta, \{a_n\}, \{b_n\} \). If the minimum of \( (\Omega_0 - \Omega_d) \) is greater than zero, the disordered phase is the thermodynamically stable phase. When the minimum of \( (\Omega_0 - \Omega_d) \) is negative, the ordered state characterized by \( \{a_n\} \) and \( \{b_n\} \) is the stable phase. The order-disorder transition occurs when the minimum of \( (\Omega_0 - \Omega_d) \) is zero, since the equality of \( T, V, \) and \( \mu \) for the two phase was imposed in the derivation above.

2.3 Lamellar Ordering of Diblock Copolymers

Experimental investigations focusing on the determination of the molecular weight dependence of the domain spacing, \( D \), have produced conflicting results. While most of the investigators [1,6,16] claim to have found the strong segregation law, \( D \propto N^{2/3} \), others[13,15] have found, \( D \propto N^{0.8} \). In one recent study[14] the \( N \) scaling exponent of \( D \) had been found to be close to \( 2/3 \) in agreement with the strong segregation theories, although a part of the data used in obtaining this result actually belonged to the weak
segregation limit. Here, the density functional theory developed in Section 2.2 will be applied to the lamellar ordering of a symmetric diblock copolymer. The range of the strong and weak segregation limits will be determined, as well as the nature of the crossover between these limits.

Since this section of the dissertation is concerned solely with the lamellar morphology, the minimization of \((\Omega_o - \Omega_d)\) in equation (2.17) may be simplified by parameterizing the density profile in terms of a small number of adjustable parameters. A general reduced density profile, \(f_A(r)\), for the lamellar phase may be constructed by convoluting a normalized Gaussian function with a square wave function[44]. The resulting expression is,

\[
f_A(z) = \frac{\rho_A(z)}{\rho_d} = f + \sum_{n=1}^{\infty} \frac{1}{\pi n} \sin(2\pi nf) \cos\left(\frac{2\pi n z}{D}\right) e^{-2\pi^2 n^2 \left(\frac{\sigma_0}{D}\right)^2}
+ \sum_{n=1}^{\infty} \frac{1}{\pi n} \left[1 - \cos(2\pi nf)\right] \sin\left(\frac{2\pi n z}{D}\right) e^{-2\pi^2 n^2 \left(\frac{\sigma_0}{D}\right)^2},
\]

(2.18)

where \(D\) is the domain spacing or lamellar repeat distance and \(\sigma_0\) characterizes the sharpness of the interface between A-rich and B-rich domains. \(z\) is the position variable perpendicular to the A-B lamellar domains. A sharp interface corresponds to \(\sigma_0<<1\) and as \(\sigma_0\) increases the interface becomes increasingly diffuse.
By comparing equations (2.16) and (2.18) the order parameters, \( a_n \) and \( b_n \), are identified to be:

\[
a_n = \frac{1}{\pi n} \sin(2\pi nf) e^{-2\pi^2 n^2 \left( \frac{\sigma_0}{D} \right)^2}
\]

\[
b_n = \frac{1}{\pi n} \left[ 1 - \cos(2\pi fn) \right] e^{-2\pi^2 n^2 \left( \frac{\sigma_0}{D} \right)^2}
\]

\( \sigma_0 / D \) is considered a variational parameter for the determination of the minimum of \( \Omega_0 - \Omega_d \) in equation (2.17). The domain spacing, \( D \), also enters the calculation through \( F(x,f) \) in equation (2.17) where,

\[
x = k^2 R_g^2 = 4\pi^2 n^2 \left( \frac{R_g}{D} \right)^2
\]

\[
R_g^2 = \frac{N f^2}{6}
\]

Therefore, present parameterization of the density profile has allowed the equilibrium structure of the lamellar morphology to be determined by only two variational parameters, \( \sigma_0 / D \) and \( R_g / D \). Note that the domain spacing, \( D \), is expressed in units of \( R_g \) which is proportional to \( N^{0.5} \).

In summary, there are three variational parameters \( \sigma_0 / D \), \( R_g / D \), and \( \eta \) and four experimental variables \( R_g \), \( \chi N \), \( f \) and \( \rho_d \). As was emphasized above, this section is concerned only with the ordering to the lamellar morphology. For a given choice of the experimental variables, \( (\Omega_0 - \Omega_d) \) of equation (2.17) needs to be
minimized with respect to $\sigma_0/D$, $R_g/D$, and $\eta$. Upon minimization of $(\Omega_0 - \Omega_d)$, the equilibrium density $\rho_0$ of the ordered phase along with the characteristics of the reduced density profile $f_A(z)$ (i.e. $\sigma_0/D$ and $R_g/D$) are obtained. The phase with the lowest grand potential $\Omega$ is the thermodynamically stable phase. A flow chart of the computer program used to minimize $(\Omega_0 - \Omega_d)$ for the lamellar morphology is provided in Appendix B.

The results of calculations performed in order to determine the onset of microphase separation and the characteristics of the microphase separated state for $\chi N > (\chi N)_t$ will now be presented for a symmetric diblock copolymer (i.e. $f = 0.5$) ordering to the lamellar morphology. In Section 2.4, results will be presented for a range of copolymer compositions ordering to the various morphologies. For all the calculations, the infinite Fourier expansion for the reduced density, $f_A(z)$, in equation (2.16) was truncated at a finite number of terms determined by the requirement that all the sums contained in equation (2.17) had completely converged.

The order-disorder transition occurs at $(\chi N)_t = 10.495$ in agreement with the original prediction of Leibler[27]. No volume change (i.e. $\eta = 0$) was predicted at the transition. Therefore, the transition is second order, again in agreement with Leibler. Preliminary results[12] for other diblock copolymer compositions have shown that a small volume change accompanies the transition for $f \neq 0.5$ and the transition is first order. The features of the reduced density profile, $f_A(z)$, for $\chi N > (\chi N)_t$ will now be considered. Initially, the discussion will be restricted to the case where the volume change is zero (i.e. $\eta = 0$). Later, this constraint will be lifted.
The equilibrium values of the domain spacing, D, and $\sigma_0$, the parameter characterizing the sharpness of the interface, are given in Table 2.1 and plotted in Figures 2.1 and 2.2. In Table 2.1, the minimum values of $(\Omega_0-\Omega_d)$ for the range of $\chi N$ examined is also provided. Although the figures contain the same information as Table 2.1, the raw data is provided for convenience to the reader. In Figure 2.1, $\ln(D/R_g)$ is plotted against $\ln(\chi N)$. It is clear from the figure that there are three distinct regimes for the molecular weight dependence of the domain spacing D.

For values of $\chi N$ in the range 10.495 to 12.5, $D/R_g(=3.231)$ is independent of $\chi N$. Since the domain spacing, D, is proportional to $R_g$, D is proportional $N^{0.5}$ for $10.495 \leq \chi N \leq 12.5$. In addition, D is independent of $\chi$ in this regime. The regime, $10.495 \leq \chi N \leq 12.5$, is identified to be the weak segregation regime of Leibler[27]. Note that the range of the weak segregation limit in $\chi N$ has clearly been determined. Within the weak segregation limit the A segment density is considered to vary in a sinusoidal fashion. Also the junction points between the A-type and B-type chains are distributed approximately at random in space. A typical reduced density profile, $f_A(z)=\rho_A(z)/\rho$, in the weak segregation regime is plotted in Figure 2.3 against z/D for $\chi N=11.00$. For this value of $\chi N$, $D/R_g=3.23$ and $\sigma_0/D=0.23324$. Notice the approximately sinusoidal nature of the density profile. It is also obvious from Figure 2.2 that for $10.495 \leq \chi N \leq 12.5$, a simple power law for the $\chi N$ dependence of interface parameter $\sigma_0$ cannot be established. In fact $\sigma_0$ diverges as $\chi N$ approaches the critical value $(\chi N)_c=10.495$, although a critical exponent was not extracted.
Table 2.1  Equilibrium values for the variational parameters $D/R_g$ and $\sigma_0/D$ calculated using density functional theory for the lamellar morphology with $f=0.5$ and $\eta=0$. $\beta N\Delta\Omega/\rho_d V$ is the dimensionless grand potential difference per chain between the ordered and disordered phases.

<table>
<thead>
<tr>
<th>$\chi N$</th>
<th>$D/R_g$</th>
<th>$\sigma_0/D$</th>
<th>$\beta N\Delta\Omega/\rho_d V$</th>
</tr>
</thead>
<tbody>
<tr>
<td>10.495</td>
<td>3.231</td>
<td>0.54969</td>
<td>-0.3875 $(10)^{-9}$</td>
</tr>
<tr>
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<td>-0.1547 $(10)^{-5}$</td>
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<td>-0.2368 $(10)^{-2}$</td>
</tr>
<tr>
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<td>3.231</td>
<td>0.19205</td>
<td>-0.02368</td>
</tr>
<tr>
<td>12.000</td>
<td>3.231</td>
<td>0.16228</td>
<td>-0.05335</td>
</tr>
<tr>
<td>12.500</td>
<td>3.231</td>
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<td>0.039396</td>
<td>-3.234</td>
</tr>
<tr>
<td>35.000</td>
<td>3.976</td>
<td>0.034275</td>
<td>-4.277</td>
</tr>
<tr>
<td>40.000</td>
<td>4.090</td>
<td>0.030544</td>
<td>-5.345</td>
</tr>
<tr>
<td>45.000</td>
<td>4.184</td>
<td>0.027729</td>
<td>-6.431</td>
</tr>
<tr>
<td>50.000</td>
<td>4.283</td>
<td>0.025409</td>
<td>-7.531</td>
</tr>
<tr>
<td>55.000</td>
<td>4.357</td>
<td>0.023594</td>
<td>-8.643</td>
</tr>
<tr>
<td>65.000</td>
<td>4.505</td>
<td>0.020714</td>
<td>-10.89</td>
</tr>
<tr>
<td>75.000</td>
<td>4.630</td>
<td>0.018585</td>
<td>-13.17</td>
</tr>
<tr>
<td>95.000</td>
<td>4.843</td>
<td>0.015592</td>
<td>-17.79</td>
</tr>
<tr>
<td>105.00</td>
<td>4.938</td>
<td>0.014482</td>
<td>-20.12</td>
</tr>
<tr>
<td>125.00</td>
<td>5.102</td>
<td>0.012766</td>
<td>-24.81</td>
</tr>
<tr>
<td>145.00</td>
<td>5.236</td>
<td>0.011499</td>
<td>-29.54</td>
</tr>
<tr>
<td>175.00</td>
<td>5.420</td>
<td>0.010064</td>
<td>-36.68</td>
</tr>
<tr>
<td>195.00</td>
<td>5.525</td>
<td>0.93314 $(10)^{-2}$</td>
<td>-41.47</td>
</tr>
<tr>
<td>225.00</td>
<td>5.666</td>
<td>0.84490 $(10)^{-2}$</td>
<td>-48.66</td>
</tr>
<tr>
<td>255.00</td>
<td>5.797</td>
<td>0.77412 $(10)^{-2}$</td>
<td>-55.88</td>
</tr>
<tr>
<td>285.00</td>
<td>5.917</td>
<td>0.71625 $(10)^{-2}$</td>
<td>-63.13</td>
</tr>
<tr>
<td>335.00</td>
<td>6.079</td>
<td>0.64173 $(10)^{-2}$</td>
<td>-75.25</td>
</tr>
</tbody>
</table>
Figure 2.1 Plot of $\ln(D/R_g)$ vs $\ln(\chi N)$ for the lamellar morphology with $f=0.5$ and $\eta=0$. $\alpha$ refers to the $N$ scaling exponent of the domain spacing, $D$. 
Figure 2.2 Plot of $\ln(\sigma_0/D)$ vs $\ln(\chi N)$ for the lamellar morphology with $f=0.5$ and $\eta=0$. 
Figure 2.3  Plot of the reduced density $f_A(z/D)$ vs $z/D$ for $\chi N = 11$ ($D/R_g = 3.231$ and $\sigma_o/D = 0.233$).
Far from the order-disorder transition, characterized by $\chi N > 105$, the scaling behavior observed for $D/R_g$ from Figure 2.2 is,

$$\frac{D}{R_g} \propto (\chi N)^{0.17 \pm 0.01}.$$  
(2.19)

For $\chi N > 335$ the asymptotic result, $\frac{D}{R_g} \propto (\chi N)^{0.17}$, is achieved, therefore, the domain spacing scales as

$$D \propto N^{0.67} \chi^{0.17}.$$  
(2.20)

The $N$ exponent, 0.67, is in good agreement with the previous theories [17-26] of the strong segregation limit. Thus, the region $\chi N > 100$ has been determined to be the strong segregation regime. The reduced density profile, $f_A(z)$, for a representative value in the strong segregation limit of $\chi N = 195$ is shown in Figure 2.4. The values of two variational parameters $D/R_g$ and $\sigma_0/D$ are 5.525 and 0.93314(10)$^{-2}$ respectively. The strong segregation regime is characterizing by well defined A and B domains separated by a very narrow interface. In the strong segregation limit, $\sigma_0$, the parameter that characterizes the breadth of the interface, varies with $\chi N$ according to the power law (see Figure 2.2),

$$\frac{\sigma_0}{D} \propto (\chi N)^{-0.69 \pm 0.01}.$$  
(2.21)
Figure 2.4  Plot of the reduced density $f_A(z/D)$ vs $z/D$ for $\chi N=195$ ($D/R_g=5.525$ and $\sigma_0/D=0.00933$).
Again for $\chi N>335$ the asymptotic result, \( \frac{\sigma_0}{D} \propto (\chi N)^{0.67} \), is obtained.

So that, $\sigma_0$, the parameter characterizing the breath of the interface, scales as

\[
\sigma_0 \propto \chi^{-0.50 \pm 0.02}
\]

(2.22)

where the result of equation(2.20) was used. Since $\sigma_0$ is proportional to the interfacial thickness, the interface thickness is independent of molecular weight and varies as $\chi^{-0.5}$ in the strong segregation regime. This too is in agreement with previous theories \[12-26\] of the strong segregation regime.

Between the weak and strong segregation limits it is possible to clearly identify from Figure 2.1 an intermediate regime with features distinctly different from those of weak and strong segregations regimes. The scaling law for the domain spacing, $D$, in this crossover regime is,

\[
D \propto N^{0.72 \pm 0.22} \chi
\]

(2.23)

for values of $\chi N$ in the range $17 \leq \chi N \leq 75$. Note that the $N$ exponent of $D$ is higher in the intermediate regime than in the strong segregation limit. A density profile for a typical value of $\chi N=35$ within the intermediate regime is presented in Figure 2.5, where $D/R_g=3.976$ and $\sigma_0/D=0.0343$. Although the interface is narrow, it is not very sharp in comparison with a typical density profile in the strong
Figure 2.5  Plot of the reduced density $f_A(z/D)$ vs $z/D$ for $\chi_N=35$ ($D/R_g=3.976$ and $\sigma_0/D=0.0343$).
segregation regime. The details of the interfacial region for $\chi N = 35$ and 195 are compared in Figure 2.6. The N scaling exponent of the domain spacing with a power greater than 2/3 is attributed to the coarsening of the density profile as $\chi N$ is increased from the weak segregation limit. To accomplish this, the junction points between the diblock chains must move into the interfacial region. In addition, because the interfacial region in the intermediate regime is spread over a wider range of space than with the strong segregation limit (see Figure 2.6.), the junction points are not completely localized in the intermediate regime. These effects, coupled with the stretching of the chains that arises from the requirement that the total segment density, $\rho$, be uniform in space gives rise to the N exponent of D being greater than for the strong segregation limit. Lastly, it is clear from Figure 2.2 that a single power law cannot be used to accurately describe the $\chi N$ dependence of the interfacial parameter, $\sigma_0/D$, in the intermediate regime. However, it was found that $\sigma_0$ is only weakly dependent on N in the intermediate regime.

The results presented above for $\chi N > (\chi N)_t$ assumed that the volume change parameter, $\eta$, was zero. Allowing for $\eta$ to be a free variational parameter, produced $\eta=0$ for $\chi N < 18$, which should be expected since polymeric liquids are relatively incompressible and the amount of chain stretching for $\chi N < 18$ is minimal. For $\chi N = 18$, the value of $\eta$, determined by the requirement that $(\Omega_0-\Omega_d)$ be a minimum in $D/R_g, \sigma_0/D$ and $\eta$, was predicted to be 0.0145 with $D/R_g=3.390$ and $\sigma_0/D=0.42991(10)^{-1}$ while at $\chi N = 30$, $\eta$ was determined to be 0.20 with $D/R_g=3.390$ and $\sigma_0/D=0.42991(10)^{-1}$. When
Figure 2.6  Plot of the reduced density $f_A(z/D)$ vs $z/D$ in the interfacial region for, •, $\chi_N=35$ ($D/R_g=3.98$ and $\sigma_0/D=0.0343$) and □, $\chi_N=195$ ($D/R_g=5.52$ and $\sigma_0/D=0.00933$).
The anomalous large volume change predicted as \( \chi N \) is increased, is a direct consequence of the absence of compressibility effects in the RPA calculated excess Helmholtz free energy, \( F_{ex} \) (equation 2.13). In addition, the present model for the diblock copolymer melt embodied in \( F_{ex} \) of equation (2.13) lacks a "hard-core" for the segments comprising the polymer which would prevent unphysically large volume changes. However, the general trends observed for the variation of \( D \) and \( \sigma_0 \) should be correct. Table 2.2 provides a comparison between the calculated values of \( D/R_g \) and \( \sigma_0 \) for \( \eta=0 \) with those determined when \( \eta \) is a free variational parameter. In general, the effect of the volume change is to decrease \( D \) while \( \sigma_0 \) increases. Also, the magnitude of the deviation in the values of \( D/R_g \) and \( \sigma_0/D \) calculated when \( \eta \) is a free variational parameter from those determined for \( \eta=0 \) is anti-
ipated to decrease when the local structure of the copolymer segments is included in $F_{ex}$. Therefore, the zero volume change (i.e. $\eta=0$) results should more than adequately describe the microphase separated state of block copolymers.

Now consider one possible modification to the excess Helmholtz free energy, $F_{ex}$, implemented in the density functional theory developed in this dissertation. Leibler[27] determined the excess Helmholtz free energy of the ordered diblock copolymer phase (equation 2.13) by expanding about a disordered phase devoid of compositional fluctuations. Fredrickson and Helfand[29] modified Leibler's free energy, taking into account only those compositional fluctuations with wave vector $q^*$ using a self-consistent Hartree approximation. The wave vector $q^*$ is determined by the peak of the RPA calculated structure factor for the disordered phase. The inclusion of fluctuations leads to the structure factor, $S(q)$, of a symmetric diblock copolymer melt to be given by,

$$\frac{N}{S(q)} = F(x,f) - 2\chi N + \frac{256.785}{(\epsilon N)^{0.5}},$$

(2.24)

where $N$, $F(x,f)$ and $\chi$ were previously defined and $\epsilon$ satisfies,

$$0 = 20.990 - 2\chi N - \epsilon + \frac{256.785}{(N\epsilon)^{0.5}}.$$

(2.25)
Note, the addition of fluctuations has introduced N dependence into the description of the diblock copolymer system. In addition, the use of the Hartree approximation rigorously limits the application of equation (2.24) to $N \geq 10^{10}$. Incorporating the Fredrickson-Helfand structure factor into the density functional theory developed in Section 2.2, modifies the second order term in equation (2.17) from,

$$-\frac{1}{4} (1+\eta)^2 (1-\eta+\eta^2) \sum_{k_n} (a_n^2 + b_n^2) [2\chi N - F(x,f)]$$

to

$$-\frac{1}{4} (1+\eta)^2 (1-\eta+\eta^2) \sum_{k_n} (a_n^2 + b_n^2) \left[ 2\chi N - F(x,f) - \frac{256.785}{(eN)^{0.5}} \right]$$

for a symmetric diblock copolymer. Table 2.3 gives the values of $\chi N$, $\sigma_o/D$, $R_g/D$ at the order-disorder transition for a symmetric diblock copolymer as a function of the number of statistical segments, N, calculated using density functional theory with the fluctuation corrections of Fredrickson and Helfand included in $F_{ex}$. The transition shifts to higher values of $\chi N$ as N is decreased, consistent with the notion that the free energy attributed to fluctuations increases with decreasing N. Table 2.3 also provides $\chi N$ at the order-disorder transition predicted from the weak segregation theory of Fredrickson and Helfand[29]. Similar to the weak segregation theory of Leibler, Fredrickson and Helfand assumed that ordered phase could be described by a single wave vector $q^*$. 
Previous results of Section 2.3 which employed Leibler’s excess Helmholtz free energy indicated that the single vector approximation is fairly accurate within the weak segregation limit. Notice that the predictions based on density functional theory differ substantially from the transitions determined by Fredrickson and Helfand for $N<10^{10}$.

Table 2.3 $\chi_N$, $\sigma_0/D$ and $R_g/D$ calculated at the order-disorder transition using density functional theory with the fluctuation corrections to the structure factor, $S(q)$, determined by Fredrickson and Helfand[29]. $\chi_N(F-H)$ refers to the values of $\chi_N$ at the transition calculated using the weak segregation theory of Fredrickson and Helfand.

<table>
<thead>
<tr>
<th>$N$</th>
<th>$\chi_N$</th>
<th>$\sigma_0/D$</th>
<th>$R_g/D$</th>
<th>$\chi_N (F-H)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$10^8$</td>
<td>11.288</td>
<td>0.67642</td>
<td>0.3096</td>
<td>10.583</td>
</tr>
<tr>
<td>$10^9$</td>
<td>10.746</td>
<td>0.63196</td>
<td>0.3096</td>
<td>10.536</td>
</tr>
<tr>
<td>$10^{10}$</td>
<td>10.575</td>
<td>0.59795</td>
<td>0.3096</td>
<td>10.514</td>
</tr>
<tr>
<td>$10^{14}$</td>
<td>10.496</td>
<td>0.53039</td>
<td>0.3096</td>
<td>10.496</td>
</tr>
<tr>
<td>$10^{18}$</td>
<td>10.495</td>
<td>0.51528</td>
<td>0.3096</td>
<td>10.495</td>
</tr>
<tr>
<td>$10^{22}$</td>
<td>10.495</td>
<td>0.51133</td>
<td>0.3096</td>
<td>10.495</td>
</tr>
</tbody>
</table>

The primary origin of the discrepancy between the predictions of density functional theory with fluctuation corrections and the theory of Fredrickson and Helfand[29] is that the latter theory implicitly includes some fluctuation corrections to the higher order correlation functions which were neglected in the density functional theory. Also, $N<10^{10}$ is strictly beyond the limits of the Hartree
approximation[29]. In addition, fluctuations with wave vector different from \( q^* \) will become more important as \( N \) is decreased. When the transition is close to the spinodal, \((\chi N)_S\), defined as the value of \( \chi N \) where the Leibler structure factor evaluated at \( q^* \) diverges, the dominant fluctuations in the disordered phase will indeed have wave vector \( q^* \). However, as \( N \) is decreased and the transition moves away from the spinodal, fluctuations with wave vector different from \( q^* \) will also make a contribution to the free energy and should be included in \( F_{ex} \). Since density functional theory includes contributions to the free energy with all wave vectors and the weak segregation theory of Fredrickson and Helfand employs only a single wave vector \( q^* \), it is expected that the transition predicted by the two theories would differ when \((\chi N)_t > (\chi N)_S\).

Finally, for \( \chi N > (\chi N)_t \) the fluctuation corrections to \( F_{ex} \) as prescribed by Fredrickson and Helfand fail to yield a transition from the weak segregation limit. Consider equation (2.25) which determines \( \varepsilon \), for \( \chi N > (\chi N)_S \) \( \varepsilon \) will be a small positive number. As \( \chi N \) is increased further equation (2.25) becomes

\[
0 = 20.990 - 2\chi N + \frac{256.785}{(Ne)^{0.5} \langle Ne \rangle},
\]

therefore, the structure factor, \( S(q) \), reduces to,

\[
\frac{N}{S(q)} = F(x,f) - 20.990.
\]
The net effect of the fluctuation corrections of Fredrickson and Helfand is to drive the system toward the spinodial (i.e. $10.495=(\chi N)_s$), thus suppressing a transition from the weak segregation limit.

A comparison will now be made between the results of the present density functional theory and some recent experimental investigations. The prediction that the N scaling exponent of D is higher than that of the strong segregation limit as $\chi N$ is increased from the weak segregation limit is in qualitative agreement with the value of 0.8 for this exponent reported recently by Almdal et al. [15] and also in the past by Hadizianonou and Skoulios[13]. However, these investigations had not observed the crossover from the intermediate regime to the strong segregation regime. It remains unclear at present whether the observed result in these experiments is truly the intermediate regime or an asymptotic limit with an entirely different mechanism dominating the ordering process. One possible origin of the slight discrepancy between the experimental value of 0.8 and the value of 0.72 predicted by density functional theory could be chain stiffness. Another possibility is that the average conformation assumed by the diblock copolymer in the disordered phase is not Gaussian. Recall that within the density functional theory developed here the domain spacing, D, was expressed in terms of $D/R_g$, where $R_g$ is the average root mean square radius of gyration of the copolymer in the disordered phase and was assumed to be proportional to $N^{0.5}$. If in fact the copolymer chains are slightly stretched in the disordered phase, as has been suggested by a recent Monte Carlo simulation[45] and
the experiments of Almdal et al., this would lead to the N dependence of $R_g$ scaling with a power greater than 0.5. Thus, the N scaling exponent of $D$ would likewise increase. In addition, if there is stretching of the diblock copolymers in the disordered phase, it is expected to be a non-universal effect with the amount of chain stretching being a function of the local chemical structure of the copolymer chains.

Now consider the puzzling conclusion of the experiments Anastasiadis et al.[14] who observed, $D \propto N^{0.65}$, apparently in agreement with strong segregation theories even though their lowest molecular weight sample (used in obtaining the N scaling exponent of the domain spacing) was demonstrated to be in the weak segregation regime at the temperature of their study. This conclusion is merely a reflection of a lack of a complete set of data. They used only four samples with $\chi N=10.5$ (f=0.5), $\chi N=35$ (f=0.496), $\chi N=42$ (f=0.473), and $\chi N=105$ (f=0.534) in their investigation. In these experiments f was the fraction of styrene segments in a polystyrene-polymethylmethacrylate diblock copolymer. In addition, all four samples considered by Anastasiadis et al. were of the lamellar morphology. By comparing with Figure 2.1., it is clear that with their lowest molecular weight sample ($\chi N=10.5$ and f=0.473) in the weak segregation regime, the two samples corresponding to $\chi N=35$ (f=0.496) and $\chi N=42$ (f=0.473) lie in the intermediate regime. Their highest molecular weight sample $\chi N=105$ (f=0.534) is at the leading edge of the strong segregation regime. As a consequence an apparent exponent between 0.5, 0.72 and 0.67 for the N scaling of the domain spacing $D$ was observed. To explore
this issue further, calculations were performed using the density functional theory developed here for the particular values of \( f \) and \( \chi N \) considered in the experiments of Anastasiadis et al. The results are presented in Table 2.4. An apparent exponent of 0.68 (i.e. \( D \propto N^{0.68} \)) was obtained in remarkable agreement with their reported value of 0.65. Of course, this is only an averaged result between the weak segregation limit, intermediate regime and strong segregation limit and definitely is not due to the occurrence of the strong segregation limit.

Lastly, a few technical remarks are in order. The particular parameterization of the density profile for the lamellar morphology, equation (2.18), makes the infinite sum rapidly convergent.

Table 2.4. Equilibrium values for the parameters \( D/R_g \) and \( \sigma_0/D \) calculated using density functional theory for block copolymer compositions \( f \) and \( \chi N \) values considered in reference 14.

<table>
<thead>
<tr>
<th>( f )</th>
<th>( \chi N )</th>
<th>( D/R_g )</th>
<th>( \sigma_0/D )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.50</td>
<td>10.5</td>
<td>3.231</td>
<td>0.54969</td>
</tr>
<tr>
<td>0.496</td>
<td>35.0</td>
<td>3.976</td>
<td>0.034294</td>
</tr>
<tr>
<td>0.473</td>
<td>42.0</td>
<td>4.124</td>
<td>0.029642</td>
</tr>
<tr>
<td>0.534</td>
<td>105.0</td>
<td>4.950</td>
<td>0.014437</td>
</tr>
</tbody>
</table>

Furthermore, it was found that the 4th order term in the expansion for \( \beta N \Delta \Omega / \rho_d V \) makes less than a 1% contribution to the total value of \( \beta N \Delta \Omega / \rho_d V \) in the strong segregation limit. The convergence observed here with density functional theory should be contrasted
with other theories for the strong segregation limit based on expansions in the composition difference order parameter[34] where the convergence was much slower. Suffice to say, density functional theory includes all wave vectors in the expression for the grand potential of the ordered phase. In addition, all the previous theories for the weak segregation limit employed the single dominant wave vector approximation to describe the ordered state. Within the present calculational scheme, the single wave vector approximation was determined to be valid only for $\chi N < 12.0$. Therefore, phase diagrams calculated based on the previous weak segregation theories should only be reliable for $\chi N < 12.0$ when the composition of the block copolymer is near 0.5.

In summary, the density functional theory of block developed in Section 2.2 was applied to the lamellar ordering of a symmetric diblock copolymer. The most significant result emerging from the theory was the prediction of three distinct regimes in the micro-phase separated state. The first regime, characterized by

$$(\chi N)_t = 10.495 \leq \chi N \leq 12.5$$

$D \propto N^{0.5}$

is referred to as the weak segregation limit[27]. $\chi N > 100$ was determined to be the strong segregation limit[17-26] where,

$D \propto N^{0.67}$,

and the interfacial thickness is proportional to $\chi^{0.5}$ and independent
of molecular weight. Between these two limits, there exist another regime characterized by

\[ 12.5 < \chi N \leq 95 \]

\[ D \propto N^{0.72} \]

Within this intermediate regime, which spans almost a decade in $\chi N$, the $N$ scaling exponent of the domain spacing, $\alpha$, is higher than even in the strong segregation limit. Furthermore, much of the experimental data reported in the literature actually falls within the weak segregation limit and intermediate regime, yielding an effective exponent $\alpha$ of around $2/3$, thus fortuitously implying strong segregation behavior.

2.4 Determination of the Phase Diagram for Diblock Copolymers

Given the success of density functional theory at predicting the properties of the lamellar morphology at and below the microphase transition temperature, the theory developed in Section 2.2 will be extended to the determine the phase behavior of diblock copolymers as a function of the copolymer composition, $f$, and $\chi N$. In particular, the onset of microphase separation along with the prevailing morphology is calculated. In addition, the structural characteristics of the thermodynamically stable phase for $\chi N > (\chi N)_t$ and the range of the weak segregation limit are determined. Only
the body-centered-cubic (BCC) spheres, hexagonal cylinders and lamellar microphases will be addressed and because most experiments on diblock copolymers are restricted to the weak and intermediate regimes, the calculations will only address these regimes. Lastly, it will be assumed that no volume change (i.e. \( \eta=0 \)) accompanies the transition. The results of Section 2.3 demonstrated that this assumption should be accurate for diblock copolymers, since polymeric liquids are, in general, relatively incompressible.

The description of the change in the grand potential for a diblock copolymer ordering to the lamellar morphology is straightforward. For a given value of \( \chi N \) and block copolymer composition, \( f \), equation (2.17) for \( \beta N \Delta \Omega / \rho_d V \) is minimized with respect to the order parameters \( \{a_n\} \) and \( \{b_n\} \) given by,

\[
a_n = \frac{1}{\pi n} \sin(2\pi nf) e^{-2\pi^2 n^2 \left( \frac{\sigma_0}{D} \right)^2}
\]

\[
b_n = \frac{1}{\pi n} [1 - \cos(2\pi fn)] e^{-2\pi^2 n^2 \left( \frac{\sigma_0}{D} \right)^2}
\]

Only two variational parameters \( \sigma_0/D \) and \( R_g/D \) were required to specify the thermodynamic state of the lamellar morphology. The more complicated geometry of the BCC spheres and the hexagonal cylinders does not permit such a simple description of their respective reduced density profiles. Instead, each order parameter, \( \{a_n\} \) and \( \{b_n\} \), must be varied in order to ascertain the minimum of the change in the grand potential for the microphase separation.
process. To specify the morphology being examined, the required input into equation (2.17) is the reciprocal lattice vectors \( \{ k_n \} \) of the morphology of interest.

For the hexagonal cylinders, the reciprocal lattice vectors are generated from,

\[
k = n \mathbf{g}_1 + m \mathbf{g}_2 ,
\]

(2.26)

where \( n \) and \( m \) are integers while \( \mathbf{g}_1 \) and \( \mathbf{g}_2 \) are the unit vectors of the reciprocal lattice. The vectors \( \mathbf{g}_1 \) and \( \mathbf{g}_2 \) are determined from the primitive vectors of the hexagonal lattice through

\[
\mathbf{R}_i \cdot \mathbf{g}_j = 2\pi \delta_{ij}.
\]

\( \{ \mathbf{R}_i \} \) are the primitive vectors of the hexagonal lattice:

\[
\mathbf{R}_1 = \frac{\sqrt{3}}{2} a \mathbf{x} + \frac{1}{2} a \mathbf{y},
\]

\[
\mathbf{R}_2 = a \mathbf{y},
\]

where \( a \) is the distance between the cylinders on the lattice. \( \mathbf{x} \) and \( \mathbf{y} \) are the unit vectors along the \( x \) and \( y \) coordinate directions respectively.

Generation of the reciprocal lattice vectors according to equation (2.26) will yield a number of vectors with the same magnitude but different component vectors. All vectors with the same magnitude that are related by one of the symmetry operations of the reciprocal lattice are said to be in the same "shell". It
follows, applying one of the symmetry operations of the reciprocal lattice to equation (2.16) for the A segment density profile, \( \rho_A(r) \), should leave \( \rho_A(r) \) invariant. Consequently, order parameters corresponding reciprocal lattice vectors within a given shell must be identical. This result will be implemented in the determination of the phase diagram of diblock copolymers using density functional theory. One additional simplification follows from the symmetry of the unit cells for the BCC spheres and the hexagonal cylinders namely, the order parameters \( \{b_n\} \) are all zero.

For the BCC spheres, the reciprocal lattice vectors are generated from

\[
k = n \mathbf{g}_1 + m \mathbf{g}_2 + l \mathbf{g}_3
\]

(2.27)

where \( n, m \) and \( l \) are integers and the primitive vectors are given by

\[
\mathbf{g}_1 = \frac{2\pi}{a} (y + z),
\]

\[
\mathbf{g}_2 = \frac{2\pi}{a} (z + x),
\]

\[
\mathbf{g}_3 = \frac{2\pi}{a} (x + y).
\]

Here \( a \) is the linear dimension of the BCC unit cell and \( \hat{x}, \hat{y} \) and \( \hat{z} \) denote unit vectors along the three coordinated directions respectively. In Table 2.5 the total number of reciprocal lattice vectors and the maximum value of \( x = |k|^2 R_g^2 \) as a function of the number of shells of reciprocal lattice vectors considered, is provided for the
Table 2.5  The total number of reciprocal lattice vectors and the value of \( x = |kl|^2 R_g^2 \), as a function of the number of shells of vectors considered for the cylindrical and spherical morphologies.

### Hexagonal Cylinders

<table>
<thead>
<tr>
<th>number of shells of vectors</th>
<th>total number of vectors</th>
<th>( x )</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>9</td>
<td>( 4\pi^2(R_g^2/a^2) )</td>
</tr>
<tr>
<td>11</td>
<td>36</td>
<td>( 4\pi^2(R_g^2/a^2) )</td>
</tr>
<tr>
<td>24</td>
<td>42</td>
<td>( 4\pi^2(R_g^2/a^2) )</td>
</tr>
<tr>
<td>42</td>
<td>75</td>
<td>( 4\pi^2(R_g^2/a^2) )</td>
</tr>
<tr>
<td>45</td>
<td>81</td>
<td>( 4\pi^2(R_g^2/a^2) )</td>
</tr>
</tbody>
</table>

### BCC Spheres

<table>
<thead>
<tr>
<th>number of shells of vectors</th>
<th>total number of vectors</th>
<th>( x )</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>43</td>
<td>( 4\pi^2(R_g^2/a^2) )</td>
</tr>
<tr>
<td>15</td>
<td>160</td>
<td>( 4\pi^2(R_g^2/a^2) )</td>
</tr>
<tr>
<td>21</td>
<td>229</td>
<td>( 4\pi^2(R_g^2/a^2) )</td>
</tr>
</tbody>
</table>
hexagonal and spherical morphologies. Tables C.1 and C.2 contain the reciprocal lattice vectors for the hexagonal cylinders with 24 shells of vectors and the BCC spheres with 21 shells respectively. In summary, assuming no volume change for the transition (i.e. \( \eta = 0 \)), the minimization of \( \beta N \Delta \Omega / \rho_d V \) in equation (2.17) for the hexagonal and spherical morphologies requires the variation of the order parameters \( \{ a_n \} \), since \( \{ b_n \} = 0 \) for these structures. For a given value of \( \chi N \) and \( f \), the phase with the lowest grand potential is the thermodynamically stable phase. The necessary number of shells of reciprocal lattice vectors is dictated by the requirement that all the sums in equation (2.17) are convergent within a designated level of accuracy. In the results to follow, up to 45 shells of vectors for the cylindrical morphology and 21 shells of vectors for the spherical morphology were retained in the calculation of \( \beta N \Delta \Omega / \rho_d V \).

One of the difficulties with minimizing \( \beta N \Delta \Omega / \rho_d V \) for the cylindrical and spherical morphologies by the method outlined above is that a large quantity of computational time is required if more than fifty order parameters are used. Recall that within the development of the density functional theory for diblock copolymers in Section 2.2, the choice of the ideal free energy, \( F_{id} \), is not unique. In an attempt to simplify the computation of the phase diagram for diblock copolymers for \( \eta = 0 \) an alternative \( F_{id} \) may be
proposed. Considering the following thermodynamic path for the transition from the homogeneous state to one of the ordered states in the absence of potential interactions (i.e. $\chi=0$) and assuming incompressibility (i.e. $\rho_A(r) + \rho_B(r)=\rho$):

\[\text{Homogeneous diblock copolymer } \rho, \rho_{A_o} \xrightarrow{\Delta F_0} \text{Phase separated block copolymer } \rho, \rho_A(r)\]

\[\text{dissociate blocks} \quad \Delta F_I \quad \text{Associate blocks at constant } \rho, \rho_A(r) \quad \Delta F_{II}\]

\[\text{Homogeneous blend } \rho, \rho_{A_o} \xrightarrow{\Delta F_{III}} \text{Blend with total segment density } \rho \text{ and A segment density } \rho_A(r) \]

with $\Delta F_0=\Delta F_I + \Delta F_{II} + \Delta F_{III}$, where $\Delta F_0$ is the change in the Helmholtz free energy energy upon microphase separation in the absence of potential interactions and $\rho=\rho_d=\rho_o$ is the total segment density. Although $\Delta F_0$ would be the definitive choice for the ideal free energy, the determination of $\Delta F_0$ in a closed form is very tedious. As a simplification, the ideal free energy will be taken to be $\Delta F_{III}$. The effects of the dissociation of the A and B blocks at uniform density $\rho_{A_o}$ and the association of the blocks at density
\[ \rho_A(r) \text{ contained in } \Delta F_I \text{ and } \Delta F_{II} \text{ respectively, are relegated to the excess free energy, } F_{ex}. \Delta F_{III}, \text{ the change in the Helmholtz free energy for a mixture of A and B polymers going from a homogeneous state with total density } \rho \text{ and A segment density } \rho_A = f \rho \text{ to a state with periodic density } \rho_A(r) \text{ and total segment density } \rho, \text{ is assumed to be the change in the Flory-Huggins[46] entropy of mixing between the two states:} \]

\[ \Delta F_{id} = \Delta F_{III} = \rho \frac{\beta}{N} \int \left\{ \frac{\rho_A(r)}{\rho} \ln \left( \frac{\rho_A(r)}{\rho} \right) + \frac{[\rho - \rho_A(r)]}{\rho (1-f)} \ln \left[ \frac{1 - \rho_A(r)}{\rho} \right] \right\} dr. \]  

(2.28)

It is anticipated that the selection of the ideal free energy provided in equation (2.28) should fairly accurately describe the diblock copolymer system near the weak segregation limit. Therefore, deriving a density functional theory for diblock copolymers with equation (2.28) serving as the ideal free energy and truncating the functional Taylor series for \( F_{ex} \) after the second order contribution yields,

\[ \frac{\beta N \Delta \Omega}{\rho V} = \frac{1}{V} \int \left\{ \frac{f(r)}{f} \ln f(r) + \frac{1-f(r)}{1-f} \ln[1-f(r)] \right\} dr - \ln (1-f) - \ln f \]

\[ -\frac{1}{4} \sum_{k_n} \left( a_n^2 + b_n^2 \right) \left\{ 2\chi N - F(x,f) + \frac{1}{f^2} + \frac{1}{(1-f)^2} \right\} \]

(2.29)
where \( f(r) \) is reduced density profile of the order state. The integrals in equation (2.29) are over the unit cell of the morphology of interest. Although with the hexagonal microphase the primitive cell is a triangle of side \( a \), it proves more convenient to take the unit cell to be a parallelogram formed by two of the fundamental triangular units. The unit cell of the BCC spheres is a cube of side \( a \). Also note that for the density functional theory developed in Section 2.2, the expansion for \( \beta N \Delta \Omega / \rho_d V \) was extended out to fourth order while equation (2.29) is expanded just to second order.

As a test of the accuracy of the density functional theory for diblock copolymers expressed in equation (2.29) a comparison will be made between the predictions of this theory with those of the more elaborate description provided in equation (2.17). To avoid confusion, equation (2.29), will be referred to as DFT-II while equation (2.17) will be denoted by DFT-I throughout the remainder of this section. Figures 2.7 and 2.8 give a comparison between the calculated values for \( D/R_g \) and \( \sigma_0/D \) as a function of \( \chi N \) for DFT-I and DFT-II. The agreement is excellent considering the simplicity of DFT-II. There is one limitation for the application of DFT-II to the study of the microphase separation in diblock copolymers. The theory cannot be applied to address the strong segregation limit owing to the numerical difficulties encountered as \( \chi N \) is increased well beyond the microphase transition. In addition, the same numerical problems may exist for the determination of the properties of an ordered state for \( f<<0.5 \) using DFT-II.
Figure 2.7  Plot of $\ln(\sigma_0/D)$ vs $\ln(\chi N)$ for the lamellar morphology with $f=0.5$ and $\eta=0$. □ denotes calculations using DFT-II, while + are the predictions based on DFT-I.
Figure 2.8 Plot of $\ln(D/R_g)$ vs $\ln(\chi N)$ for the lamellar morphology with $f=0.5$ and $\eta=0$. □ denotes calculations using DFT-II, while + are the predictions based on DFT-I.
The utility of DFT-II in describing the lamellar ordering of a symmetric diblock copolymers has been demonstrated by comparison to DFT-I. One of the advantages of DFT-II over DFT-I is the reduced computational time required to determine the minimum of the grand potential. Therefore, DFT-II was used to facilitate the determination of the phase behavior of diblock copolymers as a function of f and χN for the three morphologies, BCC spheres, hexagonal cylinders and lamellae. Flow diagrams for the computer programs that apply DFT-I and DFT-II to determine βNΔΩ/ρV for a specific morphology are provided in Appendix B.

The phase diagram for an A-B diblock copolymer, calculated using density functional theory, is shown in Figure 2.9. Tables D.1-D.6 in Appendix D provide data complementary to what is presented in Figure 2.9. Although not detectable from Figure 2.9, density functional theory (DFT-II) predicts the existence of small compositional windows where it is possible to pass directly to the various ordered phases. For 0.50< f<0.4996 transitions directly to lamellae occur and for 0.4996< f<0.4975 transitions directly to hexagonal cylinders are found. Table D.3 and D.4 in Appendix D give f, χN, the change in the grand potential potential at the transition, βNΔΩ/ρV, and the equilibrium lattice spacing, a, expressed in terms of Rg~N^{0.5}. In addition, the values of χN at the order-disorder to BCC spheres, the equilibrium lattice spacing parameter, Rg/a, and the first six order parameters are provided in Tables D.1 an D.2 of Appendix D.
Figure 2.9 The phase diagram for an A-B diblock copolymer calculated using density functional theory. The regions marked DIS (disordered phase), BCC (body-centered-cubic spheres), HEX (hexagonal cylinders), LAM (lamellae), and refer to the thermodynamically stable phase in that region. $\chi$ is the Flory interaction parameter, $N$ is the number of statistical segments, and $f$ is the fraction of A segments contained in the A-B diblock copolymer. DFT-II, developed in section 2.4, was used to determine the thermodynamically stable phase for $0.3 \leq f < 0.5$ and $\chi N < 18$. All other regions of the phase diagram were determined by DFT-I (density functional theory of Section 2.2).
Comparing the predictions of Leibler’s theory[27] (Tables A.2-A.4 of Appendix A) with those of density functional theory in Tables D.1, D.3, D.4 show that the values of \( \chi N \) at the transition are in very good agreement. One subtle difference is the small compositional windows where transitions directly to lamellae and hexagonal cylinders are predicted using density functional theory. The existence of the compositional windows is attributed to the application of DFT-II to describe the microphase transition. Use of the more elaborate density functional theory developed in Section 2.2 (DFT-I) failed to identify any compositional ranges where it is possible to pass directly to lamellae or hexagonal cylinders. In contrast to the weak segregation theory of Fredrickson and Helfand [29] where compositional windows were only predicted for finite \( N \), the windows are independent of \( N \) within the density functional theory of Section 2.4 (DFT-II). It remains to be seen what the effects of including fluctuations into DFT-II would have on the predicted phase diagram. In addition, the slight deviation in the predicted transitions using density functional theory from the results of Leibler’s theory increase as the copolymer composition, \( f \), decreases. This is attributed to the greater importance of the order parameters corresponding to the larger reciprocal lattice vectors as \( f \) is decreased. For example, at \( f=0.215 \) Leibler’s theory gives \( (\chi N)_t=22.5 \) while DFT-I with 21 shells of order parameters predicts \( (\chi N)_t=21.5 \). For the purpose of comparing the order parameters from density functional theory with the single order parameter in Leibler’s theory, inspection of equations (1.5) and (2.16) shows that the order parameters from density functional theory must be
divided by two in order to have them on the same basis as the
order parameter from the theory of Leibler[27]. Table 2.6 gives
1/2 the value of the order parameters calculated using density
functional theory along with the order parameter from the theory
of Leibler for f=0.40 and f=0.215. Notice from the calculated value
via DFT-I that the series diminishes more slowly for f=0.215 then
for 0.40. Table 2.6 also demonstrates two general trends observed
for the calculations using density functional theory. First of all,
even though the transition predicted by Leibler and density func-
tional theory are in good agreement, the microscopic details of the
phase separated state differ for DFT-I, DFT-II, and the theory of
Leibler owing to the difference in the order parameters. The first
order parameter from DFT-I and the single order parameter from
Leibler’s theory compare very well, however; density functional
theory has additional order parameters that clearly are non-zero.
In fact, the order parameters determined from DFT-I differ from
those of DFT-II. The difference between the predictions of the
various theories may be observable in scattering experiments
where the A segment density profile, \( \rho_A(r) \), may be determined.
Subsequently, the order parameters for the expansion of \( \rho_A(r) \) in
terms of the reciprocal lattice vectors specific to the morphology of
interest can be extracted and compared to theoretical predictions.

The results for the lamellar ordering of a symmetric diblock
copolymers demonstrated that Leibler’s theory was only accurate in
describing the microphase separated state in the weak segregation
regime. Figure 2.10 shows the phase diagram determined using
density functional theory with the calculated weak segregation
Table 2.6 One-half the value of the order parameters for the BCC spheres at the order-disorder transition calculated using density functional theory for $f=0.40$ and $0.215$. $a_n$ refers to the order parameter of reciprocal lattice vectors from shell $n$. The $n=1$ shell contains reciprocal lattice vectors with the smallest magnitude possible. Vectors for $n=1$ and higher along with the degeneracy of the shells is provided in Appendix B Table B.2. $a$(Leibler) is the single order parameter predicted using the theory of Leibler[27]. DFT-I refers to the density functional theory developed in Section 2.2 and DFT-II is the density functional theory developed in Section 2.4.

\[ f=0.40 \]

\[
\begin{array}{ccccccc}
  a_{1/2} & a_{2/2} & a_{3/2} & a_{4/2} & a_{5/2} & a_{6/2} \\
  \text{DFT-I} & 1.76e-2 & 1.54e-3 & 2.09e-3 & 1.23e-6 & -6.04e-5 & -3.80e-5 \\
  \text{DFT-II} & 2.70e-2 & 2.37e-3 & 3.54e-4 & 4.52e-5 & -7.25e-5 & -4.67e-5 \\
\end{array}
\]

$a$(Leibler)=$1.70e-2$


\[
\begin{array}{ccc}
  \chi N_l & \text{Leibler} & \text{DFT-I} & \text{DFT-II} \\
  11.25 & 11.25 & 11.24 \\
\end{array}
\]

\[ f=0.215 \]

\[
\begin{array}{ccccccc}
  a_{1/2} & a_{2/2} & a_{3/2} & a_{4/2} & a_{5/2} & a_{6/2} \\
  \text{DFT-I} & 2.17e-2 & 6.60e-3 & 1.14e-3 & -1.85e-4 & -4.05e-4 & -3.85e-4 \\
  a$(Leibler)$=2.543e-2$
\]

\[
\begin{array}{cc}
  \chi N_l & \text{Leibler} & \text{DFT-I} \\
  22.5 & 21.5 \\
\end{array}
\]
Figure 2.10 The phase diagram for an A-B diblock copolymer calculated using density functional theory. The shaded region was determined to be the weak segregation regime of Leibler. The regions marked DIS (disordered phase), BCC (body-centered-cubic spheres), HEX (hexagonal cylinders), LAM (lamellae), and refer to the thermodynamically stable phase in that region. $\chi$ is the Flory interaction parameter, $N$ is the number of statistical segments, and $f$ is the fraction of A segments contained in the A-B diblock copolymer. DFT-II, developed in section 2.4, was used to determine the thermodynamically stable phase for $0.3 \leq f < 0.5$ and $\chi N < 18$. All other regions of the phase diagram were determined by DFT-I (density functional theory of Section 2.2).
regime defined by the shaded region. The transition from BCC spheres to hexagonal cylinders determined by density functional theory is in good agreement with the predictions of the theory of Leibler (compare Appendix D Table D.6 with Appendix A Table A.2) which is expected since the spheres to cylinders transitions all lie within the weak segregation limit. The predicted cylinder to lamellae transitions using density functional that occur for $\chi N$ above the weak segregation regime are substantially different from Leibler’s predictions as may be seen by contrasting Figure 2.10 (and Table D.5 of Appendix D) and Figure 1.3 (and Table A.4 of Appendix A). For example, at $f=0.38$ Leibler’s theory predicts a transition from cylinders to lamellae at $\chi N=14.8$ whereas, Table 2.7 demonstrates no transition from cylinders to lamellae was predicted using DFT-I out to $\chi N=40$. This is a consequence of the onset of the intermediate regime. In section 2.3, the $N$ scaling exponent of the domain spacing, $D$, was found to be 0.72 for symmetric diblock copolymers in the intermediate regime. Indeed, the same value 0.72 was found for the lamellar morphology at other copolymer compositions. For example, the domain spacing $D/R_g$, where $R_g$ is proportional to $N^{0.5}$, calculated using DFT-I for the lamellar morphology with $f=0.42$ is plotted in Figure 2.11 (Table D.7 of Appendix D), demonstrating $D \propto N^{0.72}$ behavior. For $f=0.4$, Figure 2.12 shows that for the hexagonal cylinders morphology the domain spacing, $D$, also scales as $N^{0.72}$. In this case the results were obtained using DFT-II. At the same composition, $f=0.4$, calculations using DFT-I (see Table 2.7) yielded, $D \propto N^{0.66}$, even
Table 2.7 Comparison of the change in grand potential, $\beta N \Delta \Omega / \rho V$, calculated using DFT-I for the cylindrical and lamellar microphases with $f=0.38$. 42 shells of vectors were used to characterize the cylindrical morphology and 300 vectors were used for the lamellae microphase.

<table>
<thead>
<tr>
<th>$\chi N$</th>
<th>Cylinders</th>
<th>Lamellae</th>
<th>Cylinders</th>
<th>Lamellae</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Rg/a</td>
<td>$\beta N \Delta \Omega / \rho V$</td>
<td>Rg/D</td>
<td>$\beta N \Delta \Omega / \rho V$</td>
</tr>
<tr>
<td>18</td>
<td>0.2610</td>
<td>-0.66066</td>
<td>18</td>
<td>0.2905</td>
</tr>
<tr>
<td>19</td>
<td>0.2590</td>
<td>-0.886655</td>
<td>19</td>
<td>0.2875</td>
</tr>
<tr>
<td>20</td>
<td>0.2570</td>
<td>-1.1485</td>
<td>20</td>
<td>0.2830</td>
</tr>
<tr>
<td>21</td>
<td>0.2550</td>
<td>-1.44683</td>
<td>21</td>
<td>0.2795</td>
</tr>
<tr>
<td>22</td>
<td>0.2534</td>
<td>-1.782212</td>
<td>22</td>
<td>0.2765</td>
</tr>
<tr>
<td>23</td>
<td>0.2514</td>
<td>-2.1551287</td>
<td>23</td>
<td>0.2735</td>
</tr>
<tr>
<td>24</td>
<td>0.2498</td>
<td>-2.565987</td>
<td>24</td>
<td>0.2710</td>
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<tr>
<td>25</td>
<td>0.2482</td>
<td>-3.0151732</td>
<td>25</td>
<td>0.2680</td>
</tr>
<tr>
<td>26</td>
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<td>-3.503015</td>
<td>26</td>
<td>0.2665</td>
</tr>
<tr>
<td>27</td>
<td>0.2450</td>
<td>-4.029805</td>
<td>40</td>
<td>0.2415</td>
</tr>
</tbody>
</table>
Figure 2.11 Plot of \( \ln(D/R_g) \) vs \( \ln(\chi N) \) for the lamellar morphology with \( f=0.42 \) and \( \eta=0 \). \( \alpha \) refers to the N scaling exponent of the domain spacing, D. Calculations were performed using the density functional theory developed in Section 2.2(DFT-I).
Figure 2.12  Plot of $\ln(a/R_g)$ vs $\ln(\chi N)$ for the cylindrical morphology with $f=0.4$ and $\eta=0$.  $a$ refers to spacing between cylinders and $\alpha$ is to the $N$ scaling exponent of the domain spacing, $D$.  Calculations were performed using the density functional theory developed in Section 2.4(DFT-II).  45 shells of order parameters were retained in the calculations.
though the range of $\chi N$ examined should be well within the range of the intermediate regime as determined in Section 2.3. A number of plausible explanations exist for the discrepancy. For instance, the range of the intermediate regime may be shorter for the the cylinders than the lamellae. Another possibility is that not enough shells of vectors were considered in the calculation of the equilibrium structure of the cylindrical microphase for the range of $\chi N$ considered in Table 2.7. However, this may be ruled out since the convergence behavior for the cylindrical microphase with $f=0.38$ and $18<\chi N<35$ was examined for calculations with 24 and 42 shells of vectors. The calculated lattice spacings, $R_g/a$, were nearly identical for 24 and 42 shells of vectors. The last possibility is that the determined minimum of the grand potential for the ordered phase with respect to variations in $R_g/a$, as prescribe by Flow Chart 6 in Appendix B, may not be sufficiently accurate to ensure a precise prediction of the N scaling exponent of the lattice spacing, $a$.

As $\chi N$ is increase beyond the weak segregation limit the grand potential of the order phase becomes less sensitive to small variations in $R_g/a$, therefore; the exact position of the minimum of $\beta N \Delta \Omega / \rho V$ is difficult to determine.

Lastly, the phase diagram in Figure 2.9 determined using density functional theory shows that for $\chi N >> (\chi N)_t$ the observed transition between cylinders and lamellae occurs at a composition of 0.38. Table 2.8 provides the copolymer composition, $f$, where the transition from cylinders to lamellae is predicted from a number of strong segregation theories.
Table 2.8 Diblock copolymer composition, f(cyl-lam), where the transition from cylinders to spheres is predicted to occur from a number of strong segregation theories.

<table>
<thead>
<tr>
<th>Theory</th>
<th>f(cyl-lam)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Helfand [18-21]</td>
<td>0.25</td>
</tr>
<tr>
<td>Ohta&amp;Kawasaki [33]</td>
<td>0.36</td>
</tr>
<tr>
<td>Semenov [32]</td>
<td>0.28</td>
</tr>
</tbody>
</table>

Notice the value f=0.38 found from density functional theory is higher than the predictions of all the strong segregation theories, but is in fairly good agreement with the experimental[6] result of 0.35.

2.5 Conclusions

In the first half of this dissertation, density functional theory of first order transitions was successfully applied to the order-disorder transition in block copolymers. The general density functional formalism for A-B block copolymers was developed in Section 2.2. Here, the grand potential of an ordered state with total segment density, \( \rho_0 \), and A segment density profile, \( \rho_A(r) \), was expanded about the disordered phase with the same chemical potential, \( \mu \), as the ordered phase and total segment density \( \rho_d \). The equilibrium grand potential of a given phase was found by minimizing the grand potential with respect to a finite number of
parameters characterizing the phase of interest. The phase with the lowest grand potential is the thermodynamically stable phase. In Section 2.3, the resulting formalism was applied to the lamellar ordering of symmetric A-B diblock copolymers and in Section 2.4 other diblock copolymer compositions along with the cylindrical and spherical morphologies were considered.

The results for symmetric diblock copolymers indicated that there exists three regimes in the microphase separated state, each with distinctly different properties from the others. The first regime $10.495 < \chi N < 12.5$ was determined to the weak segregation limit of Leibler. Within the weak segregation regime, the domain spacing, $D$, is proportional to $N^{0.5}$, where $N$ is the number of statistical segments comprising the copolymer. The $N$ dependence of $D$ is a direct consequence of the copolymer chains in the phase separated state assuming conformations near those found in the disordered state. Also, the spatial variation of the A and B segment densities is approximately sinusoidal in the weak segregation regime. For $\chi N > 105$, the $N$ scaling exponent of the domain spacing was found to be $2/3$. Here, there exists well defined A-rich and B-rich micro-domains separated by a very narrow interfacial region. The interfacial thickness was found to be independent of $N$ but proportional to $\chi^{0.5}$. It was concluded that the regime $\chi N > 105$ is the strong segregation limit pioneered by Meier and Helfand. Between these limits, for $15 < \chi N < 95$ a new regime with characteristics distinctly different from those of the weak and strong segregation regimes was found. Within this "intermediate" regime, $D$ is proportional to $N^{0.72}$. In addition, the interfacial thickness was
found to be weakly dependent on N. The N scaling exponent of D with a power greater than the strong segregation result of 2/3 is attributed to the coarsening of the segment density profiles as the system moves away from the weak segregation limit. To accomplish this task, the junction points between the A block and B block segments must become localized in the developing interfacial region. The effect of the localization of the junction points coupled with the stretching of the chains arising, also from the formation of well defined domains, leads to the N scaling exponent of D with a power greater than 2/3. It was also pointed out that much of the previous experimental work on diblock copolymers was restricted to the weak and intermediate regimes. Furthermore, recent experiment results of Anastasiadis et al. where apparent strong segregation behavior was observed (i.e. $D \sim N^{0.67}$) were demonstrated to actually be averaged results between the three regimes determined using density functional theory.

For block copolymer compositions, $f \neq 0.5$, the cylindrical and spherical morphologies also needed to be considered when determining the state of the system. The limits of the weak segregation were determined as a function of the copolymer composition, $f$, and morphology. In addition the N scaling exponent for the hexagonal cylinders intermediate regime was determined to be 0.72, in agreement with the result for the lamellar microphase. The predicted order-disorder transitions using density functional theory are in good agreement with the original predictions of Leibler for the weak segregation limit. One subtle difference was the existence of small compositional windows where it is possible to
pass directly to the lamellar or cylindrical morphologies. For temperatures below the order-disorder transition, the order-order transitions predicted using density functional theory which fell within the bounds of the weak segregation limit were also in agreement with the theory of Leibler. However, for $\chi N$ greater than the weak segregation limit, the calculated order-order transitions were as expected quite different from the predictions of Leibler. Lastly, for $\chi N >> (\chi N)_t$ but still well within the intermediate regime the predicted copolymer composition, $f$, at which there is a transition from hexagonal cylinders to lamellae as $f$ increased was $f=0.38$. This too is in reasonable agreement with the experiments of Hashimoto.
References of Chapter 2


(22) Semenov, A.N., Soviet Physics JETP, 61, 733(1985).
(38) Baus, M.; Colot, J.L., Molecular Physics, 55, 653(1985).
3.1 Some Suggestions for Future Studies

There is a multitude of directions that may be pursued for future research in the area of density functional theory of polymers. Within the realm of order-disorder transitions of block copolymers, other questions concerning the phase behavior could be considered. In Section 2.2 the density functional theory developed employed the RPA free energy of Leibler. In addition, the wave vector dependence of the third and fourth order correlation functions in $F_{ex}$ was neglected. The density functional theory developed here could be easily be modified to consider the effects of including the wave vector dependence in the third and fourth order correlation functions. Also, the effects of fluctuations in the disordered phase were considered briefly in the context of the theory of Fredrickson and Helfand who considered only fluctuations with a single wave vector, $q^*$. However, the inclusion of these fluctuation corrections into $F_{ex}$ led to the absence of any transition from weak segregation behavior. Therefore, a more comprehensive theory looking at fluctuations on all length scales may be performed. Section 2.4 demonstrated that by making a clever choice for the ideal free energy, the computation of the phase
behavior can be simplified. Therefore, other ideal free energy could be tried as input for the density functional theory. In addition the effect of fluctuations on the predictions of density functional theory with the ideal system of Section 2.4 could be studied.

More practical questions could also be addressed within the density functional formalism developed here such as considering the phase diagram for star block copolymers. The investigation of the relative stability of other morphologies, such as ordered-bicontinuous double diamond, could easily be undertaken. In addition, the density functional theory developed here could be modified to study the phase behavior of copolymers in contact with a surface. Also a density functional theory could be developed to study interfaces between incompatible polymers and polymer blends near a surface, and the formation of micelles in a mixture of an A-B block copolymer with either homopolymer A and B.
CHAPTER 4

INTRODUCTION TO COMPUTER SIMULATIONS OF POLYELECTROLYTE ELECTROPHORESIS

4.1 Experimental Set-up and Parameters

Gel electrophoresis has proved to be a valuable separation technique for biological polymers[1]. Recently, the method has also been applied to synthetic polyelectrolytes[2,3] with great success. The technique is depicted in Figure 4.1. The experiment consists of a polymer sample being introduced into a gel with an external electric field applied across the gel. The separation is achieved due to the differing rates with which charged polymers with different molecular weights migrate through the gel. Typically, the electric field is applied across the gel for an amount of time ranging from a few hours to a day depending on the molecular weight of the polymers in the sample, the gel concentration, and the electric field strength. After the electric field has been applied, the gel is stained with the various molecular weight fractions of the polymer sample appearing as bands. Figure 4.2 presents the results of a typical gel electrophoresis experiment[3]. Here N is the degree polymerization and the mobility, $\mu$, is defined to be the steady state velocity of a band divided by the electric field strength.
Figure 4.1. Schematic diagram of a gel electrophoresis apparatus. The tube or slab containing the gel is connected to buffer reservoirs at different electric potentials. The sample is applied to the top of the gel. Electrophoresis runs from top to bottom of the gel. The gel may be either agarose or crosslinked polyacrylamide (from reference 4).
Figure 4.2. The results of a typical gel electrophoresis experiment. The gel was 0.6% agarose. The ionic strength of the buffer solution was 0.03 M and an electric field of 1.3 volts/cm was applied across the gel. N refers to the degree of polymerization of the charged polymer, sulfonated polystyrene, and \( \mu \) is the electrophoretic mobility (from reference 3).
From the previous experimental work on polyelectrolyte gel electrophoresis[1-7], the variables influencing the relative separation achieved are: (1) the gel concentration, (2) the electric field strength, and (3) the ionic strength of the buffer solution. In addition, the effect of temperature variations has been shown to be relatively weak[6].

Existing theories for polyelectrolyte gel electrophoresis have focused on extending the reptation model[8-10] for the dynamics of a neutral polymer in a gel or the melt to included the effects of the electric field[11-17]. Although some predictions of the reptation theory for gel electrophoresis appeared to have been observed in a number of experiments[5,7], it remains an open question whether or not reptation is the dominant transport mechanism in gel electrophoresis of high molecular weight polyelectrolytes. With this in mind one of the objectives of the second half of this dissertation is to perform computer simulations of a single polyelectrolyte in gel electrophoresis in order to test the predictions of reptation theory. In addition, these simulations will also study the variation of the chain mobility as a function of molecular weight of the polymer with the results being compared to experiments. The rest of the dissertation is organized as follows. In Section 4.2 previous theoretical work on electrophoresis will be reviewed. Section 4.2.1 discusses the reptation theory for gel electrophoresis, while Section 4.2.2 reviews previous computer simulations. Chapter 5 deals with the stretching of a polyelectrolyte in an electric field with one end of the polymer held fixed. The model is developed in order to obtain an understanding of the effect an external electric field has
on the equilibrium dimension of a polyelectrolyte. Chapter 6 introduces the computer simulation model employed in the dissertation. In Sections 6.3 and 6.4 the model developed is used to investigated polyelectrolyte dynamics in an electric field. The second half of the dissertation concludes with Chapter 7 where some suggestions for future studies are made.

4.2 Previous Theoretical Investigations

In view of the practical importance of gel electrophoresis in biopolymer research, the problem of understanding the molecular mechanism responsible for the separation of charged polymers in gel electrophoresis has recently attracted a great deal of interest from a theoretical perspective[11-17]. In addition a number of computer simulations[19-22] have been performed. The existing theories used to describe the motion of a charged polymer in gel electrophoresis are based on the reptation model of polymer dynamics[7-9] which has been used in the past to describe the diffusion of a neutral polymer in a gel and the melt. In Section 4.2.1 the details of the reptation theory for gel electrophoresis will be examined. One method of investigating the dynamics on a microscopic scale is to perform computer simulations. Simulations allow a researcher to systematically study a problem under strict controls imposed by the investigator. If properly constructed, computer simulations can also be used to check existing theories for
a physical process. Therefore, in Section 4.2.2 the previous computer simulations of gel electrophoresis will also be examined.

4.2.1 Biased Reptation Model for Gel Electrophoresis

The reptation theories of gel electrophoresis are commonly referred to as biased reptation theories[14-16]. Reptation theories for gel electrophoresis assert that a long polyelectrolyte chain moves under the influence of the external electric field in a snake-like fashion. One end of the charged polymer moves through the gel while the rest of the chain follows the path created by the leading end. Specifically, reptation theories[7-13] of gel electrophoresis assume that a charged polymer of uniform charge, Q, is confined to a tortuous tube of length, L, formed by the topological constraints of the gel. The motion of the chain, constrained to move only along the contour of the tube as is depicted below, is considered to be "biased" in the field direction.
With the electric field along the x coordinate direction, reptation predicts the average electrophoretic mobility, \( \mu \), to be given by,

\[
\mu = \frac{Q \langle R_x^2 \rangle}{L^2 f} \propto N^{2\nu - 2}
\]

(4.1)

The variables in equation (4.1) are defined as follows:

\( \langle R_x^2 \rangle = \) mean-square-end-to-end distance of the chain in the direction of the applied field over the duration of the chain migration,

\( \nu = \) scaling exponent for the molecular weight dependence of \( \langle R_x^2 \rangle \),

\( f = \) translational friction coefficient, and

\( N = L/l \), the number of statistical segments, where \( l \) is the step length of the primitive chain.

For a Gaussian chain \( \nu = 1/2 \), and therefore, according to reptation theory, the mobility will scale as \( N^{-1} \). In some experiments with long DNA fragments, the \( 1/N \) dependence for \( \mu \) has been observed. Assuming that the chain statistics of a very long DNA molecule are Gaussian, this experimental result for the molecular weight dependence of the mobility has been taken as verification of reptation. However, other workers[6] were not able to fit their results with a simple \( 1/N \) dependence for the mobility. In general, it is expected that the size of the charged polymer is to be signifi-
cantly modified by the external electric field, even if the field is relatively weak. In order to determine whether reptation is the dominant transport mechanism involved in the movement of a charged polymer in gel electrophoresis it is of vital interest to monitor the individual components of the reptation theory for gel electrophoresis, viz. \(<R_x^2>\) and \(\mu\). One of the objectives of the second half of this dissertation is examine the detailed dynamics of a polyelectrolyte in gel electrophoresis in order to ascertain whether reptation is the dominant transport mechanism. Before proceeding with the development of a computer simulation model the previous computer simulations will be reviewed.

4.2.2 Computer Simulations

The first computer of gel electrophoresis was performed by Olvera de la Cruz et al.[18] using the Monte Carlo method[23]. These workers modeled the gel by a cage of infinitely long bars (see Figure 4.3) forming a perfect lattice. The polymer chain was modeled as a random walk of \(N\) steps on a cubic lattice embedded in the network. The spacing of the network was taken to be the same as the step length of the polymer. The points where the random walk come directly back onto itself were labelled "kinks". The authors prescribed the dynamics of the model to be the free movement of the ends of the polymer and of the kinks; otherwise the monomers were frozen due to the presence of the bars.
Figure 4.3 Two-dimensional representation of the model for gel electrophoresis constructed by Olvera de la Cruz et al. The dots represent bars that make-up the cage. The polymer is modeled by a series of "kinks" and straight sections. Only the kinks and the ends of the polymer are free to move (from reference 18).
Without the electric field, their model is identical to that of Evans and Edwards[24], who found the diffusion coefficient of the center of mass of a chain, D, within the confines of the above model to obey the reptation law, \( D \sim N^{-2} \). The work of Olvera de la Cruz et al. followed the above reptation model, with the inclusion of the effect of a uniform external electric field. The procedure implemented by these investigators was the following:

(A) Choose a segment on the chain at random.

(B) If the segment chosen is not a kink, the program carries out the next iteration.

(C) If a kink is selected, it is flipped to one on the six possible positions on the lattice. For kinks at the end of the chain, the end segment is flipped to one of the six possible positions.

(D) The change in the energy for the movement of the kink is calculated \( \Delta E = E*\Delta x \), where \( \Delta x \) is the change in the x coordinate for the kink moved and the electric field is assumed to be along the x-direction. If \( \Delta E < 0 \), the new configuration is accepted. If \( \Delta E > 0 \), the new configuration is accepted with probability \( \exp(-\Delta E/kT) \) where \( T \) is the temperature and \( k \) is the Boltzmann constant.

After completing a required number of iterations, the whole process is repeated for different initial configurations. One limitation of the model employed by Olvera de la Cruz et al. is that intersegment interactions were ignored and the interactions of the chain with the network were accounted for only through the above choice of the dynamics of the kinks.
Even with such a simplified model, computer simulations are difficult, due to the fact that the chain gets trapped in metastable configurations. The authors found that the relaxation time, the time taken by the chain to lose its correlation with the original configuration, has an exponential dependence on the chain length and that the mean square displacement of the chain varies logarithmically with time. Furthermore, the polymer was found to move slower at higher electric fields.

These results are not similar to those found in experimental investigations of gel electrophoresis. Notice, this simulation had reptation built in from the start and adapted in the modifications of the electric field. Thus the question of whether reptation is the dominant transport mechanism in gel electrophoresis could not be answered. Also, the choice of the spacing of the network making the entanglements to be the same as the step length of the chain is too severe a constraint and consequently forced the chain to be trapped in the metastable states for substantial intervals of time over the length of the simulation. Nevertheless, the most important information emerging from this study is that the time taken for the chain to escape from a metastable state is $\exp(ENc)$, where $c$ is a numerical constant less than unity, $E$ is the strength of the electric field, and $N$ is the number of segments comprising the polymer chain, and that their Monte Carlo simulation method cannot be employed to study such problems if the simulation is not run for times much longer than $\exp(ENc)$. 
The next important step in the computer simulation of gel electrophoresis was carried out by Deutsch and Madden[19]. The primary purpose of this work was to circumvent the difficulties encountered in the previous Monte Carlo simulation in terms of the appearance of the metastable states. These authors used a Langevin equation to describe the dynamics of the polymer chain in the presence of a regular array of point obstacles. The Langevin equation describing the motion of the chain generically contains forces arising from friction, the connectivity of the chain, the electric field, the potential force from the gel, and the random force. The resulting differential equation is then numerically solved subject to the constraint that the distance between two adjacent beads remains constant and that the random force obeys Gaussian statistics.

While the principle behind the computational technique is superior to the Monte Carlo method of reference 18, the actual model used in this calculation is primitive. In the work of Deutsch and Madden, the gel is represented as a two-dimensional periodic lattice of discs, and the polymer chain is modeled as a freely jointed chain of N beads devoid of any excluded volume interactions. The beads interact with the discs via a short-range repulsive force. Note that the effects of gel heterogeneity are ignored. For this model with a relatively strong electric field strength, the authors found that the motion of the chain is not confined to a tube-like region as postulated in the reptation model. But, since the topological constraints of the entanglements are truly a three-dimensional effect, the three-dimensional version of the Langevin simulation of
Deutsch and Madden would need to be performed in order to ascertain whether reptation is the dominant transport mechanism in gel electrophoresis.

In addition, an essentially identical simulation to that of Deutsch and Madden was independently performed by Shaffer and Olvera de la Cruz[20]. The only significant difference was that the chain connectivity was taken into account by introducing a Gaussian potential between adjacent segments of the polymer chain. As will be demonstrated in Chapter 5 of the dissertation, the Gaussian potential leads to unrealistic stretching of the polymer chain at moderate to high electric field strengths. Thus, the results of Shaffer and Olvera del la Cruz should be considered only qualitative at best since they employed relatively high electric field strengths in their simulations. As expected, their results are in qualitative with those of Deutsch and Madden.

There are also two important simulations by Zimm[21] and Duke[22] which addressed the consequences arising from field inversion gel electrophoresis. These simulations are still based on extending the original reptation model. Also as with the simulations above, they ignored any potential interaction between the charged polymer segments.

Thus, the basic questions raised in the beginning of this section regarding gel electrophoresis, such as the size and shape of the polyelectrolyte chain in a gel, the dependence of the chain mobility on chain length and field strength, and whether reptation is the dominant mechanism, are still not answered by the above simulations for experimentally relevant physical conditions. This
failure is due to the inherent difficulties of the techniques and the choices of the models employed in these studies.

4.3 Conclusions

In the absence of the electric field, previous computer simulations of Baumgarner and Muthukumar[25,26] demonstrated that the dynamics of a chain in a random medium are different from those obtained when the obstacles are arranged in a periodic array in three dimensions. To be specific, consider a random medium where the volume fraction of solid phase is 0.5. If the solid phase is created randomly according to the random site percolation method[27], the diffusion coefficient of the center of mass in such a percolating random medium decays exponentially with chain length. The chain dynamics is non-reptative and controlled by entropic barriers located at random within the space of the medium. On the other hand, if the solid phase is created as a regular periodic network, the chain dynamics is reptative and $D \sim N^{-2}$. Thus, the spatial heterogeneity is an important contributing factor. In addition, the space dimension plays a crucial role on entanglement effects, leading to different dynamics depending on the space dimension (compare results of reference 24 with those of reference 28). Furthermore, intersegment interactions must also be accounted for to avoid any spurious aggregation observed in earlier simulations.
In Chapter 6 Monte Carlo simulations based on a model that accounts for the three features described above, namely, network heterogeneity, space dimension of three, and potential interactions between segments of the polymer chain and between chain segments and the network will be performed. Next, in Chapter 5 a model is developed for the stretching of a charged polymer chain in an external electric field with one end of the polymer held fixed in space. This will provide an estimate of the amount of chain stretching that can be observed in electrophoresis simulations when part of the polymer becomes pinned on an obstacle or obstacles that model the gel.
References of Chapter 4


CHAPTER 5

STRETCHING OF A POLYELECTROLYTE IN AN ELECTRIC FIELD WITH ONE END OF THE CHAIN ANCHORED

5.1 Introduction

As a simplified model for the stretching of a polyelectrolyte pinned on an obstacle in gel electrophoresis, this chapter considers the determination of the average size of a model polyelectrolyte in an electric field. One end of the polymer is held fixed while the other segments are free to interact with the electric field. The model ignores potential interactions between segments and only takes into account the chain connectivity of the polymer. The results for the case where there is a Gaussian potential (Section 5.2) between adjacent segments will be discussed in light of the computer simulations for electrophoresis by Shaffer and Cruz[1]. It is demonstrated that this model predicts unphysical stretching of the polymer chains at moderate to high electric field strengths. To circumvent this deficiency, a model for the polymer chain consisting of segments with fixed bond lengths is developed in Section 5.3 and the predictions are compared to the results of Section 5.2.
5.2 Path Integral Approach

Consider a uniformly charged polymer chain with N segments, each of charge q, interacting with a constant electric field, \( \mathbf{E} \), directed along the x-coordinate direction. In the absence of inter-segment interactions the probability density for the the end-to-end distance of the chain, \( P(R,N) \) is given by the Edwards path integral[2],

\[
P(R,N) \sim \int_{0,0}^{R,N} \text{d}[\mathbf{r}(n)] \exp \left\{ \frac{3}{2l^2} \int_0^N \left( \frac{\partial \mathbf{r}(n)}{\partial n} \right)^2 \text{d}n + E' \int_0^N \mathbf{r}(n) \text{d}n \right\},
\]

(5.1)

where \( l \) is the statistical segment length of the polymer and \( E' = qE/kT \) is the dimensionless electric field strength with \( T \) being temperature and \( k \) is the Boltzmann constant. The first term in the exponential takes into account the chain connectivity through a Gaussian potential for neighboring points on the chain and the second term is the added effect of the electric field. The current model is exactly solvable[3-5], with \( P(R,N) \) being given by

\[
P(R,N) = \exp \left\{ -\frac{3}{2l^2N} (R_x^2 + R_y^2 + R_z^2) \right\} \exp \left\{ -\frac{E'R_x}{2} (N+1) \right\}.
\]

(5.2)

Note electric field is taken to be along the x-coordinate direction.
In addition, the average x-component of the end-to-end distance squared, \( <R_x^2> \), was determined\([4,5]\) to be

\[
\frac{3}{Nl^2} <R_x^2> = 1 + \frac{E^2 Nl^2}{3} \left( 1 + \frac{N_1 N_2}{4} \right).
\]

(5.3)

Notice that at high electric fields the size of the polymer scales as \( N^4 \) which is unphysical, since \( <R_x^2> \) for a completely extended chain scales as \( N^2 \). The unphysical nature of the current model may be attributed to the Gaussian potential employed to ensure polymer chain connectivity. Accordingly, the segments comprising the polymer chain may support very large extensions under large forces, with the whole chain being allowed to extended substantially beyond its contour length, \( L=NL \). An analogous problem arises in rubber-elasticity at high extensions. If all the charge on the polymer were to be localized on the segments at each end of the polymer, this would be equivalent to the situation in rubber elasticity. Alternately, Gaveau and Shulman\([5]\) suggest that the unphysical stretching results from the lack of a fundamental length scale to the "Brownian path" described by equation 5.1. In the next section this problem is rectified by modeling the polymer as a string of segments separated by a fixed bond length, \( l \). The implications to electrophoresis simulations is that if the interbead potential is assumed to be Gaussian, as employed by Shaffer and Cruz\([1]\) in their simulations, the stretching of the chain will be greatly over-estimated.
5.3 Discretized Representation of the Polymer

Here the polymer is model by a succession of N beads separated by a distance \( l \) which is fixed. All other variables are the same as described above. Realizing that the potential of a given conformation only depends on the center of mass of the polymer, the resulting expression for \( P(R,N) \) is given by

\[
P(R,N) = P_0(R,N) \exp \left\{ -\frac{R_x E'}{2} (N+1) \right\}
\]

(5.4)

The electric field is directed along the x direction and \( P_0(R,N) \) is given by[7],

\[
P_0(R,N) = \frac{1}{2^{N+1} (N-2)! \pi l^2 |R|} \sum_{k=0}^{k \leq 0.5} (-1)^k \binom{N}{k} \binom{N-2k-\frac{|R|}{l}}{N-2}^{N-2}
\]

(5.5)

A similar result was found by other investigators[3,5]. Now \( <R_x^2> \) may determined from,

\[
<R_x^2> = \frac{\int R_x^2 P(R,N) dR}{\int P(R,N) dR}
\]

(5.6)
by numerical integration. The results for \( <R_x^2> \) as a function of \( E' = qE/kT \) are plotted in Figures 5.1 to 5.3. Figure 5.1 demonstrates for a chain of 10 segments that the size of the polymer saturates as the electric field is increased. As the number of segments comprising of the polymer is increased, Figures 5.2 and 5.3 show that the plateau of \( <R_x^2> \) is reached at progressively weaker electric fields. From the data in Figure 5.2 at high electric fields where \( <R_x^2> \) has saturated for all values of \( N \), \( <R_x^2> \) is proportional to \( N^2 \). Therefore, the unphysical results of Section 5.2 are avoided, at high fields the size of the polymer along the field direction scales as a rod as expected.

Finally, Figures 5.4 to 5.6 provided a comparison between the predictions of the discretized model for the polymer presented here and the results of Section 5.2 where a Gaussian potential between the segments was employed to ensure chain connectivity. The figures demonstrate that the model of Section 5.2 is fairly accurate for small chains at low electric fields (Figure 5.4) with the model breaking down either as \( N \) is increased (Figure 5.6) or as the electric field is increased.

5.4 Conclusions and Future Work

A model for a polyelectrolyte chain stretched by an electric field was developed for two cases. In the first case the polymer chain connectivity was imposed through a Gaussian potential
between segments. It was demonstrated that this model leads to an unphysical results, namely $<R_x^2> \sim N^4$. The problem was rectified by employing a discrete model for the polymer chain and at high electric field strengths $<R_x^2>\sim N^2$.

The addition of potential interactions between the segments of the charged polymer chain and the inclusion of the random medium would be natural continuations of the present work relevant to gel electrophoresis.
Figure 5.1 A plot of $3\frac{<R_x^2>}{Nl^2}$ vs $qE/kT$ for a chain of 10 beads calculated using the discrete representation of the polymer.
Figure 5.2 A plot of $\frac{3<R_x^2>}{Nl^2}$ vs $qE/kT$ for chains of 10(●), 40(+), 70(●) and 80(●●) beads calculated using the discrete representation of the polymer.
Figure 5.3 A plot of $3 <R_x^2>/NI^2$ vs qE/kT for chains of 10(□), 40(＋), 70(●) and 80(○) beads calculated using the discrete representation of the polymer. The results are at weak electric fields.
Figure 5.4 Comparison between the predictions for $3\langle R_x^2 \rangle / N l^2$ as a function of the electric field strength $qE/kT$ obtained from the discrete representation of the polymer (○) with those predicted from the model of Section 5.2 (●) for a chain 10 segments. In Section 5.2 the polymer chain connectivity was taken into account through a Gaussian potential between segments.
Figure 5.5 Comparison between the predictions for $3\frac{\langle R_x^2 \rangle}{Nl^2}$ as a function of the electric field strength $qE/kT$ obtained from the discrete representation of the polymer (•) with those predicted from the model of Section 5.2 (○) for a chain 40 segments. In Section 5.2 the polymer chain connectivity was taken into account through a Gaussian potential between segments.
Figure 5.6 Comparison between the predictions for $3\frac{<R_x^2>}{Nl^2}$ as a function of the electric field strength $qE/kT$ obtained from the discrete representation of the polymer (○) with those predicted from the model of Section 5.2 (●) for a chain 80 segments. In Section 5.2 the polymer chain connectivity was taken into account through a Gaussian potential between segments.
References of Chapter 5


(4) Melenkevitz and Muthukumar (unpublished results, 1989)


CHAPTER 6

MONTE CARLO SIMULATIONS OF POLYELECTROLYTE ELECTROPHORESIS

6.1 Introduction

Previous computer simulations[1-6] of gel electrophoresis have been confined to two dimensions for chains without excluded volume or any other type of potential interactions. As already mentioned in Chapter 4, these simulations employed a periodic array of obstacles to model the gel, even though it has been demonstrated[28] that agarose gels closely resemble a random porous medium. In addition, it has been shown using Monte Carlo simulations[7] that the dynamics of an uncharged polymer in a random porous medium are different from the dynamics of a chain obtained when the obstacles form a periodic array. Recall from the discussion in Chapter 4 that the space dimension has an important influence on entanglement effects, so the dynamics is highly dependent on the space dimension.

In the model presented here, a uniformly charged polymer chain of N beads moves in a three-dimensional random medium with an applied electric field. The beads interact via a screened coulombic potential, where the Debye-Huckel length is an experimental parameter accounting for the presence of counterions and
added low-molecular-weight salts. The random medium is modeled by cubic obstacles distributed at random in space. The density of the obstacles is such that there is always continuous space through which the chain moves. The chain moves in the empty space and performs off-lattice motion. The interaction between the chain and the random medium is taken to be pure excluded volume. Thus the chain dynamics is determined by the chain connectivity, the interbead screened coulombic potential, the potential interaction between the beads and the external constant electric field, and the excluded volume interactions between the beads and the random medium. The time evolution of the chain is monitored by the standard Monte Carlo technique[8]. Details of the model are provided in Section 6.2.

In Section 6.3, simulations will be performed for a single model polyelectrolyte chain in random porous media with an applied electric field in order to test the predictions of the biased reptation theory for gel electrophoresis. The variation of the chain mobility, \( \mu \), with \( N \) at constant electric field and ionic strength will be determined in order to make a qualitative comparison between the results of the computer simulations with typical gel electrophoresis experiments. Lastly, because previous computer simulations of gel electrophoresis [1-6] employed a periodic array obstacles to model the gel, a comparison will be made in Section 6.4 between the relative separation achieved for polyelectrolytes of different molecular weights when the obstacles of the model gel are arranged randomly with the separation obtained with a regular array of obstacles.
6.2 Model Employed

The model for gel considered here consists of a random array of impenetrable cubes of side \( d \). The cubes are distributed at random with probability \( 1-p \) (\( 0<p<1 \)) on a cubic lattice with a lattice spacing \( d \) (see Figure 6.1), according to the random site percolation algorithm\([9]\). The size of the lattice is taken to be \( 100d \) throughout the current work and the infinite size of the system is approximated by imposing periodic boundary conditions on the original cube. Also notice that the obstacles are not points. In any particular realization of the random medium the obstacles appear as a collection of polydispersed lattice animals. After the cubic obstacles are placed on the original cubic lattice, the empty lattice sites are taken to be a continuum, and the polymer is allowed to occupy any region of the continuous phase. For the present work the porosity \( p \), the volume fraction of unoccupied space, is 0.7 (unless otherwise noted), which is well above the percolation threshold for the empty space, \( p_c \), of 0.3117. Note that the model for the gel chosen is akin to agarose gels\([10]\) which are fairly rigid from the prospective of the polymer navigating through the gel in electrophoresis. In addition, the gel fibers are arranged approximately at random in space\([10]\).

The polymer, depicted in Figure 6.2, is modeled as a "pearl-necklace" chain \([8]\) of \( N \) beads with diameter \( \sigma \) and charge \( q \), separated by distance, \( l \). For the work considered here \( d/\sigma=2 \) and \( l/\sigma=1.2 \). The beads \( i \) and \( j \) separated by a distance \( |\mathbf{r}_{ij}| \) interact via
Figure 6.1 Two-dimensional representation of the random medium use to model the gel. The cubic obstacles (black) of side $d$ are introduced on the lattice according to the random site percolation algorithm[9].
a Debye-Huckel potential:

\[
V(|r_{ij}|) = \begin{cases} 
\frac{q^2 e^2}{4\pi \varepsilon |r_{ij}|} \exp(-\kappa |r_{ij}|) & |r_{ij}| > \sigma \\
\infty & |r_{ij}| \leq \sigma 
\end{cases}
\]

\[
\kappa^2 = \frac{e^2 N_A}{\varepsilon kT} \sum_i q_i^2 c_i
\]

where \( e \) is the electron charge, \( \varepsilon \) is the dielectric constant of the medium, \( N_A \) is Avogadro's number, \( k \) is the Boltzmann constant, \( T \) is the absolute temperature, and \( c_i \) is the concentration of the \( i \)th ion of the charge \( q_i \). \( \kappa^{-1} \) is the screening length which includes the contribution of counterions of the polyelectrolyte that are not part of the condensed fraction as well as added low-molecular-weight salts. The polymer is allowed to move through the continuous phase of the porous medium with chain configurations generated using the kink-jump technique[8]. A bead is chosen at random and the chain configuration is changed locally by attempting a rotation of two successive links around the axis, joining their end beads by a random angle, \( \phi \), chosen to be in the interval \((0, 2\pi)\). If an end bead is chosen, the terminal link is rotated to a new position by specifying the angle \( \phi \) as above, along with an angle \( \Theta \), chosen such that the \( \cos \Theta \) is equally distributed in the interval \((-1, 1)\). Subsequent to a bead move, its new position is checked for violation
Figure 6.2 "Pearl-necklace" model for a polyelectrolyte chain. Each bead is of diameter $\sigma$ and contains charge $q$. The beads are separated by a distance $l$. Only the excluded volume of the beads restricts the bond angles that may assumed for a given conformation of the chain.
of the excluded volume constraint with the random medium. If the excluded volume constraint is violated, the procedure of the dynamic Monte Carlo method[8] is implemented, therefore, the bead is returned to its original position and this is counted as the new configuration. Next, the Metropolis test is used to accept configurations for moves that have not violated the excluded volume constraint with the random medium. For the movement of the m\textsuperscript{th} bead with the electric field along the x direction the change in the total interaction energy of the model polyelectrolyte, $\Delta E_m$, is calculate:

$$
\Delta E_m = \sum_{i<j} V(|r_{ij}|)_{new} - \sum_{i<j} V(|r_{ij}|)_{old} + qeE (x_{m,\text{new}}-x_{m,\text{old}})
$$

where $V(|r_{ij}|)_{\text{new}}$ and $V(|r_{ij}|)_{\text{old}}$ are the Debye-Huckel potentials when bead m is in its new and old positions, respectively. The other term, $qeE (x_{m,\text{new}}-x_{m,\text{old}})$, is the change in the electrical potential for the charged polymer in the electric field. If $\Delta E_m < 0$ the move is accepted; otherwise the move is accepted if,

$$
\exp(-\Delta E_m/kT) \geq w,
$$

where w is a random number chosen in the interval (0,1). If the trial is not accepted, the bead is returned to its original position and the configuration is counted as the new one.
In the results presented in the following sections N will assume values in the range of 10 to 70 while the other parameters for the model are,

\[ \kappa l = \frac{2}{3} \]

\[ \frac{q^2 e^2}{4\pi \varepsilon kT l} = 8.33 \times 10^{-3}. \]

At constant temperature, the effect of varying \( \kappa \) is to change the average size of the chain at zero field from a rod \( (\kappa \to 0) \) to a self-avoiding walk \( (\kappa \to \infty) \). The effect of the electric field is to stretch the polymer out along the field direction. The two parameters above were selected such that the N scaling exponent of the radius of gyration of polyelectrolyte chain was close to the value observed for DNA solutions employed in gel electrophoresis experiments.

With the electric field along the x direction, the mobility is given by \( \mu = \dot{X}_{cm}/E \) where \( \dot{X}_{cm} \) is the steady-state velocity of the x component of the center-of-mass of the polymer. In order to approach a steady state, the simulations were allowed to "warm-up" for 100,000 Monte Carlo steps for the shortest chains and up to 600,000 Monte Carlo steps for the longest chains. One Monte Carlo step(\text{ms}) is defined as N attempted moves for a chain of N beads. The "warm-up" time refers to the number of Monte Carlo steps taken at the beginning of the simulation where no information on the polymers configuration is retained for the purpose of determining average quantities of the polymer for the simulation. In
general, the "warm-up" time is incorporated into a computer simulation to eliminate any correlations with the initial configuration of the polymer. The steady-state velocity was obtained from the slope of the plot of the root-mean-square displacement of the x-component of the center-of-mass against Monte Carlo time. In the current study 1 Monte Carlo time(mt) was define as 100 Monte Carlo steps. The resulting mobility was averaged over five realizations of the porous media. The average quantities, such as mean square radius of gyration, x-component of the mean-square-end-to-end distance, and the time-dependent mean square displacement of the center of mass of the chain, were obtained by averaging over the various polymer configurations and different realizations of the porous media.

In the next section the model developed here will be used to study the dynamics of a single polyelectrolyte chain in a random medium with an applied external electric field, E. First the properties of the charged polymer will examined in the absence of the electric field to ascertain the effects of the random medium on the polyelectrolytes average size. Next, the effect the electric field on the polymer properties in the absence of the random medium will be studied. Lastly, the polyelectrolyte properties in the random medium with the applied electric field will investigated to determined the N dependence of the mobility, μ, and how the size of the polymer in influenced by the combined effects of the electric field and random environment. In Section 6.4, the electrophoresis of a polyelectrolyte in a regular array of obstacles will be examined to
demonstrate that the observed dynamics is indeed different from the dynamics in a random environment.

6.3 Polyelectrolyte Electrophoresis in a Random Medium

First of all, for the model polyelectrolyte chain with $\kappa l=2/3$

and $\frac{q^2 e^2}{4\pi \varepsilon kT l} = 8.33 \times 10^{-3}$ in the absence of an external electric field, Figure 6.3 shows that the effective scaling exponent, $v$, for the molecular weight dependence of the average radius of gyration squared, $<R_g^2>$, is 0.64 independent of $p$, provided $p>p_c$, in agreement with previous theoretical predictions[11-14]. Now consider the effect of the electric field, $E$, on the properties of the polyelectrolyte chain described above when no obstacles are present (i.e. $p=1$). The steady state velocity $X_{cm}$ is given by

$$X_{cm} = \frac{F}{f} = \frac{qEN}{f},$$

where $F$ is the total force acting on the polymer chain due to the electric field, $f$ is the translational friction coefficient, and $q$ is the charge on each bead comprising the polymer of $N$ beads. Since the dynamic kink-jump method is known to yield Rouse dynamics for
Figure 6.3  Double logarithmic plot of $\langle R_g^2 \rangle$ vs N. (○) is for $p=1$ and (●) is for $p=0.7$. $\kappa l=2/3$, $q^2 e^2/4\pi \varepsilon \kappa T=8.33(10)^{-3}$ and the electric field strength, $\mathbb{E}=0$. 
E=0.0 and \( p=1 \)[24], the Rouse friction coefficient, \( f \), is expected to be proportional to \( N \), leading to

\[ \dot{X}_{cm} \propto EN^0. \]

Figure 6.4 demonstrates for a chain \( N=10 \) that the "free-draining" behavior is indeed observed in the present simulations. In addition, Figure 6.5 shows that for a chain composed of 10 beads with \( p=1 \), the polymer chains do not elongate as the electric field strength is increase; therefore, any stretching observed for the simulations with \( p\neq1 \) will be mediated through the porous medium. Lastly, the "free-draining" dynamics also implies that \( \dot{X}_{cm} \) is independent of \( N \) at constant electric field strength. Figure 6.6 verifies that \( \dot{X}_{cm} \) is indeed independent of molecular weight when \( p=1 \).
Figure 6.4 Variation of the steady state velocity of the center of mass, $X_{cm}$, with electric field strength, $qE/kT$, for a chain of 10 beads. $\kappa l=2/3$, $q^2e^2/4\pi\epsilon kT=8.33(10)^{-3}$ and the electric field is along the $x$ direction.
Figure 6.5  Plot of the x-component of the mean-square radius of gyration, $\langle R_{g_x}^2 \rangle$ (○), and $\langle R_g^2 \rangle$ (■) vs electric field strength, qEl/kT, for a chain of 10 beads. $\kappa l=2/3$, $q^2e^2/4\pi\varepsilon_0kT=8.33\times10^{-3}$ and the electric field is along the x direction.
Figure 6.6  The variation of $X_{cm}$ with the number of beads $N$ for, $qE/kT = 0.012 (+), 0.06 (○),$ and $0.12 (■).$ $q^2e^2/4\pi\varepsilon_0kT = 8.33(10)^{-3},$ $\kappa l = 2/3$ and the electric field is along the $x$ direction.
Now the case where the polymer is present in the random medium with \( p=0.7 \) and an external electric field is applied along the \( x \)-coordinate direction will be investigated. First of all, for a chain of 10 beads, the effect of the electric field strength on chain properties was studied. Figures 6.7 and 6.8 show that as the electric field strength is increased, both the chain mobility and the \( x \)-component of the mean-square radius of gyration reach a plateau. This demonstrates the coupling between the average size of the chain and its mobility. Also, the effect of field strength is not simply a minor perturbation as suggested by some recent theoretical work[10]. The results for \( 10 \leq N \leq 70 \) and \( qEI/kT=0.12 \) are plotted in Figure 6.9, and similar trends are observed for other values of the electric field. They are in qualitative agreement with actual experimental data[15,16] (see Figure 4.2) It is possible to recognize three different regimes for the molecular weight dependence of mobility:

**Region 1:** For \( N<20 \), chains are smaller than the average pore size and the mobility of the chains is that of structureless particles, influenced primarily by collisions with obstacles that are arranged randomly in space.

**Region 2:** For \( 30>N>20 \), the average size of the chain is comparable to the average pore size so that the chain mobility is also affected by entropic barriers associated with the polymer moving through different size pores. In the weak field limit, the diffusion coefficient of a chain moving through different size pores is related to the partition coefficient, \( K \sim \exp (-\Delta F/kT) \) where \( \Delta F \) is the difference in free energy for a chain confined in two different size.
Figure 6.7 x-component of the mean-square radius of gyration 
$\langle R_{gx}^2 \rangle$ vs dimensionless electric field $qEl/kT$ for a chain of 10 beads. $\kappa l=2/3$, $q^2e^2/4\pi\varepsilon_0 kT=8.33(10)^{-3}$ and the porosity $p=0.7$. 
Figure 6.8 The electrophoretic mobility, $\mu$, vs dimensionless electric field $qE_l/kT$ for a chain of 10 beads. $q^2e^2/4\pi\varepsilon lkT=8.33(10)^{-3}$, $k_l=2/3$ and the porosity $p=0.7$. 
Figure 6.9  $\ln N$ plotted against the electrophoretic mobility, $\mu$, for $\kappa l = 2/3$, $q^2 e^2 / 4\pi \epsilon l kT = 8.33 \times 10^{-3}$, $qE l / kT = 0.12$ and the porosity $p = 0.7$. 
The free energy of a chain is increased when a chain is confined to a smaller volume due to the reduction in the number of configurations available. More details on entropic barriers in the absence of an electric field may be found in references 7 and 17. By making use of the Einstein relation $D = kT/f$ (the mobility is proportional to $D$ in the zero field limit), it is concluded that entropic barriers contribute to the decrease in chain mobility in region 2. Also from a practical perspective, it would be advantageous to perform the separation of polymers in region 2, since the change in mobility is relatively large for only a small change in molecular weight. From the arguments above, it should be possible to adjust the gel concentration in gel electrophoresis in order to operate in region 2.

**Region 3:** For $N>30$, the chain size is much larger than the average pore size. In addition to the effects present in regions 1 and 2, the chains also becomes entangled with obstacles. In fact, the chain is stretched more readily in this regime by the electric field. Figure 6.10 demonstrates the effect of the electric field on chain dimensions. For the electric field strength $qEl/kT = 0.12$, Figures 6.10(a) and 6.10(b) show that the electric field increases the average dimensions of the chains relative to the zero field size (see Figure 6.3) with $v=0.76$ ($<R_g^2>\sim N^{2v}$). Also the stretching is highly anisotropic with $v_\parallel=0.95$ ($<R_x^2>\sim N^{2v_\parallel}$).
Continued, next page
Figure 6.10(b) Double logarithmic plot of $<R_x^2>$ vs $N$, for $k=2/3$, $q^2e^2/4\pi\epsilon\lambda kT=8.33(10)^{-3}$, $q\epsilon\lambda/kT=0.12$ and the porosity $p=0.7$. 
Consider region 3 in more detail. Here simple reptation in a tube is not observed. Using the reptation prediction for the mobility from Chapter 4, \( \mu \approx N^{2\nu_H-2} \), with \( \nu_H = 0.95 \) yields, \( \mu \approx N^{-0.10 \pm 0.08} \), however, from the data for \( N > 30 \) at \( qE/lkT = 0.12 \), it is observed that \( \mu \approx N^{-0.27 \pm 0.04} \) in the range of \( N \) studied. The lack of conformance to reptation is expected in light of the reptation assumption that the motion of the chain be confined along the tube formed by the obstacles.

In order to study the dynamics in the high-molecular-weight region more closely, the time evolution for a chain of 54 beads (\( qE/lkT = 0.12 \) electric field along the x direction) will be followed, recording the bead coordinates at each Monte Carlo time step. Figure 6.11 shows a typical cross section for the time evolution of the x-component of the center-of-mass and the x-component of the end-to-end distance. The motion is characterized by regions where the chain is stretched, followed by durations where the chain is contracted. The findings of this section are corroborated with a series of pictures shown in Figures 6.12-19. The pictures correspond to specific times for the data of Figure 6.11. These are two-dimensional projections of the positions of beads and obstacles. Only those obstacles that come a distance 2l or less from a bead on the chain over the complete time evolution are shown. Further, the size of the obstacles has been reduced in these figures by a factor of 2 in order to allow for greater visibility of the chain. From the pictures simple reptation in a tube is not observed, i.e, the motion is not dominated by the movement of the ends of the chain. The pictures also show that at some instances the leading end of the
Figure 6.11  \( x \) component of the center-of-mass(o) and \( x \) component of the end-to-end distance \( |R_x| \) (●) against Monte Carlo time(\( mt \)) for a chain with 54 beads and the electric field along the \( x \) direction. \( qE_l/kT=0.12, \ \kappa l=0.66, \) and \( q^2e^2/4\pi\varepsilon lkT=8.33\times10^{-3} \). The simulations were allowed to "warm-up" for 600,000 Monte Carlo steps (1\( mt=100\)ms).
Figure 6.12 Two-dimensional (x,y) projections of a chain of 54 beads for different Monte Carlo times (mt). The electric field is along the x direction. The values of the x coordinate of the center of mass (X_{cm}) for the chain are: 701.50 (mt=661), 703.93 (mt=671), and 704.75 (mt=681).
Figure 6.13 Two-dimensional (x,y) projections of a chain of 54 beads for different Monte Carlo times (mt). The electric field is along the x direction. The values of the x coordinate of the center of mass (X_{cm}) for the chain are: 705.64 (mt=691), 708.16 (mt=701), and 710.46 (mt=711).
Figure 6.14 Two-dimensional \((x,y)\) projections of a chain of 54 beads for different Monte Carlo times \((mt)\). The electric field is along the \(x\) direction. The values of the \(x\) coordinate of the center of mass \((X_{cm})\) for the chain are: 709.60 \((mt=721)\), 710.47 \((mt=731)\), and 712.60 \((mt=741)\).
Figure 6.15 Two-dimensional (x,y) projections of a chain of 54 beads for different Monte Carlo times (mt). The electric field is along the x direction. The values of the x coordinate of the center of mass (X_{cm}) for the chain are: 713.81 (mt=751), 715.04 (mt=761), and 716.37 (mt=771).
Figure 6.16 Two-dimensional (x,y) projections of a chain of 54 beads for different Monte Carlo times (mt). The electric field is along the x direction. The values of the x coordinate of the center of mass (X_{cm}) for the chain are: 717.32 (mt=781), 718.41 (mt=791), and 718.77 (mt=801).
Figure 6.17 Two-dimensional (x,y) projections of a chain of 54 beads for different Monte Carlo times (mt). The electric field is along the x direction. The values of the x coordinate of the center of mass (X cm) for the chain are: 719.63 (mt=811), 719.68 (mt=821), and 720.81 (mt=831).
Figure 6.18 Two-dimensional (x,y) projections of a chain of 54 beads for different Monte Carlo times (mt). The electric field is along the x direction. The values of the x coordinate of the center of mass (X_cm) for the chain are: 721.13 (mt=841), 721.90 (mt=851), and 723.79 (mt=861).
Figure 6.19 Two-dimensional $(x,y)$ projections of a chain of 54 beads for different Monte Carlo times $(mt)$. The electric field is along the $x$ direction. The values of the $x$ coordinate of the center of mass $(X_{cm})$ for the chain are: 726.66 $(mt=871)$, 730.01 $(mt=881)$, and 734.39 $(mt=891)$.
chain, that is the end which is furthest downfield, actually turns back against the field, contrary to the results of the biased reptation theory[18-20]. These pictures show a situation where movement by reptation is clearly not observed. Here rather than moving through its ends, the center of the chain escapes downfield through bottlenecks. It is also obvious from Figure 6.11 that our Monte Carlo simulations do not suffer from the difficulties encountered by Olvera de la Cruz et al.[1] with regard to metastabilities. This is primarily due to the fact that our simulations are very long-time simulations, compared to the time necessary to anneal a metastable state, and that our simulations are performed off-lattice with a smaller fraction of space occupied by the obstacles as compared to reference 1. This will be further demonstrated by considering the dynamics in a regular array of obstacles in the next section.

6.4 Polyelectrolyte Electrophoresis in a Regular Array of Obstacles

In the last section, electrophoresis of polyelectrolytes in random media was considered. It was demonstrated that the sensitivity of the separation achieved for polyelectrolytes of different molecular weights depended on the average size of the polymer relative to the average pore size in the random medium. A single random medium contains a broad distribution of pore sizes. Now the consequences of performing electrophoresis when
the obstacles are arranged to form a regular network or "cage" will be considered. The unit cell for the periodic array of obstacles employed here is shown below.

![Diagram of a regular network or cage](image)

The size scale for both the cubic obstacles comprising the periodic array and the model polymer chain is the same as previously used for the electrophoresis in random media of Section 6.3 (i.e. \( d/\sigma = 2 \) and \( l/\sigma = 1.2 \)). The electric field, \( E \), is directed along the \( x \) direction. Here \( p = 0.259 \), which is slightly smaller than the value 0.3 used for the electrophoresis in random media (Section 6.3). Also as before the Deybe-Huckel potential with,

\[
\kappa l = \frac{2}{3}
\]

\[
\frac{q^2 e^2}{4\pi \varepsilon kT l} = 8.33 \times 10^{-3}
\]
is employed to model the interactions between the beads comprising the polymer chain. Because earlier computer simulations of electrophoresis[1,3&4] were concerned primarily with high molecular weight chains, only chains which had been demonstrated to be within region III of Figure 6.9, Section 6.3, will be studied. Table 6.1 provides the simulation data for the electrophoresis in a regular array of obstacles with dimensionless electric field strengths, qEl/kT< 0.12 and N=42, 54, and 68.

Table 6.1 The average x-component of the radius of gyration squared, \( <\text{R}_{gx}^2> \), the average radius of gyration squared, \( <\text{R}_g^2> \), the average x-component of the end-to-end distance squared, \( <\text{R}_x^2> \), and the mobility, \( \mu \), as a function of the number of beads, N, and the electric field strength, qEl/kT, for electrophoresis in a "cage" of obstacles. The values of N were selected to be within region III(N>30) of Figure 6.9 (Section 6.3).

<table>
<thead>
<tr>
<th>N</th>
<th>qEl/kT</th>
<th>( &lt;\text{R}_{gx}^2&gt; )</th>
<th>( &lt;\text{R}_g^2&gt; )</th>
<th>( &lt;\text{R}_x^2&gt; )</th>
<th>( \mu )</th>
</tr>
</thead>
<tbody>
<tr>
<td>42</td>
<td>0.030</td>
<td>11.115</td>
<td>26.683</td>
<td>74.430</td>
<td>12.740</td>
</tr>
<tr>
<td>42</td>
<td>0.060</td>
<td>13.900</td>
<td>27.493</td>
<td>93.410</td>
<td>15.490</td>
</tr>
<tr>
<td>42</td>
<td>0.120</td>
<td>20.250</td>
<td>30.375</td>
<td>132.85</td>
<td>20.650</td>
</tr>
<tr>
<td>54</td>
<td>0.060</td>
<td>22.660</td>
<td>39.380</td>
<td>153.90</td>
<td>15.05</td>
</tr>
<tr>
<td>54</td>
<td>0.030</td>
<td>17.130</td>
<td>38.485</td>
<td>118.86</td>
<td>11.670</td>
</tr>
<tr>
<td>68</td>
<td>0.060</td>
<td>41.710</td>
<td>65.200</td>
<td>289.50</td>
<td>15.260</td>
</tr>
<tr>
<td>68</td>
<td>0.030</td>
<td>27.920</td>
<td>54.575</td>
<td>193.125</td>
<td>11.120</td>
</tr>
</tbody>
</table>

First of all, from Table 6.1 for N=42 , as the electric field strength is increased, the mobility increases demonstrating again that these simulations do not suffer from the difficulties encountered with the
lattice Monte Carlo simulations of Olvera del la Cruz et al[1].

Contrary to electrophoresis experiments[15] and the results of Table 6.1, these workers[1] found that the polymer chains actually move slower at higher electric fields. Comparing the results from Figures 6.9 and 6.10 (Section 6.3) for electrophoresis in a random array of obstacles to the results of Table 6.1 shows that for N=42 and qEl/kT=0.12, the mobility, $\mu$, is much higher for electrophoresis in a regular array of obstacles than electrophoresis in random media ($\mu=20.65$, regular array vs. $\mu=10.500$, random media). In addition, although the average size of the chain is larger for electrophoresis in random media relative to electrophoresis in a regular array of obstacles ($<R_g^2>=29.67$, random media vs. $<R_g^2>=20.35$, regular array), the chain stretching is much more anisotropic for electro-phoresis in a regular array of obstacles ($<R_x^2>=132.85$, regular array vs $<R_x^2>=91.104$, random media). It appears that the orientation of the electric field with respect to the unit cell of the regular array of obstacles (see top of page 159) serves to facilitate the alignment of sections of the chains in the field direction. Previously[17], it had been demonstrated that the dynamics of a polymer chain in the presence of a regular array of obstacles and no electric field are reptative. Assuming reptation still describes the dynamics when the electric field is non-zero, then $\mu \approx <R_x^2>/N^2$ and therefore, greater stretching of the chains along the field direction will lead to less of a relative separation for polymers of different molecular weights. For the regular array of obstacles, no separation was achieved for qEl/kT=0.12. In fact, for an electric field qEl/kT=0.06 Table 6.1 also indicates that no separation is
achieved. Thus, the effect of the randomness of the porous medium serves to allow for larger fluctuations in the size of the polymer chain in the high molecular weight regime, inducing a more efficient separation than that obtained for the regular array of obstacles. This follows as a consequence of the presence of entropic barriers in random media. A feature common to both electrophoresis in random media and electrophoresis in a regular array of obstacles is the time evolution of the x-component of the end-to-end distance. Comparing Figure 6.20 for electrophoresis in a regular array of obstacles with Figure 6.11, Section 6.3, demonstrates that independent of the arrangement of the obstacles the polymer chains are stretched out at times, then pass through durations where the chains are contracted. However, y-x, y-z, and z-x projections of a polymer chain of 54 beads for data corresponding to Figure 6.20 provided in Figures 6.21-32 demonstrate that there are qualitative differences between the time evolution of a polymer chain in electrophoresis in a regular array of obstacles with the motion of a chain in a random medium (see Figures 6.13-19, Section 6.3). Notice from the y-x projections in Figures 6.21-32 that the polymer moves through its ends and there is never a situation analogous to Figures 6.13-16 where the center of the chain escapes through an entropic barrier. Therefore, a proper model of gel electrophoresis must include the effects gel heterogeneity.
Figure 6.20 x component of the center-of-mass(o) and x component of the end-to-end distance |Rx| (●) against Monte Carlo time(mt) for a chain with 54 beads and the electric field along the x direction. qE/kT=0.12, κα=0.66, and q²e²/4πε_lkT=8.33x10⁻³. The obstacles comprising the medium form a regular array and the simulations were allowed to "warm-up" for 600,000 Monte Carlo steps (note for this figure 1mt=200ms).
Figure 6.21 Two-dimensional projections, (y,x), (y,z) and (z,x), of a chain of 54 beads for mt=221. The electric field is along the x direction and the x coordinate of the center of mass ($X_{cm}$) for the chain is 59.91.
Figure 6.22 Two-dimensional projections, (y,x), (y,z) and (z,x), of a chain of 54 beads for mt=241. The electric field is along the x direction and the x coordinate of the center of mass ($X_{cm}$) for the chain is 62.40.
Figure 6.23 Two-dimensional projections, $(y,x)$, $(y,z)$ and $(z,x)$, of a chain of 54 beads for $m = 261$. The electric field is along the $x$ direction and the $x$ coordinate of the center of mass ($X_{cm}$) for the chain is 62.46.
Figure 6.24 Two-dimensional projections, (y,x), (y,z) and (z,x), of a chain of 54 beads for mt=281. The electric field is along the x direction and the x coordinate of the center of mass ($X_{cm}$) for the chain is 61.88.
Figure 6.25 Two-dimensional projections, (y,x), (y,z) and (z,x), of a chain of 54 beads for nt=301. The electric field is along the x direction and the x coordinate of the center of mass \((X_{cm})\) for the chain is 60.91.
Figure 6.26  Two-dimensional projections, \((y,x), (y,z)\) and \((z,x)\), of a chain of 54 beads for \(mt=321\). The electric field is along the \(x\) direction and the \(x\) coordinate of the center of mass \(X_{cm}\) for the chain is 60.35.
Figure 6.27 Two-dimensional projections, \((y,x), (y,z)\) and \((z,x)\), of a chain of 54 beads for \(mt=341\). The electric field is along the \(x\) direction and the \(x\) coordinate of the center of mass \(X_{cm}\) for the chain is 61.18.
Figure 6.28 Two-dimensional projections, \((y,x), (y,z)\) and \((z,x)\), of a chain of 54 beads for \(mt=361\). The electric field is along the \(x\) direction and the \(x\) coordinate of the center of mass \((X_{cm})\) for the chain is 64.37.
Figure 6.29  Two-dimensional projections, (y,x), (y,z) and (z,x), of a chain of 54 beads for mt=381. The electric field is along the x direction and the x coordinate of the center of mass (X_{cm}) for the chain is 64.85.
Figure 6.30 Two-dimensional projections, (y,x), (y,z) and (z,x), of a chain of 54 beads for mt=401. The electric field is along the x direction and the x coordinate of the center of mass ($X_{cm}$) for the chain is 68.29.
Figure 6.31 Two-dimensional projections, \((y,x)\), \((y,z)\) and \((z,x)\), of a chain of 54 beads for \(mt=421\). The electric field is along the \(x\) direction and the \(x\) coordinate of the center of mass \(X_{cm}\) for the chain is 69.91.
Figure 6.32  Two-dimensional projections, \((y,x)\), \((y,z)\) and \((z,x)\), of a chain of 54 beads for \(mt=441\). The electric field is along the \(x\) direction and the \(x\) coordinate of the center of mass \((X_{cm})\) for the chain is 69.76.
6.5 Conclusions

Monte Carlo simulations were performed in order to study the dynamics of a polyelectrolyte chain in random porous media with an applied external electric field. It was found that the dependence of the chain mobility, $\mu$, on the number of segments comprising the polymer, $N$, is in qualitative agreement with actual gel electrophoresis experiments. Further, three regions for the $N$ dependence of the mobility were identified and determined to be a function of the average size of the polyelectrolyte in relation to the average pore size in the random medium. In the region of small $N$, the mobility is influenced primarily by collisions with the random media. As the average size of the polymer becomes comparable to the average pore size, the existence of entropic barriers has the effect of introducing a strong dependence of the mobility on $N$. In the high $N$ regime, the polymer chains become significantly entangled with the random medium, further impeding the motion of the chains. However, in this high $N$ regime, the chain dynamics cannot be explained by reptation. Also, the size of the polyelectrolyte chains were found to be significantly stretched for the electrophoresis in a random medium and the stretching was found to be highly anisotropic. It was found that in the absence of the random medium there was no chain stretching even as the electric field was increased dramatically. Therefore, any stretching of the chains was mediated through the random medium. Lastly, it was demonstrated that the chain dynamics of a polyelectrolyte in the
presence of a regular array of obstacles with an applied external electric field defers from the dynamics of a chain in a random environment. Indeed, it was demonstrated that the presence of random medium gave rise to a much more efficient separation of polyelectrolytes of different N.
References of Chapter 6

(20) Slater, G.W.; Rousseau, J.; Noolandi, J., Biopolymers, 26, 863 (1987).
CHAPTER 7

FUTURE WORK

7.1 Suggestions for Future Studies

One aspect of electrophoresis that may be studied systematically using computer simulations is the role of disorder in the medium used for electrophoresis. Starting with a regular array of obstacles, the separation achieved for model polyelectrolytes in electrophoresis may be monitored as a function of the amount of disorder introduced in the porous medium.

Another area of electrophoresis that may be studied is field inversion gel electrophoresis (FIGE). Here an electric field with strength, $E_1$, is applied across the gel for a time $T_1$, followed by the application of an electric field, $E_2$, for a time $T_2 (T_2 < T_1)$ in the direction opposite to the first "pulse". Experimentally, for very large chains FIGE has been found to yield much better separation for polyelectrolytes of different molecular weights than electrophoresis in a constant field. Here too some computer simulations have been performed but suffer from the deficiencies of previous constant field electrophoresis simulations noted in Chapter 4.
Lastly, the electrophoresis of polyelectrolytes with different topologies may be examined. Computer simulations could determine whether it is experimentally feasible to separate polyelectrolytes differing only in the topology (i.e. linear, ring, knot, stars, ...etc.).
APPENDIX A

ORDER PARAMETERS CALCULATED FROM THE WEAK SEGREGATION THEORY OF LEIBLER

Table A.1  Values of the parameters $x^*$, $\chi N_s$, c, $\mu$ and $\lambda$ as a function of copolymer composition, f, pertinent to Leibler's theory for the microphase separation in the weak segregation limit.

<table>
<thead>
<tr>
<th>f</th>
<th>$x^*$</th>
<th>$\chi N_s$</th>
<th>c</th>
<th>$\mu$</th>
<th>$\lambda$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.50</td>
<td>3.78524</td>
<td>10.4949</td>
<td>1.10196</td>
<td>-6.3291</td>
<td>115.831</td>
</tr>
<tr>
<td>0.45</td>
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<td>10.6978</td>
<td>1.10769</td>
<td>-10.303</td>
<td>120.959</td>
</tr>
<tr>
<td>0.42</td>
<td>3.82202</td>
<td>11.0266</td>
<td>1.11790</td>
<td>-13.149</td>
<td>129.267</td>
</tr>
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<td>3.84330</td>
<td>11.3440</td>
<td>1.12556</td>
<td>-16.857</td>
<td>137.352</td>
</tr>
<tr>
<td>0.35</td>
<td>3.92071</td>
<td>12.5620</td>
<td>1.15712</td>
<td>-21.047</td>
<td>168.597</td>
</tr>
<tr>
<td>0.30</td>
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<td>14.5620</td>
<td>1.20596</td>
<td>-31.010</td>
<td>222.684</td>
</tr>
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<td>0.25</td>
<td>4.21383</td>
<td>18.1719</td>
<td>1.27805</td>
<td>-44.824</td>
<td>317.593</td>
</tr>
<tr>
<td>0.215</td>
<td>4.41944</td>
<td>23.3250</td>
<td>1.36383</td>
<td>-56.651</td>
<td>411.169</td>
</tr>
<tr>
<td>0.20</td>
<td>4.47084</td>
<td>24.6133</td>
<td>1.38524</td>
<td>-66.217</td>
<td>497.157</td>
</tr>
</tbody>
</table>

Table A.2  The predicted order-disorder transitions to BCC spheres calculated using the theory of Leibler. Only those values of $f$ that are compared to the predictions of the density functional theory constructed in this dissertation are shown.

<table>
<thead>
<tr>
<th>f</th>
<th>$\chi N_{trans}$</th>
<th>a6</th>
<th>$\Phi(a6)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.45</td>
<td>10.674</td>
<td>8.9098e-3</td>
<td>-1.8081e-7</td>
</tr>
<tr>
<td>0.40</td>
<td>11.25</td>
<td>0.0171042</td>
<td>-1.30768e-6</td>
</tr>
<tr>
<td>0.35</td>
<td>12.36</td>
<td>0.0228420</td>
<td>-2.9329916e-5</td>
</tr>
<tr>
<td>0.25</td>
<td>17.6</td>
<td>0.0265700</td>
<td>-1.982252e-4</td>
</tr>
<tr>
<td>0.215</td>
<td>22.5</td>
<td>0.0254280</td>
<td>-1.421364e-4</td>
</tr>
</tbody>
</table>
Table A.3 Transitions from BCC spheres to hexagonal cylinders calculated using the theory of Leibler. Only those values of f that are compared to the predictions of density functional theory are shown. a6 and a3 refer to the order parameters at the transition for the spheres and cylinders respectively.

<table>
<thead>
<tr>
<th>f</th>
<th>χtrans</th>
<th>a6</th>
<th>a3</th>
<th>Φ</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.45</td>
<td>10.72</td>
<td>0.0163860</td>
<td>0.025601</td>
<td>-8.6e-5</td>
</tr>
<tr>
<td>0.40</td>
<td>11.41</td>
<td>0.0290133</td>
<td>0.045030</td>
<td>-9.1e-4</td>
</tr>
<tr>
<td>0.35</td>
<td>12.70</td>
<td>0.0376212</td>
<td>0.058317</td>
<td>-3.1e-3</td>
</tr>
<tr>
<td>0.25</td>
<td>18.6</td>
<td>0.0427780</td>
<td>0.066396</td>
<td>-0.0100</td>
</tr>
<tr>
<td>0.215</td>
<td>23.9</td>
<td>0.0415650</td>
<td>0.064445</td>
<td>-0.0113</td>
</tr>
</tbody>
</table>

Table A.4 The predicted transitions from hexagonal cylinders to lamellae calculated using the theory of Leibler. Only those values of f that are compared to the predictions of density functional theory are shown. a3 and a1 refer to the order parameters at the transition for the spheres and cylinders respectively.

<table>
<thead>
<tr>
<th>f</th>
<th>χtrans</th>
<th>a3</th>
<th>a1</th>
<th>Φ</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.45</td>
<td>11.8</td>
<td>0.882510</td>
<td>0.1723537</td>
<td>-0.0266</td>
</tr>
<tr>
<td>0.42</td>
<td>12.5</td>
<td>0.102839</td>
<td>0.191012</td>
<td>-0.04302</td>
</tr>
<tr>
<td>0.40</td>
<td>13.6</td>
<td>0.122773</td>
<td>0.227724</td>
<td>-0.0924</td>
</tr>
</tbody>
</table>
APPENDIX B

FLOW CHARTS OF DENSITY FUNCTIONAL THEORY
COMPUTER PROGRAMS

Flow Chart 1 (Method I for Hard Sphere Freezing)

1. Generate reciprocal lattice vectors for structure of interest.

2. Sort reciprocal lattice vectors by magnitude, smallest to largest.

3. Sort vectors with the same magnitude into "shells". (i.e. vectors with the same magnitude related by a symmetry operation of the reciprocal lattice are in the same shell)

4. Set the $\rho_\text{s}$ in equation (1.16).

5. Input initial value for $\rho_\text{I}$ in equation (1.12).

6. Input two initial guesses for $\alpha$ in equation (1.16) to bracket minimum of $\Delta \Omega$.

7. Implement bisection method to determine the local minimum of $\Delta \Omega$ in equation (1.12).

8. Increment $\rho_\text{I}$ and repeat steps 6. & 7. until the global minimum of $\Delta \Omega$ is found for the value of $\rho_\text{s}$ set in step 4.
Flow Chart 2  (Method II for Hard Sphere Freezing)

1. Generate reciprocal lattice vectors for structure of interest.

2. Sort reciprocal lattice vectors by magnitude, smallest to largest.

3. Sort vectors with the same magnitude into "shells". (i.e. vectors with the same magnitude related by a symmetry operation of the reciprocal lattice are in the same shell)


5. Using

$$\ln \frac{\rho(r)}{\rho_1} = \int C^{(2)}(r_1, r_2) [\rho(r_2) - \rho_1] \, dr_2$$

combine with equation (1.14) to determine $\{A_q\}$ & $\rho_s$ at the global minimum for the system with liquid density, $\rho_1$.

6. Calculate $\Delta \Omega$ from equation (1.12).
Flow Chart 3  (Modified Method II for Hard Sphere Freezing)

1. Generate reciprocal lattice vectors for structure of interest.
2. Sort reciprocal lattice vectors by magnitude, smallest to largest.
3. Sort vectors with the same magnitude into "shells". (i.e. vectors with the same magnitude related by a symmetry operation of the reciprocal lattice are in the same shell)
4. Set the $\rho_S$ in equation (1.16).
5. Input initial value of $\rho_1$.
6. Combine equation (1.14) with equation (1.12) and determine the local minimum of $\Delta\Omega$ using Newton's Method.
7. Increment $\rho_1$ and repeat steps 5. & 6. until the global minimum of $\Delta\Omega$ is found for the value of $\rho_S$ set in step 4.
Flow Chart 4 (Lamellar Morphology, DFT-I)

1. Set the value of the reduced density, $\eta$.

2. Substitute

$$a_n = \frac{1}{n \pi} \sin(2\pi fn) e^{-2\pi^2 n^2 \left(\frac{\sigma_0}{D}\right)^2}$$

$$b_n = \frac{1}{n \pi} \left[1 - \cos(2\pi fn)\right] e^{-2\pi^2 n^2 \left(\frac{\sigma_0}{D}\right)^2}$$

into equation (2.17) for $\Delta\Omega$.

3. Input initial value for $R_g/D$.

4. Input two initial guesses for $(\sigma_0/D)$ to bracket the minimum of $\Delta\Omega$.

5. Implement bisection method to determine the local minimum of $\Delta\Omega$.

6. Increment $R_g/D$ and repeat steps 4. & 5. until global minimum of $\Delta\Omega$ is found for the value of $\eta$ set in step 1.
Flow Chart 5  (Diblock Copolymer, DFT-I)

1. Generate reciprocal lattice vectors for structure of interest.

2. Sort reciprocal lattice vectors by magnitude, smallest to largest.

3. Sort vectors with the same magnitude into "shells". (i.e. vectors with the same magnitude related by a symmetry operation of the reciprocal lattice are in the same shell)

4. Within each shell retain $k_n$ and discard $-k_n$ for sums in equation (2.17).

5. Set the value of $\eta$.

6. Input initial value for $R_g/D$.

7. Minimize $\Delta \Omega$ in equation (2.17) with respect to $\{a_n\}$ & $\{b_n\}$ using Newton's Method.

8. Increment $R_g/D$ and repeat steps 6. & 7. until global minimum of $\Delta \Omega$ is found for the value of $\eta$ set in step 5.
Flow Chart 6  (Diblock Copolymer, DFT-II)

1. Generate reciprocal lattice vectors for structure of interest.

2. Sort reciprocal lattice vectors by magnitude, smallest to largest.

3. Sort vectors with the same magnitude into "shells". (i.e. vectors with the same magnitude related by a symmetry operation of the reciprocal lattice are in the same shell)

4. Within each shell retain $k_n$ and discard $-k_n$ for sums in equation (2.17).

5. Input initial value of $R_g/D$.

6. Minimize $\Delta \Omega$ in equation (2.29) with respect to $\{a_n\}$ & $\{b_n\}$ using Newton's Method.

7. Increment $R_g/D$ and repeat steps 5. & 6. until the global minimum of $\Delta \Omega$ is found.
APPENDIX C

TABLES OF RECIPROCAL LATTICE VECTORS FOR
BODY-CENTERED-CUBIC SPHERES AND
HEXAGONAL CYLINDERS

Table C.1 The reciprocal lattice vectors multiplied by \( \frac{a}{2\pi} \) for the hexagonal cylinders morphology. The components of one vector \((k_x, k_y)\) in each shell is provided along with the degeneracy of that shell. 24 shells of vectors are represented.

<table>
<thead>
<tr>
<th>Shell</th>
<th>((a/2\pi)*k_x)</th>
<th>((a/2\pi)*k_y)</th>
<th>number of vectors in shell</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.577</td>
<td>1.000</td>
<td>4</td>
</tr>
<tr>
<td>2</td>
<td>1.155</td>
<td>0.000</td>
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<tr>
<td>3</td>
<td>0.000</td>
<td>2.000</td>
<td>2</td>
</tr>
<tr>
<td>4</td>
<td>1.732</td>
<td>1.000</td>
<td>4</td>
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<td>2.000</td>
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<td>7</td>
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<td>12</td>
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<td>13</td>
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<td>2.000</td>
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<td>17</td>
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<td>5.196</td>
<td>1.000</td>
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<tr>
<td>24</td>
<td>1.732</td>
<td>5.000</td>
<td>4</td>
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</table>
Table C.2  The reciprocal lattice vectors multiplied by $a/2\pi$ for the body-centered-cubic spheres morphology. The components of one vector $(k_x, k_y, k_z)$ in each shell is provided along with the degeneracy of that shell. 21 shells of vectors are represented.

<table>
<thead>
<tr>
<th>shell</th>
<th>$(a/2\pi)*k_x$</th>
<th>$(a/2\pi)*k_y$</th>
<th>$(a/2\pi)*k_z$</th>
<th>number of vectors in shell</th>
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<tbody>
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<td>1.000</td>
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<td>2.000</td>
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</tr>
<tr>
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<td>1.000</td>
<td>1.000</td>
<td>2.000</td>
<td>24</td>
</tr>
<tr>
<td>4</td>
<td>2.000</td>
<td>0.000</td>
<td>2.000</td>
<td>12</td>
</tr>
<tr>
<td>5</td>
<td>0.000</td>
<td>1.000</td>
<td>3.000</td>
<td>24</td>
</tr>
<tr>
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<td>2.000</td>
<td>2.000</td>
<td>2.000</td>
<td>8</td>
</tr>
<tr>
<td>7</td>
<td>1.000</td>
<td>2.000</td>
<td>3.000</td>
<td>48</td>
</tr>
<tr>
<td>8</td>
<td>0.000</td>
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<td>4.000</td>
<td>6</td>
</tr>
<tr>
<td>9</td>
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<td>0.000</td>
<td>3.000</td>
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</tr>
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</tr>
<tr>
<td>11</td>
<td>0.000</td>
<td>2.000</td>
<td>4.000</td>
<td>24</td>
</tr>
<tr>
<td>12</td>
<td>3.000</td>
<td>3.000</td>
<td>2.000</td>
<td>24</td>
</tr>
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<td>13</td>
<td>2.000</td>
<td>2.000</td>
<td>4.000</td>
<td>24</td>
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<tr>
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<td>1.000</td>
<td>3.000</td>
<td>4.000</td>
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</tr>
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<td>21</td>
<td>4.000</td>
<td>4.000</td>
<td>2.000</td>
<td>24</td>
</tr>
</tbody>
</table>
APPENDIX D

TABLES OF ORDER PARAMETERS

Table D.1. Order-disorder transitions to BCC spheres calculated using density functional theory. $\chi N_S$ is the spinodal calculated using the theory of Leibler, $Rg/a$ is the spacing of the BCC spheres at the transition, and $\Delta w$ is the value of the change in the dimensionless grand potential, $\beta N \Delta \Omega / \rho dV$, at the transition. All results are for $\eta=0$. For the compositions marked with an asterisk, the calculations were performed using the density functional theory developed in Section 2.2 (DFT-I). The remainder of the results was calculated using DFT-II of Section 2.4.

<table>
<thead>
<tr>
<th>f</th>
<th>$\chi N_{\text{trans}}$</th>
<th>$\chi N_S$</th>
<th>Rg/a</th>
<th>$\Delta w$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.495</td>
<td>10.4967</td>
<td>10.4949</td>
<td>0.2190</td>
<td>-1.12e-9</td>
</tr>
<tr>
<td>0.490</td>
<td>10.5021</td>
<td>10.5029</td>
<td>0.2190</td>
<td>-7.66e-9</td>
</tr>
<tr>
<td>0.485</td>
<td>10.5111</td>
<td>10.5129</td>
<td>0.2190</td>
<td>-2.80e-8</td>
</tr>
<tr>
<td>0.480</td>
<td>10.5237</td>
<td>10.5269</td>
<td>0.2190</td>
<td>-8.00e-8</td>
</tr>
<tr>
<td>0.475</td>
<td>10.5400</td>
<td>10.5450</td>
<td>0.2190</td>
<td></td>
</tr>
<tr>
<td>0.470</td>
<td>10.5600</td>
<td>10.5670</td>
<td>0.2190</td>
<td>-4.73e-7</td>
</tr>
<tr>
<td>0.465</td>
<td>10.5830</td>
<td>10.5940</td>
<td>0.2190</td>
<td>-7.52e-8</td>
</tr>
<tr>
<td>0.460</td>
<td>10.6110</td>
<td>10.6240</td>
<td>0.2194</td>
<td>-1.30e-6</td>
</tr>
<tr>
<td>0.450</td>
<td>10.6760</td>
<td>10.6980</td>
<td>0.2194</td>
<td>-6.63e-7</td>
</tr>
<tr>
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<td>10.7570</td>
<td>10.7890</td>
<td>0.2194</td>
<td>-1.04e-6</td>
</tr>
<tr>
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<td>10.9670</td>
<td>11.0270</td>
<td>0.2198</td>
<td>-1.24e-6</td>
</tr>
<tr>
<td>0.400</td>
<td>11.2500</td>
<td>11.3440</td>
<td>0.2202</td>
<td>-3.65e-5</td>
</tr>
<tr>
<td>0.380</td>
<td>11.6100</td>
<td>11.7510</td>
<td>0.2206</td>
<td>-1.11e-4</td>
</tr>
<tr>
<td>0.350</td>
<td>12.3000</td>
<td>12.5620</td>
<td>0.2210</td>
<td>-1.79e-5</td>
</tr>
<tr>
<td>0.300</td>
<td>14.0450</td>
<td>14.6350</td>
<td>0.2214</td>
<td>-1.19e-4</td>
</tr>
<tr>
<td>0.250*</td>
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<td>18.2000</td>
<td>0.2222</td>
<td>-7.738e-4</td>
</tr>
<tr>
<td>0.215*</td>
<td>21.5</td>
<td>23.325</td>
<td>0.2238</td>
<td>-3.0e-3</td>
</tr>
<tr>
<td>0.400*</td>
<td>11.24</td>
<td>11.344</td>
<td>0.2202</td>
<td>-6.0e-5</td>
</tr>
</tbody>
</table>
Table D.2(a) Order parameters \( \{a_n\} \) for the first three shells of the BBC spheres at the order-disorder transition corresponding to the data in Table D.1. For the compositions marked with an asterisk, the calculations were performed using the density functional theory developed in Section 2.2 (DFT-I). The remainder of the results was calculated using DFT-II of Section 2.4.

<table>
<thead>
<tr>
<th>f</th>
<th>( a_1 )</th>
<th>( a_2 )</th>
<th>( a_3 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.495</td>
<td>3.09e-3</td>
<td>7.50e-6</td>
<td>8.90e-8</td>
</tr>
<tr>
<td>0.490</td>
<td>5.77e-3</td>
<td>5.45e-6</td>
<td>6.80e-7</td>
</tr>
<tr>
<td>0.485</td>
<td>9.09e-3</td>
<td>1.96e-5</td>
<td>2.39e-6</td>
</tr>
<tr>
<td>0.470</td>
<td>1.84e-2</td>
<td>1.59e-4</td>
<td>1.93e-5</td>
</tr>
<tr>
<td>0.465</td>
<td>1.87e-2</td>
<td>2.10e-4</td>
<td>2.83e-5</td>
</tr>
<tr>
<td>0.460</td>
<td>2.25e-2</td>
<td>3.36e-4</td>
<td>4.40e-5</td>
</tr>
<tr>
<td>0.450</td>
<td>2.69e-2</td>
<td>6.09e-4</td>
<td>8.33e-5</td>
</tr>
<tr>
<td>0.440</td>
<td>3.21e-2</td>
<td>1.04e-3</td>
<td>1.45e-4</td>
</tr>
<tr>
<td>0.420</td>
<td>4.22e-2</td>
<td>2.37e-3</td>
<td>3.45e-4</td>
</tr>
<tr>
<td>0.400</td>
<td>5.40e-2</td>
<td>4.73e-3</td>
<td>7.08e-4</td>
</tr>
<tr>
<td>0.380</td>
<td>6.45e-2</td>
<td>7.94e-3</td>
<td>1.25e-3</td>
</tr>
<tr>
<td>0.350</td>
<td>7.46e-2</td>
<td>1.35e-2</td>
<td>2.44e-3</td>
</tr>
<tr>
<td>0.300</td>
<td>9.07e-2</td>
<td>2.60e-2</td>
<td>5.82e-3</td>
</tr>
<tr>
<td>0.250*</td>
<td>4.428e-2</td>
<td>1.248e-2</td>
<td>2.414e-3</td>
</tr>
<tr>
<td>0.215*</td>
<td>4.34e-2</td>
<td>1.32e-2</td>
<td>2.27e-3</td>
</tr>
<tr>
<td>0.400*</td>
<td>3.525e-2</td>
<td>3.071e-3</td>
<td>4.174e-3</td>
</tr>
</tbody>
</table>

Continued, next page
Table D.2(b) Order parameters \( \{a_n\} \) for the 4th, 5th and 6th shells of the BBC spheres at the order-disorder transition corresponding to the data in Table D.1 For the compositions marked with an asterisk, the calculations were performed using the density functional theory developed in Section 2.2 (DFT-I). The remainder of the results was calculated using DFT-II of Section 2.4.

<table>
<thead>
<tr>
<th>( f )</th>
<th>( a_4 )</th>
<th>( a_5 )</th>
<th>( a_6 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.495</td>
<td>1.20e-8</td>
<td>-2.90e-8</td>
<td>-1.50e-8</td>
</tr>
<tr>
<td>0.490</td>
<td>1.09e-7</td>
<td>-1.92e-7</td>
<td>-9.83e-8</td>
</tr>
<tr>
<td>0.485</td>
<td>3.36e-7</td>
<td>-7.50e-7</td>
<td>-3.85e-7</td>
</tr>
<tr>
<td>0.470</td>
<td>2.52e-6</td>
<td>-6.19e-6</td>
<td>-3.22e-6</td>
</tr>
<tr>
<td>0.465</td>
<td>4.90e-6</td>
<td>-6.53e-6</td>
<td>-3.43e-6</td>
</tr>
<tr>
<td>0.460</td>
<td>6.91e-6</td>
<td>-1.13e-5</td>
<td>-5.96e-5</td>
</tr>
<tr>
<td>0.450</td>
<td>1.38e-5</td>
<td>-1.90e-5</td>
<td>-1.03e-5</td>
</tr>
<tr>
<td>0.440</td>
<td>2.34e-5</td>
<td>-3.20e-5</td>
<td>-1.78e-5</td>
</tr>
<tr>
<td>0.420</td>
<td>5.27e-5</td>
<td>-7.05e-5</td>
<td>-4.17e-5</td>
</tr>
<tr>
<td>0.400</td>
<td>9.03e-5</td>
<td>-1.45e-4</td>
<td>-9.33e-5</td>
</tr>
<tr>
<td>0.380</td>
<td>1.38e-4</td>
<td>-2.34e-4</td>
<td>-1.71e-4</td>
</tr>
<tr>
<td>0.350</td>
<td>3.02e-4</td>
<td>-3.34e-4</td>
<td>-2.90e-4</td>
</tr>
<tr>
<td>0.300</td>
<td>8.16e-4</td>
<td>-4.76e-4</td>
<td>-6.62e-4</td>
</tr>
<tr>
<td>0.250*</td>
<td>5.097e-5</td>
<td>-4.66e-4</td>
<td>-4.86e-4</td>
</tr>
<tr>
<td>0.215*</td>
<td>-3.69e-4</td>
<td>-8.10e-4</td>
<td>-7.7e-4</td>
</tr>
<tr>
<td>0.400*</td>
<td>2.467e-6</td>
<td>-1.207e-4</td>
<td>-7.6e-5</td>
</tr>
</tbody>
</table>

Table D.3 Order-disorder transitions to lamellae calculated using DFT-II developed in Section 2.4. \( \chi N_S \) is the spinodial calculated using the theory of Leibler, \( Rg/D \) is the spacing of the lamellae at the transition, and \( \sigma_0/D \) characterizes the breadth of the interface. All results are for \( \eta=0 \).

<table>
<thead>
<tr>
<th>( f )</th>
<th>( \chi^{N_{\text{trans}}} )</th>
<th>( \chi^{N_S} )</th>
<th>( Rg/D )</th>
<th>( \sigma_0/D )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.50000</td>
<td>10.4949</td>
<td>10.4949</td>
<td>0.3096</td>
<td>0.52426</td>
</tr>
<tr>
<td>0.49975</td>
<td>10.4949</td>
<td>10.4949</td>
<td>0.3096</td>
<td>0.52843</td>
</tr>
<tr>
<td>0.49970</td>
<td>10.4949</td>
<td>10.4949</td>
<td>0.3096</td>
<td>0.53051</td>
</tr>
</tbody>
</table>
Table D.4  Order-disorder transitions to hexagonal cylinders calculated using DFT-II developed in Section 2.4. $\chi_{N_s}$ is the spinodal calculated using the theory of Leibler, $R_g/a$ is the spacing of the cylinders at the transition, and $\Delta w$ is the value of the dimensionless grand potential change, $\beta N \Delta \Omega / \rho d V$, at the transition. All results are for $\eta$.

<table>
<thead>
<tr>
<th>$f$</th>
<th>$\chi_{N_{trans}}$</th>
<th>$\chi_{N_s}$</th>
<th>$R_g/a$</th>
<th>$\Delta w$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.4996</td>
<td>10.4949</td>
<td>10.4949</td>
<td>0.2682</td>
<td>-2.59\times 10^{-11}</td>
</tr>
<tr>
<td>0.4995</td>
<td>10.4949</td>
<td>10.4949</td>
<td>0.2682</td>
<td>-1.49\times 10^{-11}</td>
</tr>
<tr>
<td>0.4985</td>
<td>10.4951</td>
<td>10.4951</td>
<td>0.2682</td>
<td>-4.75\times 10^{-10}</td>
</tr>
<tr>
<td>0.4975</td>
<td>10.4954</td>
<td>10.4954</td>
<td>0.2682</td>
<td>-9.02\times 10^{-10}</td>
</tr>
</tbody>
</table>

Table D.5  Transitions from hexagonal cylinders to lamellae determined using density functional theory. $R_g/D$ is the spacing of the lamellae at the transition and $\sigma_0/D$ characterizes the breadth of the lamellae interface. $R_g/a$ is the spacing of the cylinders at the transition, and $\Delta w$ is the value of the dimensionless grand potential change, $\beta N \Delta \Omega / \rho d V$, at the transition. For the compositions marked with an asterisk, the calculations were performed using the density functional theory developed in Section 2.2 (DFT-I). The remainder of the results was calculated using DFT-II of Section 2.4.

<table>
<thead>
<tr>
<th>$f$</th>
<th>$\chi_{N_{trans}}$</th>
<th>$R_g/D$</th>
<th>$\sigma_0/D$</th>
<th>$R_g/a$</th>
<th>$\Delta w$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.4996</td>
<td>10.4949</td>
<td>0.3096</td>
<td>0.5367</td>
<td>0.2682</td>
<td>-7.761\times 10^{-10}</td>
</tr>
<tr>
<td>0.4995</td>
<td>10.4950</td>
<td>0.3096</td>
<td>0.4927</td>
<td>0.2682</td>
<td>-2.651\times 10^{-8}</td>
</tr>
<tr>
<td>0.4985</td>
<td>10.4957</td>
<td>0.3096</td>
<td>0.4451</td>
<td>0.2682</td>
<td>-1.4654\times 10^{-7}</td>
</tr>
<tr>
<td>0.4975</td>
<td>10.4969</td>
<td>0.3096</td>
<td>0.4201</td>
<td>0.2682</td>
<td>-2.343\times 10^{-6}</td>
</tr>
<tr>
<td>0.4950</td>
<td>10.503</td>
<td>0.3096</td>
<td>0.3760</td>
<td>0.2682</td>
<td>-2.759\times 10^{-5}</td>
</tr>
<tr>
<td>0.4900</td>
<td>10.524</td>
<td>0.3096</td>
<td>0.3321</td>
<td>0.2682</td>
<td>-1.411\times 10^{-4}</td>
</tr>
<tr>
<td>0.4850</td>
<td>10.561</td>
<td>0.3096</td>
<td>0.2998</td>
<td>0.2682</td>
<td>-4.535\times 10^{-4}</td>
</tr>
<tr>
<td>0.4800</td>
<td>10.614</td>
<td>0.3096</td>
<td>0.2746</td>
<td>0.2682</td>
<td>-1.411\times 10^{-4}</td>
</tr>
<tr>
<td>0.450*</td>
<td>11.800</td>
<td>0.3096</td>
<td>0.14927</td>
<td>0.2678</td>
<td>-5.188\times 10^{-2}</td>
</tr>
<tr>
<td>0.420</td>
<td>13.00</td>
<td>0.3072</td>
<td>0.12517</td>
<td>0.2646</td>
<td>-1.278\times 10^{-1}</td>
</tr>
<tr>
<td>0.40</td>
<td>15.6</td>
<td>0.2970</td>
<td>0.09751</td>
<td>0.2566</td>
<td>-4.07\times 10^{-1}</td>
</tr>
<tr>
<td>0.420*</td>
<td>12.6</td>
<td>0.3180</td>
<td>0.1680</td>
<td>0.2654</td>
<td>-4.647\times 10^{-2}</td>
</tr>
</tbody>
</table>
Table D.6 Transitions from BCC spheres to hexagonal cylinders using density functional theory. \((Rg/a)_{\text{sph}}\) is the spacing of the BCC spheres at the transition. \((Rg/a)_{\text{cyl}}\) is the spacing of the cylinders at the transition, and \(\Delta w\) is the value of the change in the dimensionless grand potential, \(\beta N\Delta \Omega/\rho_d V\), at the transition. For the compositions marked with an asterisk, the calculations were performed using the density functional theory developed in Section 2.2 (DFT-I). The remainder of the results was calculated using DFT-II of Section 2.4.

<table>
<thead>
<tr>
<th>(f)</th>
<th>(\chi N_{\text{trans}})</th>
<th>((Rg/a)_{\text{cyl}})</th>
<th>((Rg/a)_{\text{sph}})</th>
<th>(\Delta w)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.35</td>
<td>12.81</td>
<td>0.2714</td>
<td>0.2210</td>
<td>-1.584e-2</td>
</tr>
<tr>
<td>0.40</td>
<td>11.43</td>
<td>0.2698</td>
<td>0.2202</td>
<td>-2.982e-3</td>
</tr>
<tr>
<td>0.25*</td>
<td>18.60</td>
<td>0.2796</td>
<td>0.2222</td>
<td>-1.1024e-2</td>
</tr>
<tr>
<td>0.40*</td>
<td>11.41</td>
<td>0.2698</td>
<td>0.2202</td>
<td>-1.400e-3</td>
</tr>
</tbody>
</table>
Table D.7  Equilibrium values of the variational parameters $R_g/D$ and $\sigma_0/D$ for the lamellar morphology calculated using the density functional theory developed in Section 2.2 (DFT-I) with $f=0.42$ and $\eta=0$. $\Delta w$ refers to the value of $\beta N \Delta \Omega/\rho_d V$.

<table>
<thead>
<tr>
<th>$\chi N$</th>
<th>$R_g/D$</th>
<th>$\sigma_0/D$</th>
<th>$\Delta w$</th>
</tr>
</thead>
<tbody>
<tr>
<td>11.3</td>
<td>0.3108</td>
<td>0.27380</td>
<td>-0.13407636e-2</td>
</tr>
<tr>
<td>11.6</td>
<td>0.3108</td>
<td>0.23631</td>
<td>-0.059776e-2</td>
</tr>
<tr>
<td>11.9</td>
<td>0.3108</td>
<td>0.21184</td>
<td>-0.13949143e-2</td>
</tr>
<tr>
<td>12.2</td>
<td>0.3108</td>
<td>0.19276</td>
<td>-0.2537852e-1</td>
</tr>
<tr>
<td>12.5</td>
<td>0.3108</td>
<td>0.17668</td>
<td>-0.40287293e-1</td>
</tr>
<tr>
<td>12.8</td>
<td>0.3104</td>
<td>0.16252</td>
<td>-0.5869638e-1</td>
</tr>
<tr>
<td>13.1</td>
<td>0.3096</td>
<td>0.14976</td>
<td>-0.80596379e-1</td>
</tr>
<tr>
<td>13.4</td>
<td>0.3092</td>
<td>0.13826</td>
<td>-0.10592265</td>
</tr>
<tr>
<td>13.7</td>
<td>0.3080</td>
<td>0.12799</td>
<td>-0.13451697</td>
</tr>
<tr>
<td>14.0</td>
<td>0.3072</td>
<td>0.11916</td>
<td>-0.16610214</td>
</tr>
<tr>
<td>16.0</td>
<td>0.2992</td>
<td>0.86665e-1</td>
<td>-0.4278724</td>
</tr>
<tr>
<td>18.0</td>
<td>0.2916</td>
<td>0.72114e-1</td>
<td>-0.73741298</td>
</tr>
<tr>
<td>20.0</td>
<td>0.2848</td>
<td>0.62712e-1</td>
<td>-0.10731037e+1</td>
</tr>
<tr>
<td>22.0</td>
<td>0.2784</td>
<td>0.55792e-1</td>
<td>-0.14269679e+1</td>
</tr>
<tr>
<td>24.0</td>
<td>0.2728</td>
<td>0.50494e-1</td>
<td>-0.17945059e+1</td>
</tr>
<tr>
<td>26.0</td>
<td>0.2676</td>
<td>0.46262e-1</td>
<td>-0.21727326e+1</td>
</tr>
<tr>
<td>28.0</td>
<td>0.2628</td>
<td>0.42797e-1</td>
<td>-0.25595429e+1</td>
</tr>
<tr>
<td>30.0</td>
<td>0.2588</td>
<td>0.39967e-1</td>
<td>-0.29534114e+1</td>
</tr>
<tr>
<td>32.0</td>
<td>0.2552</td>
<td>0.37577e-1</td>
<td>-0.33531912e+1</td>
</tr>
</tbody>
</table>
APPENDIX E

FLOW CHARTS OF POLYELECTROLYTE ELECTROPHORESIS COMPUTER PROGRAMS

Flow Chart 1  (Electrophoresis in a Random Medium)

1. Generate the random medium according to the random site percolation algorithm [Stauffer, 1985].

2. Generate the initial configuration for a polyelectrolyte with N segments within the random medium.

3. Turn on the electric field. The direction of the electric field will be taken to be along the x-direction.

4. Choose one of the N beads at random and execute a "kink-jump" [Baumgartner, 1984].

5a. Check for violations of the excluded volume constraint between the segment moved and the random medium. If the excluded volume constraint is violated, return the segment to its original position and count this as the "new" configuration.

5b. For bead moves that do not violate the excluded volume constraint with the random medium, perform the Metropolis test as described in Section 6.2.

6. Repeat steps 4 through 5b until N "kink-jumps" have been completed. N "kink-jumps" equal 1 Monte Carlo step(ms).

7. Repeat steps 4 through 6 until the pre-selected "warm-up" time has been completed.
8. Perform steps 4 through 6 until 100 Monte Carlo steps are completed. (1 Monte Carlo time (mt) = 100ms)

9. Repeat step 8, recording relevant data such as the position of the center of mass of the polymer, $\mathbf{R}_{\text{cm}}$, the radius of gyration of the chain, $R_g$, and the $x$-component of end-to-end distance of the polymer chain, $R_x$, at pre-determined intervals of Monte Carlo time (mt).
BIBLIOGRAPHY


Baus, M.; Colot, J.L., Molecular Physics, 55, 653 (1985).


Melenkevitz and Muthukumar (unpublished results, 1989).


