INTEGRAL EQUATION METHODS IN MACROMOLECULAR
SCIENCE: SELECTED APPLICATIONS

by

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<td>$R_g$</td>
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<td>Length</td>
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<tr>
<td>$\rho$, $\rho_m$</td>
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<td>$\rho^*_m$</td>
<td>Semidilute overlap concentration</td>
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<td>$\sigma$</td>
<td>Bond length or statistical segment length</td>
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<td>Isothermal compressibility</td>
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Abstract


An integral equation approach within the framework of the Polymer Reference Interaction Site Model (PRISM) is applied to two problems of interest. We investigate geometrical percolation in (i) one-component systems of linear homopolymers with different degrees of flexibility, as well as (ii) athermal mixtures of semiflexible and rod-like polymers. The volume fraction at the percolation threshold is shown to depend strongly on macromolecular architecture and dimensions. Attractive inter-segmental interactions are included in our treatment of flexible polymers, and are shown to have a pronounced effect on the threshold volume fraction in the vicinity of the theta temperature. The percolation threshold for rod-like particles dispersed in a medium of flexible polymers is investigated as a function of the particle aspect ratio. The dependence of critical volume fraction on rod aspect ratio is strikingly similar to that found for the analogous one component model. The shifts in spinodal boundaries and critical temperatures and concentrations in polymer solutions and blends subject to shear flow constitute the second problem that is investigated. For one-component linear flexible polymer solutions, it is shown that accounting for changes in the cohesive energy arising from flow-induced coil deformation may lead to non-monotonic shifts in the cloud point as a function of strain rate. For two-component homopolymer blends, the direct and pair correlation functions are calculated perturbatively in powers of the eccentricity of the radius-of-gyration tensors. Inclusion of the free energy due to chain extension, as well as modifications to the direct correlation functions to first order in the coil eccentricities, are found in most instances to enhance the blend miscibility.

Keywords: integral equations, percolation, shear flow, flexible coils, rigid rods

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CHAPTER I:

Introduction
I.1 Introduction and Overview

“The science of macromolecules has developed from primitive beginnings to a flourishing field of investigative activities within the comparatively brief span of some forty years.” I would like to open my dissertation with Flory’s words, taken from his Nobel Prize acceptance speech in 1974. As an outstanding pioneer in polymer science, P. J. Flory developed the fundamental, classical theories for the structure and thermodynamics of polymeric materials. Our understanding of the equilibrium properties of polymer solutions, melts, and alloys has evolved greatly since that time. The original incompressible lattice-based models1 proposed by Flory to describe polymer solutions and blends have been generalized to include vacancies2, making possible a treatment of compressibility and equation-of-state related questions. Continuous space theories, which avoid the expedient of assuming that the polymer segments occupy sites on a lattice, include approaches based on the Born-Green hierarchy of equations3, field theories4, as well as generalizations of the integral equation theory for small molecule liquids. The Polymer Reference Interaction Site Model (PRISM), an integral equation theory, was developed by K. S. Schweizer, J. G. Curro and collaborators5 in 1987 and will be employed in the present work in two areas of interest. One such area is the phenomenon of geometric percolation in polymeric fluids and mixtures. Another area is the behavior of polymer solutions and blends under shear flow, where substantial flow-induced shifts in the phase diagram have been observed.
This chapter aims to introduce the fundamental concepts and methodologies employed subsequently in this work. Very generic and basic concepts regarding those aspects of the physical chemistry of polymers most relevant to this work will be introduced in Sec. I.1. The modern theory of liquids, on which the PRISM methodology is based, is described in Sec. I.2. Details concerning the generalization of liquid state theory to macromolecules are presented in Sec. I.3. The work in the two areas of interest will be outlined in Sections I.4 and I.5, respectively.

I.1.1 The Basic Concepts

Polymers are a very important, and widely used, class of materials. The words “poly” and “mer” refer to “many” and “unit”, respectively. Thus, a polymer is a macromolecule which is made up by the linkage of many identical or similar units (monomers). Examples of naturally occurring polymers include proteins, celluloses, starch, and natural rubber. The first synthetic polymer was produced in the early 1900s. It was not until World War II that the field of synthetic polymers became the fastest growing material industry, owing to their ease of manufacture, good mechanical properties, and lower cost as compared to many alloys or ceramics. The number of monomers in a polymer chain is referred to as the degree of polymerization. Depending on the selection of monomers, polymers can be categorized as being either homopolymers or copolymers. Homopolymers are made up of identical monomers, whereas monomers of two or more distinct chemical structures are linked together to form copolymers. There are several basic
architectural forms adopted by the polymer backbones, e.g. linear, branched, comb-shaped, or star-shaped. This work will focus exclusively on linear homopolymers.

The reader can crudely picture a polymer chain backbone as a long piece of string of variable flexibility. The rigidity of a polymer depends on both the chemical structures of the monomers, and on the manner in which they are linked to form a chain. Two extreme cases, namely, highly flexible chains and rigid rod-like chains, are shown schematically in Figure I.1. In some circumstances, a polymer chain is modeled as a thread of beads, not unlike a necklace (Figure I.1). The number of beads in such a visualization is proportional to the degree of polymerization. In both the string and beads models, the detail structures of the monomers are neglected, and attention is limited to the topology of the chain backbone. Since monomers are linked with chemical bonds which possess rotational degrees of freedom, the conformation of an individual polymer chain in solution or in a melt varies from moment to moment, and from chain to chain at a given moment in time. Flexible polymer chains exist as coils with spherical symmetry on average owing to the equilibration among various possible conformations. The dimensions of such a polymer chain can only be characterized in a statistical manner.
Figure I.1  (a) Schematic representations of a flexible polymer chain; (b) schematic representations of a rigid rod.
The dimensions of a polymer chain are frequently characterized by two important parameters, namely, the mean squared end-to-end distance and radius of gyration. To illustrate how these parameters are defined and calculated, we begin with a very simple model. As shown in Figure I.2, a polymer chain can be represented by a set of position vectors representing the locations of the backbone monomers. For a chain with $N+1$ monomers, there are $(N+1)$ position vectors $\{\vec{R}_n\} \equiv (\vec{R}_0 \cdots \vec{R}_N)$, and therefore a set of bond vectors $\{\vec{r}_n\} \equiv (\vec{r}_1 \cdots \vec{r}_N)$, where $\vec{r}_n = \vec{R}_n - \vec{R}_{n-1}$. For a homopolymer, each vector is of equal length $\sigma$ and may point in any direction. The end-to-end vector is defined by

$$\vec{R}_{EE} = \vec{R}_N - \vec{R}_0 = \sum_{n=1}^{N} \vec{r}_n.$$  \hfill (1)

The mean squared end-to-end distance $\langle R_{EE}^2 \rangle$ is then given by

$$\langle R_{EE}^2 \rangle = \left\langle \left( \sum_{n=1}^{N} \vec{r}_n \right) \left( \sum_{m=1}^{N} \vec{r}_m \right) \right\rangle$$

$$= \sum_{n,m=1}^{N} \langle \vec{r}_n \vec{r}_m \rangle$$

$$= \sum_{n=1}^{N} \langle \vec{r}_n \vec{r}_n \rangle + 2 \sum_{n>m}^{N} \langle \vec{r}_n \vec{r}_m \rangle$$

$$= N\sigma^2 + 2 \sum_{n>m}^{N} \langle \vec{r}_n \vec{r}_m \rangle.$$  \hfill (2)
Figure I.2  Schematic representation of a simple model for a linear homopolymer. This polymer chain is represented by a set of $N+1$ position vectors $\{\vec{R}_n\} \equiv (\vec{R}_0 \ldots \vec{R}_N)$ and $N$ bond vectors $\{\vec{r}_n\} \equiv (\vec{r}_1 \ldots \vec{r}_N)$, where $\vec{r}_n = \vec{R}_n - \vec{R}_{n-1}$. The bond vectors have equal length $\sigma$. $R_{EE}$ is the end-to-end vector.
The mean squared end-to-end distance cannot usually be measured directly in experiments. By contrast, the radius of gyration is an experimentally measurable quantity. It measures the average squared distance of the monomers from the center of gravity of the chain, and is defined by

\[ R_g^2 = \frac{1}{N} \sum_{n=1}^{N} \left\langle (\bar{R}_n - \bar{R}_G)^2 \right\rangle \]  

(3)

where the position of the center of mass is given by

\[ \bar{R}_G = \frac{1}{N} \sum_{i=1}^{N} \bar{R}_i \]  

(4)

Equations (3) and (4) give

\[ R_g^2 = \frac{1}{2N^2} \sum_{n=1}^{N} \sum_{m=1}^{N} \left\langle (\bar{R}_n - \bar{R}_m)^2 \right\rangle \]  

(5)

The size and conformation of a polymer chain depend partly on the interactions between segments of the chain. The finite volume of the segments limits the accessible orientations of neighboring segments, and hence affects the size of the chain. This repulsive, steric, interaction, which has the net effect of increasing the coil dimensions, is referred to as the excluded volume interaction. Note that our use of the term “neighboring segments” includes both segments which are adjacent in terms of position along the backbone, as well as those which are in close spatial proximity. The nature of the interaction between the polymer and the solvent (for polymer solutions) also has substantial effects on the dimensions of the polymer chain. In a good solvent, the polymer is easily dissolved and spread out (swollen) by the intra-chain excluded volume interactions, while in a poor solvent the polymer is not
dissolved and its dimensions are smaller. For a given temperature, there may exist solvents whose effects on the polymer precisely counteract the excluded volume interactions. Such solvents have no influence on the size of the polymer, and such a solvent and temperature are referred to as \( \theta \) solvent and \( \theta \) temperature, respectively.

As the concentration of the polymer solution increases, the polymer chains start to overlap or entangle with each other like strands of spaghetti. Three concentration regimes are usually identified: dilute, semidilute, and concentrated. The dilute regime corresponds to concentrations low enough that individual chains can be treated as effectively independent, non-interacting coils. The concentration at which the polymer chains just begin to overlap is defined as the semidilute crossover concentration. The existence of a semidilute crossover concentration is unique to polymer solutions, and has no analog in small molecule liquids. For a polymer chain with \( N \) segments and radius of gyration \( R_g \), the semidilute crossover concentration \( \rho^* \) in terms of the number of segments per unit volume can be estimated by

\[
\rho^* = \frac{N}{\frac{4}{3} R_g^3}.
\]

The limiting state of a concentrated polymer solution is the polymer melt, which is completely devoid of all solvent whatsoever. This is an important state in the polymer industry as most polymer products are processed in this state. In a polymer melt, the intramolecular excluded volume effects are balanced by the intermolecular excluded volume interactions, with the net result that the polymer melt serves as a \( \theta \) solvent for itself.
I.1.2 Flexible Gaussian Chains

In Section I.1.1, we set up a schematic model for a linear homopolymer to define the mean squared end-to-end distance and radius of gyration of a polymer chain. The complexity of generalizations of this model depend on the extent to which restrictions on bond rotational freedom are taken into account, and on whether or not the excluded volume effects are accounted for. The simplest model is the Gaussian chain corresponding to a random walk without excluded volume effects, also referred as to an ideal chain. The bond vectors in a Gaussian chain obey a Gaussian probability distribution

\[ p(\vec{r}) = \left( \frac{3}{2\pi\sigma^2} \right)^{3/2} \exp \left( -\frac{3\vec{r}^2}{2\sigma^2} \right). \]  

(7)

As all the bond vectors are distributed in space randomly and independently, the second term \( \langle \vec{r}_n \cdot \vec{r}_m \rangle \) in Eq. (2) is zero. The mean squared end-to-end distance of a Gaussian chain therefore equals \( \langle R_{EE}^2 \rangle = N\sigma^2 \). If \( |n - m| \) is large enough, \( \vec{R}_n - \vec{R}_m \) obeys a Gaussian distribution as well, which leads to

\[ \langle (\vec{R}_n - \vec{R}_m)^2 \rangle = |n - m|\sigma^2. \]  

(8)

With Eq. (5) and (8), the radius of gyration of a Gaussian chain can be calculated easily

\[ R_g^2 = \frac{1}{6} N\sigma^2. \]  

(9)
1.2 Liquid State Theory

1.2.1 Radial Distribution Function

The integral equation theory of liquids, pioneered by Kirkwood in the 1930s, has been developed to a high level of sophistication over the past seventy years\(^6\). This theory was originally developed for monatomic and small molecule fluids, and provides a vehicle for calculating inter-particle pair correlation functions when the interaction potentials are specified. The pair correlation function, also referred to as the radial distribution function, describes the inter-particle packing and degree of correlation. The thermodynamics of the liquid can be described based on a complete knowledge of the radial distribution function.

For illustrating the physical significance of the radial distribution function, we consider the two simple cases of a monatomic and homonuclear diatomic liquid. For a simple monatomic liquid, the average density \( \rho(r) \) at a distance \( r \) from a given particle located at the origin is defined as

\[
\rho(r) = \rho g(r),
\]

(10)

where \( \rho \) is the site number density defined as the number of particles (atoms in this case) per unit volume, i.e. \( \rho = N/V \), and \( g(r) \) is the corresponding radial distribution function for the system.

For a diatomic liquid, \( \rho g(r) \) is defined as the average density of atoms at position \( r \) given that an atom which is part of a different molecule is at the origin. In this sense, \( g(r) \) is also called the inter-molecular pair distribution function, as opposed
to the intra-molecular pair correlation function where the pair of atoms is within the same molecule. Intra-molecular pair correlation functions will be introduced later.

Examples of the radial distribution functions for the above mentioned cases are shown in Figure I.3. The radial distribution function \( g(r) \) satisfies two readily understandable limiting behaviors: (i) \( g(r) \) should go to 1 at large \( r \) as the atom at the origin has little correlation with atoms at large \( r \); (ii) \( g(r) \) must be zero at very small separations \( r \), because two particles of finite volume cannot occupy the same space, a manifestation of the excluded volume effect. The only characteristic length scale for a monatomic liquid is the van der Waals diameter, \( \sigma \). In a dense liquid, it is very likely that the atom at the origin is in contact with other atoms at a distance \( \sigma \), leading to a significant peak in \( g(r) \) at \( r \approx \sigma \). The second peak at \( r \approx 2\sigma \) results from the high probability that the second atom is in contact with other atoms at a distance \( \sigma \).

For the case of a diatomic molecule, there are two characteristic length scales, \( \sigma \) and the chemical bond length \( L \). Each atom in the diatomic liquid is linked to a second atom within the same molecule. The coupling of the intermolecular and intramolecular packing leads to a shoulder in \( g(r) \) at distance \( r \approx \sigma + L \), besides the peak at \( r \approx \sigma \).
Figure I.3  Radial distribution functions for a dense fluid for an atomic fluid, left, and a homonuclear diatomic fluid, right. $\sigma$ is the van der Waals diameter, and $L$ the chemical bond length. (Ref.7)
Radial distribution functions can be measured experimentally from radiation and neutron scattering. The scattering intensity \( |F(k)|^2 \) produced by the sample at the scattering vector \( k \equiv k_f - k_i \), where \( k_i \) and \( k_f \) are the incident and scattered wave vectors respectively, is proportional to

\[
\langle |F(k)|^2 \rangle \approx \left( \frac{1}{N} \sum_i \sum_j \exp[ik \cdot (\vec{r}_i - \vec{r}_j)] \right) .
\]  

(11)

Equation (11) may be rewritten as:

\[
\left( \frac{1}{N} \sum_i \sum_j \exp[ik \cdot (\vec{r}_i - \vec{r}_j)] \right) \\
= 1 + \left( \sum_i \sum_j \exp[ik \cdot (\vec{r}_i - \vec{r}_j)] \right) \\
= 1 + \int d\vec{r} \rho_g(r) \exp(ik \cdot \vec{r}) \\
= 1 + \int d\vec{r} \rho \{g(r) - 1\} \exp(ik \cdot \vec{r}) + (2\pi)^3 \rho \delta(k) .
\]  

(12)

The \( \delta \)-function in Eq.(12) gives the contribution at zero wave vector. The scattering structure factor at all other \( k \) values is given by

\[
\hat{S}(k) = 1 + \int d\vec{r} \rho \{g(r) - 1\} \exp(ik \cdot \vec{r}) .
\]  

(13)

Eq.(13) introduces a very important function \( h(r) = g(r) - 1 \), which is frequently referred to as the total correlation function. \( \rho h(r) \) may be regarded as the surplus of (local) density \( \rho_g(r) - \rho \). Note the Fourier transform is defined by

\[
\hat{f}(k) = \int d\vec{r} f(\vec{r}) \exp(ik \cdot \vec{r}) \\
\]

\[
f(\vec{r}) = \frac{1}{(2\pi)^3} \int dk \hat{f}(k) \exp(-ik \cdot \vec{r}) .
\]  

(14)
Therefore, \( \hat{S}(k) \) is essentially the Fourier transform of the total correlation function. Eq.(13) can then be written conveniently as

\[
\hat{S}(k) = 1 + \rho \hat{h}(k).
\]  

(15)

The caret “\(^\wedge\)” denotes the Fourier transform function in \( k \) space throughout this thesis.

Given knowledge of the radial distribution function over the entire range of densities and the specific pair potential \( V(r) \), the thermodynamics of the liquid can be obtained through either of two routes:

(i) The free energy route

\[
\frac{A - A_0}{V} = \frac{\rho^2}{2} \int d\vec{r} g^0(\vec{r}) V(\vec{r}),
\]

(16)

where \( A_0 \) is the free energy of an ideal gas, and \( g^0(r) \) is the radial distribution function in the reference state (refer to I.3.3), and:

(ii) The compressibility route

\[
\rho k_B T \kappa_T = \hat{S}(k = 0) = 1 + \rho \int d\vec{r} (g(\vec{r}) - 1),
\]

(17)

where \( \kappa_T \) is the isothermal compressibility.

I.2.2 Ornstein-Zernike Equation

The radial distribution function, an experimentally measurable quantity, can be calculated theoretically within the integral equation approach. A convenient starting point is the Ornstein-Zernike equation:

\[
h(r) = c(r) + \int d\vec{r}' c(\vec{r}') \rho \ h(\vec{r} - \vec{r}').
\]

(18)
From the mathematical point of view, $h(r)$ may be viewed as the convolution of a short range function $c(r)$ and $h(r)$ itself. Equation (18) defines the direct correlation function $c(r)$. One can view the total correlation as being the sum of the direct correlation between two given particles and indirect contributions mediated by the remaining particles in the system. Using the convolution theorem, Eq.(18) can be rewritten as

$$\hat{h}(k) = \hat{c}(k) + \rho \hat{c}(k) \hat{h}(k).$$ \hspace{1cm} (19)

Equation (19) by itself is insufficient for calculating the desired functions $\hat{h}(k)$ or $\hat{c}(k)$, and an additional relationship (known as a “closure relation”) is required. The direct correlation function $c(r)$ is a short-ranged function with roughly the same range as the pair potential. One of the frequently used and relatively simple closure relations for the Ornstein-Zernike equation is the Percus-Yevick approximation:

$$c(r) \simeq [1 - \exp[\beta V(r)]]g(r).$$ \hspace{1cm} (20)

For hard spheres with diameter $d$, Eq.(20) reduces to

$$g(r) = 0 \hspace{1cm} r < d$$

$$c(r) = 0 \hspace{1cm} r > d.$$ \hspace{1cm} (21)

The first condition in Eq.(21) is the exact hard core constraint. The second condition is approximate, and states that $c(r)$ is spatially short ranged. Equation (19) together with the Percus-Yevick closure [Eq.(21)] leads to a nonlinear integral equation for determining the radial distribution function of the monatomic liquid.
I.2.3 Reference Interaction Site Model (RISM)

The liquid state integral equation theory for monatomic liquids was generalized by D. Chandler, H. C. Anderson, and their coworkers in the 1970’s to formulate the Reference Interaction Site Model (RISM) for molecular liquids. In the RISM theory, a molecule is viewed as consisting of several spherically symmetric sites (called interaction site). Unlike a monatomic liquid where each atom is an individual interaction site and a single radial distribution function can specify the structure of the liquid, the intermolecular structure of a liquid of \( M \) molecules is characterized by a matrix of radial distribution function \( g_{\alpha\gamma}(r) \) defined as

\[
\rho^2 g_{\alpha\gamma}(r) = \left\langle \sum_{i \neq j=1}^{M} \delta(\vec{r}_{i}^{\alpha}) \delta(\vec{r} - \vec{r}_{j}^{\gamma}) \right\rangle, \tag{22}
\]

where, \( \rho \) is the number density of molecules and \( \vec{r}_{i}^{\alpha} \) is the position vector of site \( \alpha \) on molecule \( i \). The \( \delta(x) \) function in Eq.(22) is a special kind of distribution function (Dirac delta function), which is infinitely narrow, infinitely tall and sharp at point \( x \) and zero otherwise. Physically, Eq.(22) represents the probability of finding site \( \gamma \) on molecule \( j \) at position \( r \) given that site \( \alpha \) on molecule \( i \) is located at the origin. It is clear from Eq.(22) that \( g_{\alpha\gamma}(r) \) is the pair correlation function for sites \( \alpha \) and \( \gamma \) on different molecules. In molecular liquids, the intramolecular chemical bonds constrain the shape and orientation of the molecule, and hence have strong effects on the intermolecular pair distribution. The key point of RISM is that an intramolecular correlation function is introduced to specify the intramolecular structure. Chandler
and Anderson generalized the Ornstein-Zernike equation for monatomic liquids to molecular liquids as follows\(^\text{7}\)

\[
\rho(r) = \int \int d\vec{r}_1 d\vec{r}_2 \omega(\vec{r}_1 - \vec{r}_2) \left[ \omega(\vec{r}_1) + \rho \omega(\vec{r}_2) \right].
\]

(23)

For molecules consisting of \(N\) sites, \(\rho(r)\), \(\omega(r)\), and \(c(r)\) in Eq.(23) are \(N \times N\) matrices, with matrix elements \(h_{\alpha\beta}(r) = g_{\alpha\beta}(r) - 1\), \(c_{\alpha\beta}(r)\), and \(\omega_{\alpha\beta}(r)\), respectively. The function \(\omega_{\alpha\beta}(r)\) is the intramolecular correlation function, also referred to as the intramolecular structure factor or form factor. Together with a Percus-Yevick type closure for the direct correlation functions in analogy with the monatomic case (or other closure relations), Eq.(23) forms a set of nonlinear integral equations which can by solved numerically. The RISM was applied by Chandler et al.\(^\text{7}\) to diatomic and small polyatomic (e.g., carbon tetrachloride) fluids, and good agreement with computer simulation and scattering experiments was found.

I.3 Polymer Reference Interaction Site Model (PRISM)

I.3.1 Generalization of RISM to Polymers

In 1987, J. G. Curro and K. S. Schweizer\(^\text{5}\) initiated the generalization of the RISM formalism to describe the equilibrium structure and properties of polymers in the bulk and in solution. This theory has come to be known as the Polymer Reference Interaction Site Model (PRISM)\(^\text{9}\). The generalization of RISM to polymers is based on the essential modification of pre-averaging chain end effects, \(i.e.\) treating every
monomer in a chain as being in an environment in which it experiences an identical
density profile of monomers from other molecules as a function of separation.

Consider a one-component polymeric fluid in which each polymer molecule
consists of \( N \) nonequivalent sites (proportional to the degree of polymerization).
When the RISM approach is applied to such a system, the intermolecular radial
distribution function \( g_{\alpha\gamma}(r) \) depends on the specific locations of site \( \alpha \) and site \( \gamma \) on
the polymer chains. Consequently, the matrix equation, Eq.(23), represents a set of
\( N(N+1)/2 \) independent nonlinear integral equations. Since \( N \) is generally of the
order \( 10^2 - 10^5 \) for polymers, this large number of coupled integral equations leads to
an intractable numerical problem. However, an approximation, in which all sites are
assumed to have equivalent interactions would make the correlation functions are
independent of where the sites (monomers) are located along the chain. Such
simplification, known as the equivalent site approximation, pre-average the chain end
effects and transforms the complex, multiple chain problem into a much simpler
single chain problem. The Ornstein-Zernike matrix equation [Eq.(23)] is then reduced
to a single scalar equation and after Fourier transform takes the simple form \(^9\)

\[
\hat{h}(k) = \hat{\omega}^2(k) \hat{c}(k) + \rho_m \hat{\phi}(k) \hat{c}(k) \hat{h}(k),
\]

(24)

where, \( \rho_m \) is the site number density defined as number of sites (monomers) per unit
volume. \( \hat{\phi}(k) \) is the Fourier transform of the intramolecular correlation function, or
the single chain structure factor. The structure factor of flexible chains will be
discussed in Sec. I.3.2. The relationships among these correlation functions are shown
schematically in Fig. I.4. The form factor $\phi(k)$ describes the correlation between sites on the same molecule, while the total correlation function $\hat{h}(k)$ represents the correlation between sites on all the molecules in the fluid taken as a whole. The total correlation comprises of two contributions: the direct correlation between sites on different molecules as specified by the direct correlation function $\phi(k)$, and indirect contributions mediated by the remaining sites in the system.
Figure I.4  Schematic representation of the correlation pathways in a molecular fluid. A thread of beads represents a polymer chain and each bead represents an interaction site. $h$, $c$ and $\omega$ are the total, direct, and intramolecular correlation functions, respectively.
For flexible polymers, the intramolecular structure is, in principle, coupled to the intermolecular packing. In other words, the intramolecular correlation function \( \omega(r) \) and the intermolecular radial distribution function \( g(r) \) depend on each other. The determination of the chain structure specified by \( \omega(r) \) should in principle be treated self-consistently with the fluid organization described by \( g(r) \). Such self-consistent generalizations of PRISM have been developed\(^\text{10}\), but will not be explored in the present work. For the work described in this thesis, the single chain structure, as specified by the form factor, will be presumed to be known in advance, and is treated as an “input” for our calculations. There are a number of situations in which this is an appropriate procedure, notably for polymer melts in which the screening of the excluded volume interactions results in ideal random walk like (Gaussian) chain statistics. The form factor \( \omega(r) \) can then be treated as known \textit{a priori}, which is also the case for perfectly rigid, inflexible, rod-like macromolecules.

**I.3.2 Form Factors**

The form factor of a single polymer chain as calculated with Eq.(25) (see below), is related to the distribution of intramolecular distances. Consider a polymer chain with \( R_n \) \((n=1,2, \ldots, N)\) representing the position vectors of the segments. In analogy with the radial distribution function, we define \( \omega_{nm}(r) \) to be the probability of finding the \( m \)th segment at position \( r \) given that the \( n \)th segment is at the origin:

\[
\omega_{nm}(r) = \sum_{m=1}^{N} \langle \delta(r - (R_m - R_n)) \rangle .
\]  

(25)
The form factor of a single chain is the average of $\omega_{nm}(r)$ over all $n, m$:

$$\omega(r) = \frac{1}{N} \sum_{n,m} \omega_{nm}(r) = \frac{1}{N} \sum_{n=1}^{N} \sum_{m=1}^{N} \langle \delta(r - (R_m - R_n)) \rangle .$$  \hspace{1cm} (26)$$

The Fourier transform of $\omega(r)$ is expressed as

$$\hat{\omega}(k) = \int d\vec{r} e^{i\vec{k} \cdot \vec{r}} \omega(r) = \frac{1}{N} \sum_{n=1}^{N} \sum_{m=1}^{N} \langle \exp[i k \cdot (R_m - R_n)] \rangle .$$  \hspace{1cm} (27)$$

It can be seen from Eq.(27) that $\hat{\omega}(k=0) = N$. Given that for an isotropic fluid, the direction of $R_m - R_n$ is random, Eq. (27) can be rewritten as

$$\hat{\omega}(k) = \frac{1}{N} \sum_{n,m} \left( \frac{\sin(k\|R_m - R_n\|)}{k\|R_m - R_n\|} \right) .$$  \hspace{1cm} (28)$$

With Eq.(27) and the Gaussian distribution function for $R_m - R_n$, the form factor for a Gaussian chain can be shown to be:

$$\hat{\omega}(k) = N f\left(k^2 R_g^2\right) ,$$  \hspace{1cm} (29)$$

where the Debye function $f(x)$ is given by

$$f(x) = \frac{2}{x^2} \left(e^{-x} - 1\right) + x .$$  \hspace{1cm} (30)$$

The Debye function is often approximated by the simple interpolating expression$^{11}$:

$$\hat{\omega}(k) = \frac{N}{1 + k^2 R_g^2 / 2} ,$$  \hspace{1cm} (31)$$

which is in error by less than 15% over the entire range of $k$ vector.

As $|R_m - R_n|$ for rigid rod is simply $|m - n|\sigma$, the form factor of rigid rod can be easily calculated from Eq.(28) numerically. For a simple, atomic, fluid, in which
each particle is represented by a single interaction site, the form factor reduces to a
Dirac delta function in position space, and the PRISM Ornstein-Zernike equation
[Eq.(24)] becomes equivalent to the more familiar expression in Eq.(19).

I.3.3 Closure Approximations

Closure approximations, which are required to solve the Ornstein-Zernike
equation, relate $g(r)$, $c(r)$, and $\omega(r)$ to the intermolecular pair (site-site) potential $V(r)$. Early closures applied within PRSIM were based on those developed successfully in
previous work on atomic fluids. Two such widely used atomic closures are the
Percus-Yervick (PY) closure\(^9\) and the Mean Spherical Approximation (MSA)\(^9\).

For the hard core potential, the PY closure is given by

\begin{align}
g(r) &= 0, \quad r < d \\
c(r) &= 0, \quad r > d,
\end{align}

where $d$ is the hard core diameter. For continuous potentials the PY closure takes the
form

\begin{align}
c(r) &= \{1 - \exp[\beta V(r)]\}g(r),
\end{align}

where $\beta = 1/k_B T$.

The Mean Spherical Approximation (MSA) is given by

\begin{align}
g(r) &= 0, \quad r < d \\
c(r) &= -\beta v(r), \quad r > d
\end{align}

where $v(r)$ is the attractive branch of the pair potential, frequently referred to as an
“attractive tail”. If $v(r) = 0$, the MSA reduces to the hard core PY closure.
The atomic closures, when applied within PRISM theory, were shown to be in qualitative error in addressing the long wavelength concentration fluctuations and the molecular weight dependence of the critical temperature of binary polymer blends. These errors resulted from the failure of the atomic closures to account for the interaction between segments which might be close in space but widely separated along the chain backbone. Molecular closures have been developed to account for the interactions mediated by the chemical bonds, and these approximations are frequently formulated within a perturbative, “reference fluid”-based, approach. In this approach, the repulsive hard core and the “soft” attractive branch of the inter-site potential are treated separately in formulating $c(r)$. The reference state refers to the state where only the purely repulsive interactions are accounted for. The direct correlation function $c(r)$ with the attractive branch of the pair potential accounted for is then modified perturbatively based on the reference (athermal) direct correlation function $c^0(r)$.

The molecular version of the PY closure, referred to as the Reference Molecular Percus-Yevick (R-MPY) closure, is given by

$$
\omega_i \ast c_{ij} \ast \omega_j (r) = \omega_i \ast c^0_{ij} \ast \omega_j (r) + \omega_i \ast \left[1 - \exp(\beta v_{ij})\right] \ast g_{ij} \ast \omega_j (r), \quad r > d_{ij}
$$

(35)

where $c^0_{ij}$ is the reference (athermal) direct correlation function between species $i$ and $j$, and $v_{ij}$ is the attractive pair potential and $d_{ij}$ the hard core diameter. The asterisks denote convolution integrals. At high temperature, $1 - \exp(\beta v_{ij}) \approx -\beta v_{ij}$, and the R-MPY closure given in Eq.(35) reduces to

25
\[ \omega_i \cdot c_{ij} \cdot \omega_j(r) = \omega_i \cdot c_{ij}^0 \cdot \omega_j(r) - \omega_i \cdot \beta v_{ij} \times g_{ij} \cdot \omega_j(r). \quad r > d_{ij} \]  

The high temperature approximation of the R-MPY closure given in Eq.(36) is denoted the R-MPY/HTA.

The molecular version of the MSA closure, the Reference Molecular Mean Spherical Approximation (R-MMSA)\(^{12}\), is given by

\[ \omega_i \cdot c_{ij} \cdot \omega_j(r) = \omega_i \cdot c_{ij}^0 \cdot \omega_j(r) - \omega_i \cdot \beta v_{ij} \cdot \omega_j(r). \quad r > d_{ij} \]  

Comparing the R-MPY/HTA with R-MMSA, one can view the R-MMSA as the R-MPY/HTA closure in the limiting case that \( g(r) = 1 \) everywhere, corresponding to a completely random, uncorrelated, distribution of molecular segments. For an atomic fluid, for which the form factors are Dirac delta functions in position space, the R-MPY/HTA and R-MMSA become equivalent to the usual PY and MSA closures, respectively.

### I.3.4 Thread and String Approximations

The Ornstein-Zernike equation, combined with closure relations and form factors, provides a means to determine the intermolecular structure of polymeric fluids. However, the solution of the integral equations is nontrivial, and in most cases can only be achieved through numerical techniques. The complexity of the model calculation arises from the extent to which local chemical structural details (or degree of coarse graining) are retained, as well as from the requirement of imposing an excluded volume restriction over a site of finite diameter by suitable choice of the direct correlation function. Analytical solutions, which in many instances have proved
to be qualitatively accurate, are possible for some situations by employing the highly coarse-grained thread or string idealizations\(^9\) shown schematically in Fig. I.5.

The thread approximation\(^9,13\) corresponds to taking the limit of hard core diameter \(d \rightarrow 0\), without, however, relaxing the excluded volume constraint in this process. Mathematically, the athermal direct correlation function is replaced by a \(\delta\)-function at the origin in space with an amplitude parameter \(C_0\):

\[
c(r) = C_0 \delta(r) .
\]  
(38)

The hard core constraint is satisfied by requiring that \(g(r) = 0\) for the reference athermal state in the limit that \(r \rightarrow 0\).

Within the string approximation\(^9,13(a)\), the hard core diameter \(d\) is treated as finite. The athermal direct correlation function is again approximated as a spatial \(\delta\)-function. However, the hard core condition is enforced over the region of the site diameter \(d\) in an average sense, by stipulating that:

\[
\int_0^d dr \ r^2 \ g(\ r \ ) = 0 ,
\]  
(39)

Equation (39) provides a method for determining the athermal direct correlation function parameter \(C_0\).

The thread and string approximations were successfully employed in previous investigations to predict the molecular weight dependence of the second and third virial coefficients for polymers in dilute solution, as well as the concentration dependence of the osmotic pressure in semidilute polymer solutions\(^{13(a)}\).
Figure I.5  Schematic representations of the thread (left) and string (right) approximations. The thread and the string represent a single polymer chain, respectively. $d$ is the hard core diameter.
I.4 Percolation

I.4.1 Introduction to Percolation

Percolation refers to the phenomenon by which infinitely extended clusters of “connected” objects or pathways are formed, which span the entire extent of the system under study. The notion of percolation has been widely used to study the phenomena, such as the spread of forest fires, the sol-gel transition in polymerization, the flow of liquid in a porous medium, and metal-insulator transitions in amorphous solids. A simple example of a system for which a percolation transition can be defined is the process of randomly filling sites on a $N \times N$ square lattice. Two occupied neighboring lattice sites are said to be “connected”, and contiguous groups of such “connected” sites are said to form clusters. There are, at first, some small clusters scattered on the lattice. As the fraction of the occupied sites increases and reaches a critical value known as the percolation threshold, the small clusters become connected and an infinitely large, fractal, network is formed which spans the lattice. Figure I.4 shows the incipient infinite cluster formed at the percolation threshold in a computer simulation of a square lattice in two dimensions$^{14}$, and provides a visual example of this phenomenon. Another example of percolation is the conductor-metal transition of a composite material which consists of metallic filler particles dispersed within an insulating matrix. At low volume fractions of the metallic filler, the filler forms many isolated, microscopic, islands and there is no continuous pathway for electron transport. Conducting isthmuses between neighboring islands appear as the volume fraction of filler increases. At the percolation threshold, the islands are
electrically connected and a conducting pathway extending throughout the composite appears abruptly.
Figure I.6  Computer simulation results showing the incipient infinite cluster formed at the percolation threshold. (Ref.14)
There are some similarities between the above two examples. (i) The phenomenon of percolation occurs in random, disordered, systems. In the lattice example, the distribution of the occupied sites is random, though the lattice itself is regular; (ii) the percolation transition occurs at a critical point, referred to as the percolation threshold, and; (iii) properties of the system (e.g., statistics of the cluster size distribution) change dramatically and sharply at the percolation threshold. These similarities are characteristic of the percolation phenomenon and are of both fundamental and practical interest.

The two examples mentioned above differ in that whereas the former involved a regular lattice, the latter system corresponded to a continuous, non-lattice based, spatial arrangement. A large body of work has addressed percolation problems in continuum systems of hard\(^\text{15}\) and adhesive spheres\(^\text{16}\), as well as binary mixtures of such model particles\(^\text{17}\). However, the development of methods for describing network formation in systems of complex, nonspherical, molecules, has received comparatively less attention. The present work will focus on the phenomenon of continuum percolation in macromolecular systems, as studied using an integral equation theory for the liquid state.

### I.4.2 Continuum Percolation in Macromolecular Systems

Interestingly enough, one of the earliest applications of the concept of a percolation transition was towards understanding the critical extent of chemical bond formation (covalent crosslinking of multifunctional monomers) required for the
formation of a network gel from a solution of monomers. The groundbreaking approach adopted by Flory for treating this problem was later identified with solving for the percolation threshold on a so-called Bethe lattice, on which no closed loops of connected sites are geometrically allowed. One of the major reasons why percolation in macromolecular systems is an active and interesting research area is that the formation of physically connected networks of “filler” particles dispersed in polymeric matrices is believed to correlate with dramatic effects on a number of material properties including the shear modulus, toughness and electrical conductivity. The possible role of percolation in the reinforcement of polymer matrices by rod-like cellulose microfibers and nanocrystals, as well as disc-like filler particles, has been strongly suggested in recent investigations. The formation of geometrically percolating networks of filler particles has been identified as a probable mechanism for great enhancements in the toughness of rubber-modified polyamides, polyethylene, and CaCO3 filled high density polyethylene. The existence of a percolation transition in polymer composites was tested by G. Wu et al. through dynamic rheological measurements. Figure I.7 provides an example of how percolation may correlate with a measurable material property. The toughness of High Density PolyEthylene (HDPE) reinforced with rubber particles increases abruptly when a critical average separation between the filler particles is reached, suggesting a role for a percolating network of filler particles connected by “ligaments” of intervening polymer.
Figure I.7  The Izod impact energy of HDPE reinforced with rubber as a function of average ligament thickness. The ligament thickness is defined as the closest distance between the surfaces of two rubber particles. (Ref. 24)
Scaling and renormalization-group approaches have been employed to elucidate universal features of the critical exponents associated with the infinite cluster at the transition$^{27}$. However, in understanding nonuniversal quantities, such as the value of the volume fraction at the percolation threshold, account must be taken of the interparticle interactions, particle structures, and the range over which short-ranged connectedness is established.

The application of percolation methods to continuum fluids within the framework of classical liquid state theory originated in a division of the Mayer $f$-bond into “connected” and “disconnected” contributions suggested nearly 50 years ago$^{28,29}$. In subsequent years, numerous contributions have been made to our understanding of this phenomenon in systems of interacting spheres$^{15}$. A connectedness analog of the Ornstein-Zernike equation (referred to in this work as the “connectedness Ornstein-Zernike equation”) for quantifying correlations between particles belonging to the same physical cluster was developed$^{29}$, which employed the usual fluid structural correlation functions as inputs. Most existing theoretical work on this subject has addressed spherical particles in isotropic situations$^{15}$. The connectedness Ornstein-Zernike approach will be generalized in the present work to study percolation in one-component fluids of linear macromolecules (flexible and rigid rod-like polymers), and results from this study will be presented in Chapter II. This investigation will be based on an existing generalization of the connectedness Ornstein-Zernike equation to non-spherical particles$^{30}$. The heuristic, analytical framework developed in Chapter II will be extended in Chapter III to two-component polymeric systems consisting of
rigid rod-like filler particles within a matrix of flexible coil-like molecules. The choice of appropriate form factors allows both matrix molecules and filler nanoparticles to be explicitly represented as non-spherical entities. The present work aims to address: (i) dependence of percolation threshold on macromolecular architecture (rigidity) and size; (ii) impact of attractive interactions on percolation thresholds; (iii) relation of connectedness percolation threshold to phase diagram; (iv) effects of including coil-like flexible matrix polymers on the percolation thresholds of rigid rod-like polymers/particles. While the integral equation methodology we adopt does permit investigating the effects of molecular architecture and interactions on the percolation threshold, it must be noted that inaccurate results for the critical exponents associated with the transition are to be expected within this framework. The failure of the integral equation approach to yield correct critical exponents for the percolation transition is analogous to the situation for the more familiar liquid-vapor critical point, where, again, the exponents obtained depend on the closure approximation employed, and typically do not agree with the exact results obtained from renormalization group analyses.

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I.5 Shear-Induced Effects on Miscibility of Polymer Mixtures

Flexible polymer chains under flow undergo deformation and orientation owing to hydrodynamic forces. The spherical symmetry of the radius of gyration tensor of an isolated flexible macromolecule under quiescent conditions is distorted into an approximately ellipsoidal structure. The process of chain deformation and orientation has been studied extensively within the Rouse and Zimm models, as well as in experiments using flow light scattering techniques.

The alterations in the chain conformation may result in significant changes in the macroscopic phase behavior of polymeric liquids. It has been known for a number of years that polymer solutions and blends subject to flow can exhibit miscibility behavior different from that observed under quiescent (stationary) conditions. Depending upon the specific system, shear flow has been reported to induce both enhanced as well as diminished miscibility for solutions of linear homopolymers. In contrast to polymer solutions, the majority of studies show flow-induced mixing for polymer blends, though flow-induced demixing has also been reported. In some instances, the direction of the change is reported to be a non-monotonic function of the rate of strain. The phase behavior of polymer solutions and blends under shear flow is of fundamental interest as well as industrial relevance, as substantial shear rates are encountered in polymer processing applications.

Existing approaches to understanding the phase diagram under flow have followed either of two pathways: (i) molecular kinetic theory, and, (ii) mean-field
descriptions of the quiescent state together with results from the thermodynamics of irreversible processes. A widely used starting point in existing work within the latter framework has been the classical Flory-Huggins incompressible lattice theory. Within the lattice framework, an empirically determined interaction parameter $\chi$ is introduced to calculate the free energy of mixing for polymer mixtures under quiescent (shear-free) conditions. The effects of flow are accounted for by an additional term in the free energy of mixing, which represents the work involved in the process of molecular deformation. Such a treatment fails to include the coupling between the shear field and chain conformation whose impact on the thermodynamics requires a treatment using the chain structure as a fundamental input.

The deformation and orientation of flexible linear polymers will be described in Chapter IV within generalizations of the Rouse and Zimm models which incorporate the constraint of finite extensibility. This work serves as a preliminary step, the results from which are inputs for our investigation of shear-induced effects on the miscibility of polymer mixtures. The Polymer Reference Interaction Site Model is employed in present work to calculate correlation functions associated with flexible polymers deformed due to shear flow in (i) one-component polymer solutions (Chapter V); and (ii) two-component polymer blends (Chapter VI). The shear field and chain conformation coupling effects neglected in previous work are accounted for by using form factors appropriate to anisotropic chains. Phase diagrams are obtained via the compressibility route.
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I.6 References


CHAPTER II:
An Integral Equation Study of Percolation in One-Component Systems of Flexible and Rigid Macromolecules
II.1 Abstract

An integral equation approach within the framework of the Polymer Reference Interaction Site Model (PRISM) and the Connectedness Ornstein-Zernike equation (C-OZ) is applied to understanding percolation in one-component fluids of linear macromolecules. We investigated geometrical percolation in fluids composed of (i) athermal flexible coil-like polymers, (ii) thermal flexible coil-like polymers, as well as (iii) athermal rigid rod-like polymers. Analytical treatments for the PRISM equation based on the thread-like polymer chain model and the string-like approximation to the C-OZ equation are developed. The analytical results are compared with findings from numerical calculations on finite hard-core diameter tangent-bead chain models. Semi-quantitative agreement is found between results from these two different methods of calculation. The volume fraction at the percolation threshold and number of direct interchain contacts necessary for percolation depend strongly on macromolecular architecture and size. The location of the static percolation threshold in the temperature-concentration plane with relation to the spinodal boundary is investigated for the case of thermal flexible polymers. The attractive segmental interactions are shown to have a pronounced effect on the percolation threshold in the vicinity of the theta temperature.
II.2 Introduction

Lattice and continuum approaches to percolation theory have reached a high level of sophistication and rigor in recent years\(^1\). A large body of work has addressed percolation problems in continuum systems of spherical particles\(^2\), employing methods similar to those used in successful theories of liquid organization and structure\(^3\). Predictions for the static percolation threshold have been obtained for the adhesive sphere model\(^4(a)\), as well as for spheres interacting through a square well potential\(^2(c),2(d)\) and for binary mixtures of adhesive spheres\(^4(b)\). Probabilistic criteria for particle connectivity have been explored in recent work on spherical particles\(^5\). Systems of rod-like\(^6\) and ellipsoidal particles\(^7\), as well as multiblock copolymers\(^8\), have been studied using integral equation techniques as well as Monte Carlo simulation methods. However, though macromolecular generalizations of traditional liquid state theory have been the subject of intensive study in recent years\(^9\), the development of methods for describing network-formation in systems of complex, non-spherical, molecules, has received comparatively less attention.

An integral equation approach employing (i) the Polymer Reference Interaction Site Model (PRISM)\(^9\), and (ii) the Connectedness Ornstein-Zernike equation (C-OZ)\(^6,10\) is employed in present work to understand percolation in one-component fluids of linear macromolecules. We investigated geometrical percolation in fluids composed of (i) athermal flexible coil-like polymers, (ii) thermal flexible coil-like polymers, as well as (iii) athermal rigid rod-like polymers. An “athermal” fluid corresponds to the limiting good solvent condition where polymer segments
interact solely via repulsive hard-core potentials. In contrast, for “thermal” conditions, the attractive branch of the pair potential is explicitly included in our calculations.

Rigorous enforcement of the excluded volume constraints over the entire hard-core diameter necessitates fully numerical methods for solving the PRISM and C-OZ equations. This method of calculation is quite time consuming and laborious, especially for complex, multi-component systems. A successful analytical method of calculation within a coarse-grained and computationally straightforward formalism was developed within our group and applied to athermal one-component fluids of coil-like and rod-like polymers\textsuperscript{11}. Since this method is closely related to the present study, a discussion of this approach is included in this chapter for completeness.

A key approximation of the analytical method lay in modeling the network connectivity in terms of a single parameter, corresponding to the connectedness analogue of the direct correlation function\textsuperscript{2,3}. This quantity was related in a coarse-grained and heuristic manner to the number of near neighbors as calculated from the usual pair correlation function\textsuperscript{12}. The hard core excluded volume constraints, as well as enforcement of equality between the usual and connectedness pair correlation functions in a literal fashion, were neglected in this approach. This analytical method is generalized to include “thermal” specific interactions for the case of flexible coil-like polymers. In the present study, the reliability of the approximate analytical treatment is assessed by comparing results from this method with those from purely numerical calculations.
The heuristic, analytical framework developed in this chapter can be extended to more complex, multi-component, polymeric systems in a computationally efficient manner. In particular, it will be used to describe the impact of altered surface chemistry on connectedness transitions in nanocomposites consisting of thermoplastic polymers reinforced by rod-like filler particles. Significant changes in the shear moduli and impact toughness of such materials have been attributed to the formation of such physical networks. The treatment of such interacting two-component systems in which both species are polymeric is the subject of the next chapter. The present work focuses on athermal and thermal one-component systems as a necessary preliminary step.

The remainder of this chapter is organized as follows. Analytical solutions to the PRISM equation based on the threadlike chain model as well as for the string-like approximation to the C-OZ equation are described in Section II.3.1. An extension of the analytical framework to include the attractive branch of the pair potential is presented in Section II.3.2. Issues relevant to the chain models investigated using purely numerical techniques are discussed in Section II.3.3. Results from the analytical methods under both athermal and thermal conditions, as well as from numerical calculations, are discussed in Section II.4, and directions of ongoing and potential future efforts are outlined in Section II.5.
II.3 Models and Methods

II.3.1 Analytical Methods

II.3.1.1 Athermal Thread Polymer Reference Interaction Site Model (PRISM) Theory

Our investigation employs the PRISM\(^9\) formalism to calculate correlation functions within an interaction site representation of macromolecular fluids. In PRISM theory, each macromolecule is subdivided into a connected set of spherical interaction sites. The definition of such sites is based on the chemical view of a macromolecule as a bonded collection of repeating units (monomers). The number of interaction sites in a single macromolecule is proportional to its degree of polymerization. Within the PRISM formalism, the site-averaged Ornstein-Zernike (OZ) equation for a one-component homopolymer fluid is written\(^9\):

\[
\hat{h}(k) = \hat{\omega}(k) \hat{\hat{c}}(k) \left( \hat{\omega}(k) + \rho_m \hat{h}(k) \right),
\]

where \(\hat{h}(k)\) and \(\hat{\hat{c}}(k)\) represent, respectively, the Fourier-transformed intermolecular site-site pair and direct correlation functions, \(\hat{\omega}(k)\) is the site-averaged intrachain structure factor (single molecule form factor), and \(\rho_m\) is the site number density (number of interaction sites per unit volume). Information relevant to the chain architecture is included through choice of the appropriate form factor \(\hat{\omega}(k)\), and liquid-state closure approximations\(^9,12,15\) are implemented at the level of the direct correlation function \(\hat{\hat{c}}(k)\). The equivalent site approximation is employed throughout the present study. This approximation corresponds to assuming the
correlation functions are independent of where the interaction sites are located along the contour of the polymer chain. Though methods have been developed for the self-consistent determination of the chain structure\textsuperscript{16} as specified by $\hat{\omega}(k)$ concomitantly with the fluid organization described by $\hat{h}(k)$, the present work foregoes this generalization and instead assumes that the molecular structure as specified by the form factor $\hat{\omega}(k)$ is known and available \textit{a priori}. The form factors employed in the present analytical approach are described in Sec. II.3.1.2.

The analytic PRISM theory of present interest can be implemented at the level of either the coarse-grained thread or string-like idealizations\textsuperscript{9(b),15}, together with an upper cutoff on the wave vector range. For a specified functional form for the form factor $\hat{\omega}(k)$, the direct correlation function is approximated as:

$$\hat{c}(k) = C_0 \text{ for } 0 < k < k_\epsilon, \text{ and } \hat{c}(k) = 0 \text{ for } k > k_\epsilon,$$

(2)

where $k_\epsilon$ represents the cutoff wave vector. The above approximation is a crude means of accounting for the existence of a finite hard-core site diameter $d$, corresponding to the chain thickness, which is defined as $d = 2\pi / k_\epsilon$. The athermal direct correlation function parameter $C_0$ is determined by enforcing the local site-site excluded volume constraint in either:

(i) a pointwise manner, referred to as the “thread-like” approximation\textsuperscript{9(b),15(b)}, which stipulates that:

$$h(r \to 0) = -1,$$

(3)

or:
(ii) in an average sense over the range of the effective site diameter $d$, described as the “string-like” approximation$^{9(b),15(a)}$, and where $C_0$ is determined by enforcing the condition that:

$$\int_{0}^{d} dr \, r^2 \, g(\, r \, ) = 0,$$

where $g(\, r \, ) \equiv 1 + h(\, r \, )$. Analytical methods and results for one-component systems derived within the thread approximation are presented in this chapter. The string-like approximation is used in treating two-component polymeric systems which are discussed in the next chapter. Prior work employing the thread approximation$^{9(b),15(b)}$ (without a wave vector cutoff) for flexible chain systems has established that, within the compressibility route$^{12}$, this method accurately describes solution thermodynamic properties for dilute and semidilute concentration conditions.

The present work shall focus primarily on site densities corresponding to dilute and semidilute polymer concentrations, and use of the wave vector cutoff is a technical approximation necessary for providing a unified treatment of flexible, semiflexible, and rigid rod-like macromolecules. The present work employs an effective one-component model description in which only the polymer molecules are treated explicitly, and solvent particles are not included. This procedure is appropriate in view of establishing the present method and approximation scheme. Solvent effects may be included within such an effective one-component model by modification of the effective potential between the interaction sites representing the polymer molecule.
For a given choice of $\hat{\omega}(k)$ as described in Sec.II.3.1.2, corresponding to specification of the polymer architecture, the approximation in Eq. (3) together with the PRISM-OZ equation [Eq. (1)] provide a means to determine the pair correlation function $g(r)$ through either analytic or computational methods. These results, based on the thread approximate closure to the PRISM-OZ equation [Eq. (1)], are used as inputs to the problem of determining connectedness and mean cluster sizes as described in Sec. II.3.1.3.

II.3.1.2 Polymer Models

In this chapter, we focus attention on one-component systems of flexible coil-like and rigid rod-like linear polymers. For flexible linear coils, we adopt the following accurate Lorentzian approximation to the Debye form factor$^{17}$:

$$\hat{\omega}(k) = \frac{N}{1 + \frac{Nk^2}{12} \Gamma^2},$$

over the entire wave vector range, where $\Gamma$ is defined by the ratio of the statistical segment length, $\sigma$, to the effective site diameter $d$, $\Gamma = \sigma / d$, and $N$ is the number of interaction sites per coil. Ideal, Gaussian coil statistics are assumed, and excluded volume interactions are included in terms of their impact on the pair correlation functions, though self-avoiding walk statistics are not employed in this work.
For rigid rod-like molecules, we adopt an expression for \( \hat{\omega}(k) \) which interpolates between a low wave vector, Guinier-like\(^{18}\), regime, and the \( \hat{\omega}(k) \approx 1/k d \) behavior characteristic of rod-like particles at high wave vector\(^{19}\):

\[
\hat{\omega}(k) = \frac{N}{1 + \frac{N^2 k^2 d^2}{24}}, \quad 0 < k < 1/N d, \\
\quad = \frac{24}{25 k d}, \quad 1/N d < k < k_c. \tag{6}
\]

The form factor in Eq. (6) reproduces the low wave vector limit behavior corresponding to Guinier’s law for a rigid particle of length \( L = N d \), and crosses over continuously to the \( \hat{\omega}(k) \approx 1/k d \) regime for length scales (wave vectors) which are small (large) compared to the rod length (reciprocal of the rod length). The expression in Eq. (6) is not intended to serve as an optimal approximation to the actual, oscillatory, form factor of rod-like particles,\(^{19}\) but rather embodies concisely the most important limiting behaviors in the low and high wave vector regimes.

The expression for \( \hat{\omega}(k) \) in Eq. (6) can be readily generalized to the case of arbitrary persistence lengths. (The persistence length corresponds to the length scale below which the molecule is assumed to have a locally rigid structure). Extensions have been suggested for treating non-isotropic orientational distributions\(^{20}\) as well. The present work shall focus on results obtained using the form factors in Eq. (5) and (6) appropriate for flexible, ideal coils and perfectly rigid, rod-like, particles, respectively. Alternative chain fractal dimensions and the effects of modulating the persistence length are being considered in ongoing work.
II.3.1.3 Connectedness Ornstein-Zernike Equation

The connectedness analogue of the Ornstein-Zernike equation\textsuperscript{3} has been widely applied to the study of percolation in systems of interacting spheres\textsuperscript{2(a)(b),5(a)(b)}. In recent work, this method has been generalized to treat non-spherical molecules within the interaction site formalism\textsuperscript{6}. For a homopolymeric system within the PRISM methodology, the Connectedness Ornstein-Zernike (C-OZ) equation is\textsuperscript{6,10}:

\[
\hat{h}_i (k) = \frac{\hat{o}^2 (k) \hat{c}_1 (k)}{1 - \rho_m \hat{o} (k) \hat{c}_1 (k)},
\]

where \(\hat{h}_i (k)\) and \(\hat{c}_1 (k)\) are the connectedness analogues of the site-averaged pair and direct correlation functions, respectively. (We reserve the subscript “1” for connectedness correlation functions). \(\hat{o} (k)\) and \(\rho_m\) have the same meanings as in Eq. (1). Closure approximations within which Eq. (7) has usually been solved\textsuperscript{2(a)(b),5(a)(b),6,10} presuppose (i) knowledge of the correlation functions \(g (r)\) and \(c (r)\), as well as (ii) criteria for defining when sites are considered to be directly “connected”. The mean connected cluster size \(S_i\) is determined from\textsuperscript{3,6,10}:

\[
S_i = 1 + 4 \pi \rho_m \int_0^\infty drr^2 h_i (r) = 1 + \rho_m \hat{h}_i (0).
\]

Divergence of the mean cluster size is used in the present work as an indicator of the percolation threshold.

Prior applications of the C-OZ formalism to interacting spheres\textsuperscript{2(a)(b),5(a)(b)} and to rod-like\textsuperscript{6} and flexible polymers\textsuperscript{10} within the Percus-Yevick (PY) or Mean Spherical Approximation (MSA) closures\textsuperscript{12} have strictly enforced the hard core excluded
volume constraint over the entire region $r < d$. Implementation of such a procedure for non-spherical particles requires the use of iterative, fully computational, methods to obtain numerical solutions for the connectedness and regular correlation functions. The present work considers a heuristically motivated generalization of the thread and string-like approximations\(^9\)\(^{\text{b,c,15}}\) to the connectedness problem. This approximate procedure permits greater progress to be made using simple analytical methods.

For the purely athermal, excluded volume-dominated, conditions of present interest, a pair of sites on different molecules shall be considered to be directly “connected” if and only if they approach within a distance $R$ from each other. All sites on distinct molecules within this range shall be considered as being directly “connected” to the tagged site. This definition of “connectedness”, together with the assumption of purely hard-core interactions, has been shown to suggest the following closure relations for the connectedness problem\(^6\)\(^{,10}\):

\[
h_1 (r) = g(r), \quad \text{for} \quad r < R, \quad \text{and} \quad c_1 (r) = 0, \quad \text{for} \quad r > R, \quad (9)
\]

analogous to the usual PY approximation\(^{12}\). The present analytical work does not enforce the core condition for the usual pair correlation functions on the hard core diameter length scale $d$ literally, but rather in the coarse-grained thread and string-like approximations introduced earlier [Eq. (3) and (4)]. In the spirit of this approximate treatment, the closure relations in Eq. (9) for the C-OZ equation are also implemented in a similar, averaged, sense:
The first line of Eq. (10) is the connectedness analogue of the thread and string-like approximations for the direct correlation function, implemented with an upper wave vector cutoff. The second line of Eq. (10) is a heuristic generalization of the string-like approximation for finite thickness chains, which enforces the closure relation for the C-OZ equation [Eq. (7)] in an average sense over the range within which sites on distinct molecules are regarded as being directly connected. Physically, Eq. (10) requires that both the regular and connectedness OZ equations predict equal numbers of sites within the range \( R \) defining direct connectedness. This approximation is in the same spirit as the previously studied \(^{9(b),15(a)}\) “string-like” model for the usual pair correlation functions. Implementing the condition in Eq. (9), \( i.e., \) enforcing strict equality of \( g(r) \) and \( h_1(r) \) for all \( r < R \), is not achievable within the present “string-like” approximation, and requires fully numerical calculations as described in Sec.II.3.3. The second line of Eq. (10) represents a new, and uncontrolled, approximation, whose validity must be adjudged by comparison with calculations in which the inner condition in Eq. (9) is strictly enforced. Earlier successes \(^{9(b),15}\) of the thread and string-like approximations in describing the thermodynamics of polymer solutions and blends suggest that the coarse-grained enforcement of the inner boundary condition represented by Eq. (10) may be of value in developing approximate theories for connectedness in polymeric systems. This

\[
\hat{c}_1(k) = C_1 \quad \text{for} \quad 0<k<k_c, \quad \text{and} \quad \hat{c}_1(k) = 0 \quad \text{for} \quad k>k_c;
\]

and

\[
\int_0^R dr r^2 h_1(r) = \int_0^R dr r^2 g(r).
\]
approach will make it possible to include detailed information regarding chain architecture, composition, and the nature of site-site interactions.

II.3.2 Inclusion of Attractive Interactions

This section considers the generalization of the aforementioned analytical work on athermal polymer fluids to include attractive interactions for flexible homopolymers. For flexible linear coils, we adopt the Debye form factor introduced in Eq. (5). For purposes of simplicity, the attractive branch of the site-site pair potential is assumed to be a square well of depth \( \varepsilon \) and range \( a \):

\[
u (r) = \begin{cases} \varepsilon, & d < r < a; \\ 0, & r > a. \end{cases}
\]  

(11)

The influence of the attractive “thermal” interactions is studied within the linearized Reference Molecular Percus-Yevick/High Temperature Approximation (RMPY/HTA) closure approximation\(^{21}\), which has been used successfully in previous investigations of demixing transitions in polymer solutions\(^{15(b)}\) and blends\(^{21(b,c)}\). This approximation is formulated as follows\(^{21}\) in terms of the athermal direct correlation function \( C^{(0)}(r) \) and the athermal pair correlation function, \( g^{(0)}(r) \) (The superscript “(0)” is reserved in this section for athermal conditions):

\[
\omega(r) * C(r) * \omega(r) = \omega(r) * C^{(0)}(r) * \omega(r) - \beta \omega(r) * u(r) g^{(0)}(r) * \omega(r), \quad r > d,
\]

(12)

where the asterisks represent \( r \)-space convolutions and \( d \) is the hard core site diameter. \( \beta \) denotes the reciprocal of the product of the Boltzmann constant \( k_B \) and
temperature $T$. Specification of the closure approximation is completed by enforcing the core condition, namely, $g(r) = 0$, in the region $r < d$.

The thread-like chain model corresponds to taking the limit $d \to 0$ and employing a Dirac delta function for the athermal direct correlation function in $r$-space. Within this framework, the convolutions in Eq. (12) may be cancelled after Fourier transformation and reduced to the following relation:

$$C(r) = C_0 \delta(r) - \beta u(r) g^{(0)}(r).$$

The direct correlation function modified by attractive interactions can be evaluated immediately in terms of the athermal direct and pair correlation functions and the pair potential. Within this thread-like approximation for flexible chains, the athermal reference pair and direct correlation functions are$^{9(b)}$:

$$C^{(0)}(r) = C_0 \delta(r),$$

$$g^{(0)}(r) = 1 + \frac{3}{\pi \rho_m \sigma^3} r \left[ e^{-r/\xi_{\rho}} - e^{-r/\xi_c} \right], \quad \frac{\xi_c}{\xi_{\rho}} = R_g / \sqrt{2},$$

$$(14)$$

$$\frac{\sigma}{\xi_{\rho}} = \frac{\sigma}{\xi_c} + \frac{\pi \rho_m \sigma^3}{3}, \quad \rho_m C_0 = \frac{1}{N} - \frac{1}{12} \left[ \frac{\pi \rho_m \sigma^3}{3} + \frac{\sigma}{\xi_c} \right]^2.$$  

In Eq. (14), $R_g$ and $\xi_{\rho}$ are the coil radius of gyration and correlation length for polymer concentration fluctuations, respectively. Note that the core condition, which is enforced in a pointwise fashion in the athermal thread model ($g^{(0)}(r \to 0) = 0$), is no longer enforced under thermal conditions at the thread level within the RMPY/HTA closure.

The spinodal boundary, which within the present one-component model corresponds physically to the demixing transition in a polymer solution, is located
from the divergence in the structure factor at zero wave vector\textsuperscript{15(b)}. Following this procedure, which has been discussed at length in a previous work\textsuperscript{15(b)}, Eq. (5) and Eqs. (11-14) yield a closed-form expression for the spinodal temperature as a function of the site density:

\begin{equation}
\rho_m C_0 + \frac{4}{3 t_s} \Phi \left[ 9 \rho_m a \sigma \left( \xi e^{-a / \xi} - e^{-a / \xi} \right) \right] \\
+ 9 \rho_m \sigma \left( \xi^2 \left( 1 + e^{-a / \xi} \right) + \xi^2 \left( 1 - e^{-a / \xi} \right) \right) + \pi \rho_m a^3 \Phi = \frac{1}{N},
\end{equation}

where $t_s \equiv k_B T / \varepsilon$ is the reduced spinodal temperature, and $\Phi \equiv \rho_m \sigma^3$ is the dimensionless site number density (The symbol $\Phi$ is reserved for the dimensionless site number density throughout this chapter). Analysis of Eqs. (14) and (15) reveals that, in the long chain limit, the critical polymer concentration behaves as: $\Phi_c \approx N^{-1/3}$, and the critical temperature approaches a finite, asymptotic value of $t_c \rightarrow 18 \left( a / \sigma \right)^4$ as $N \rightarrow \infty$. This limiting value of the critical temperature coincides with the theta temperature as defined by the vanishing of the polymer-polymer second virial coefficient. These results are in qualitative agreement with the findings of experiments\textsuperscript{22} and computer simulations\textsuperscript{23} on polymer solutions exhibiting upper critical solution temperature behavior.

From Eqs. (1), (5) and (11-14), an unwieldy expression can be obtained in closed form for the Fourier transform of the total correlation function, $\hat{h} (k)$, which we refrain from displaying explicitly. Calculation of the connectedness correlation functions now proceeds following the approximation outlined in Eq. (10), except that we now employ the pair correlation function as modified by the attractive...
interactions. The percolation threshold is identified from the condition given in Eq.

Equations (5), (7), (8), (10), and (11-14) lead to the following integral equation
which determines the static percolation threshold for a given range $R$:

$$\frac{3\sigma}{\pi}\Phi\left[\frac{R^2}{2} - \xi_c^2 + \xi_c \left(R + \xi_c\right)e^{-R/\xi_c}\right] = \frac{R^3}{3} + \frac{1}{2\pi^2}\int_0^{\infty} dk \hat{h}(k)\left[\frac{\sin(kR)}{k} - R \cos(kR)\right].$$

In the present work, Eq. (16) is solved numerically using an iterative procedure,
employing the temperature-dependent expression for $\hat{h}(k)$ obtained from Eqs. (1),
(5) and (11-14).

**II.3.3 Numerical PRISM Calculations**

In Section II.4.3, we present results from fully numerical calculations on
athermal coil and rod-like model polymers of finite thickness, as well as for flexible
coil-like molecules interacting through a hard core + square well pair potential. In all
cases, the polymers are treated as linear chains of tangent spherical beads for these
numerical calculations.

Our work involving rigid rod-like molecules employs the exact, site-averaged
form factor for a linear array of tangent hard beads. Each interaction site represents an
individual bead in our model. For the flexible coil-like molecules, we employ the
Koyama intramolecular distribution\textsuperscript{24} with zero bending energy to model the site-
averaged tangent bead chain form factor. The Koyama distribution is characterized by
three parameters, namely, (i) the number of interaction sites per molecule, (ii) the
bond bending energy, and, (iii) the bond length. The Koyama distribution for the
chain form factor is capable of interpolating between rigid-rod and Gaussian-coil
limits by suitably adjusting the bending energy.

In all cases, the range of direct connectedness, $R$, equals twice the hard-coresite diameter, $d$. The thermal calculations employ a square well potential of range $a = R = 2d$, and are performed within the linearized RMPY/HTA closure approximation. These calculations enforce the finite hard-core diameter constraint, and hence the convolutions in Eq. (12) cannot be cancelled after Fourier transformation. Previous work has shown\textsuperscript{25} that for flexible coil-like molecules, the results of such fully numerical calculations for the critical temperature and polymer site density are in close agreement with the predictions of the thread-like model for these quantities. Athermal calculations employ the atomic-like Percus-Yevick (PY) closure approximation. The regular and connectedness OZ equations are in all cases solved using the iterative Picard scheme\textsuperscript{12}.

In all situations, the coil dimensions correspond to ideal chain statistics, \textit{i.e.}, the chain conformations are assumed to be independent of temperature and reflect theta-solvent behavior under all conditions. The effect of temperature (or solvent quality) thus enters exclusively through the influence of the pair potential on the pair correlation functions. The chain swelling effect observed under good solvent conditions leads to chain statistics described instead by the self-avoiding-walk, and also modifies the functional dependence of the form factor upon wave vector\textsuperscript{17}. This
phenomenon may reasonably be expected to affect percolation thresholds under athermal conditions, and is under current investigation.

II.4 Results and Discussion

II.4.1 Results from Analytical Methods

A. Flexible coils

The pointwise thread-like closure approximation in Eq. (3) assumes the following form in $k$-space:

$$1 + \frac{1}{2} \pi^2 \int_0^{2\pi} \frac{d k}{d^3} k^2 \left[ \hat{h}(k) \right] = 0,$$  \hspace{1cm} (17)

where the wave vector $k$ has been expressed in units of $1/d$. Implementation of the thread-like closure approximation of Eq. (17) with the form factor $\hat{\omega}(k)$ in Eq. (5) for flexible coils leads to the following equation for determining the athermal direct correlation function parameter $C_0$:

$$2 \pi - \frac{8 \sqrt{2}}{3 \pi} \left[ \sqrt{(1+y)} \arctan \left( \frac{\pi \sqrt{N/3 \Gamma}}{\sqrt{(1+y)}} \right) - \arctan \left( \frac{\pi \sqrt{N/3 \Gamma}}{\sqrt{(1+y)}} \right) \right] = 0,$$  \hspace{1cm} (18)

where $y \equiv -\rho_m N C_0$, and the polymer density variable $z$ is reduced with respect to the usual semidilute overlap concentration, i.e., $z \equiv \rho_m / \rho_m^*$, $\rho_m^* = 3 N / 4 \pi R_g^3$. The coil radius of gyration, $R_g$, is given in units of the site diameter $d$ by $R_g = \sqrt{N/6 \Gamma}$. (The effective site diameter is defined in terms of the wave vector.
cutoff as \( d = 2 \pi / k_c \). In general, Eq. (18) must be solved numerically to determine \( C_0 \) as a function of the polymer site density \( z \). However, analysis of Eq. (18) in the low-density limit as \( N \to \infty \) shows that previously known results\(^{15} \) [Eq. (14)] for the athermal thread model without the wave vector cutoff are recovered, i.e.,

\[
y \approx 3 z / \sqrt{2} + 9 z^2 / 8 + O(z^3).
\]

In addition, imposition of the wave vector cutoff leads to a maximum site density corresponding to a logarithmic divergence in the compressibility route pressure, at a density given by:

\[
z_{\text{max}} = \frac{4 \Gamma \sqrt{6 N}}{9}, \quad \text{or} \quad \rho_{\text{m}}^\text{max} d^3 = \frac{12}{\pi \Gamma^2}.
\]  

It is worth mentioning that the existence of a maximal density \( \rho_{\text{m}}^\text{max} d^3 = 1.438/\Gamma^2 \) at which the isothermal compressibility vanishes is also found within the string-like closure approximation. A similar upper bound to the density with an accompanying divergence in the pressure calculated from the compressibility route has been found in earlier work employing the string-like model\(^{15} \) without an explicit cutoff wave vector.

As in that earlier work, this maximum density shall be identified loosely with the close-packing volume fraction, and the site packing fraction shall be defined as:

\[
\eta = z / z_{\text{max}}.
\]

With the athermal direct correlation strength \( C_0 \) determined from Eq. (18), the present string-like closure for the C-OZ equation [Eq. (10)] takes the form:

\[
\frac{\lambda^3}{3} + \frac{1}{2 \pi^2} \int_0^{2\pi} dk d k \left[ \frac{\hat{h}(k) - \hat{h}_1(k)}{d^3} \right] \left[ \frac{\sin(\lambda k)}{k} - \lambda \cos(\lambda k) \right] = 0,
\]

\( \lambda \)
where \( \lambda \equiv \frac{R}{d} \) is the dimensionless range of direct connectivity, and, as in Eq. (17), the wave vector \( k \) has been expressed in units of \( 1/d \).

In the present work, Eq. (20) is solved numerically to determine the mean cluster size, and the percolation threshold is located from the condition that the denominator of \( \hat{h}_1(k) \) vanish as \( k \to 0 \). However, the key results of these calculations can be obtained by an analytic argument which ignores the upper wave vector cutoff and extends the integrations in Eqs. (17) and (20) to \( k_e \to \infty \), i.e., which uses previously known results\(^ {9(b),15} \) for \( C_0 \) and \( g^{(0)}(r) \) for the athermal thread-like model. This approximation corresponds to taking the limit \( d \to 0 \) without relaxing the pointwise core condition of Eq. (3). Under these conditions (athermal thread-like closure and no upper wave vector cutoff), Eq. (20) leads to the following condition for the percolation threshold:

\[
\frac{3}{2 \pi \rho_m \sigma^3} \left( \frac{R}{\sigma} \right)^2 - \frac{1}{3} \left( \frac{R}{\sigma} \right)^3 - \frac{3}{\pi \rho_m \sigma^3} \left[ \left( \frac{\xi_\rho}{\sigma} \right)^2 - \left( \frac{R \xi_\rho}{\sigma^2} + \frac{\xi_\rho^2}{\sigma^2} \right) e^{-R/\xi_\rho} \right] = 0,
\]

(21)

where the density screening length \( \xi_\rho \) is calculated from Eq. (14).

Equation (21) for the percolation threshold simplifies in two limiting situations. (i) If we assume that the range of direct connectedness, \( R \), is of the order of the statistical segment length and much smaller than the screening length \( \xi_\rho \), the exponential on the left hand side of Eq. (21) can be expanded, leading to:
\[
\rho_m^p \sigma^3 \approx \frac{1}{\pi} \sqrt{24 \left( \frac{\sigma^2}{\xi_c R} \right) N^{-1/4}} \sqrt{\frac{\sigma}{R}}
\]  

(22)

in the long chain limit, where \( \rho_m^p \) is the site density at the percolation threshold.

Under these conditions, geometrical percolation is predicted to occur under semidilute concentration conditions. (ii) Alternatively, we explore the situation that a pair of sites are considered directly connected if their separation does not exceed the density screening length, i.e., we set \( R = \xi_\rho \). With this criterion, Eq. (21) predicts that

\[
\rho_m^p \sigma^3 \approx 1 / \sqrt{N},
\]

i.e., an infinite network of connected sites is formed at or around the polymer concentration which defines the crossover between dilute and semidilute conditions\textsuperscript{17}. This conclusion is intuitively reasonable, and consistent with the physical image of the semidilute crossover concentration as reflecting the condition that individual macromolecules begin to interpenetrate and cannot be treated even approximately as independent and non-interacting entities\textsuperscript{17,26}. Interestingly enough, if the pointwise core condition is relaxed by equating \( g(r) \) to unity on all length scales and \( C_0 \) to zero, the condition corresponding to Eq. (21) predicts that percolation is achieved at a polymer site concentration \( \rho_m^p \sigma^3 \propto 1 / \sqrt{N} \), irrespective of whether \( R \) is chosen to be proportional to the coil radius of gyration or an \( N \)– independent length scale proportional to \( \sigma \).

Results for the percolation threshold obtained from numerical solution of Eq. (20) for the thread model with the wave vector cutoff enforced are shown in Fig. II.1. Results from the string model are also shown in this figure for comparison. Inclusion
of the wave vector cutoff does not alter the asymptotic behavior of the critical site
density from that predicted by Eq. (21) for either choice of the connectivity range $R$.
Site densities for the percolation threshold predicted from the string-like model are
higher than those based on the thread-like model, owing to enforcement of the
interchain excluded volume in an average sense for $r < d$ [Eq.(4)], rather than in the
limit $r \to 0$ alone.
Figure II.1  The logarithm of the volume fraction at the percolation threshold $\eta_p$, defined as the site density at the percolation threshold normalized by the maximum permissible site density, as a function of the logarithm of the number of sites $N$ per coil-like molecule. Filled squares: thread model for flexible coils, $\lambda \equiv R/d = 1.25$; Open squares: string model for flexible coils, $\lambda = 1.25$; Filled triangles: thread model for flexible coils, with $\lambda = R_g/d$; Crosses: thread model for “ideal” coils, i.e., with $C_0 = 0$, and with $\lambda = 1.25$. In all cases, $\Gamma = 1.0$. The broken lines indicate slopes of $-1/4$ and $-1/2$. The smoothed lines are visual guides.
B. Rigid rods

Within the thread-like closure approximation, use of the approximate form factor in Eq. (6) for the case of rod-like particles leads to the following equation for the athermal direct correlation function parameter $C_0$:

\[
2 \pi - \frac{8 \sqrt{2}}{3z} \left[ \sqrt{1+y} \arctan \left( \frac{1}{2 \sqrt{6 (1+y)}} \right) - \arctan \left( \frac{1}{2 \sqrt{6}} \right) \right] - \frac{32y}{625 \sqrt{3} z} \left[ 2 \pi N - 1 - \frac{24y}{25} \left( \ln \left( \frac{2 \pi N + 24y}{25} \right) \right) \right] = 0, \tag{23}
\]

where $z \equiv \rho_m/\rho_m^* = \pi N^2 \rho_m d^3 / 18 \sqrt{3}$, and $y \equiv - \rho_m N C_0$. As in the case of the thread model for flexible coils with the imposed wave vector cutoff, Eq. (23) predicts a logarithmic divergence in the compressibility route pressure at a maximum density given by $z_{\text{max}} \approx 0.096736N^2$, or $\rho_m^\text{max} d^3 \approx 0.96$, when $N \gg 1$. The maximum site density in the string-like theory for rods when $N \gg 1$ is given by $\rho_m^\text{max} d^3 \approx 36 / 25 \pi^2$.

Results from numerical calculations based on Eq. (20) within the thread closure approximation for rod-like molecules are shown in Fig. II.2. The results shown in Fig. II.2 indicate that, for long and slender rods, the percolation density decreases inversely with the rod length, i.e., $\rho_m^\text{max} d^3 \approx 1/N$, when the connectedness range $R$ is assumed to be $N$ independent. These results are consistent with prior calculations based on the PRISM method in which the hard-core exclusion is strictly enforced within the site diameter, and also with findings from computer simulation.
studies\textsuperscript{27} and analytic calculations\textsuperscript{28} for hard rods and ellipsoids\textsuperscript{7}. Also shown in Fig. II.2 are results obtained from Eq. (20) by equating $R$ to one-half the rod length, which is in a spirit similar to setting $R \approx R_g$ for the case of coil-like molecules. This latter criterion leads to a percolation threshold proportional to the nominal semidilute crossover concentration for rods, i.e., now $\rho_m^p \approx 1 / N^2$, a result which is intuitively consistent with the usual picture of the semidilute crossover\textsuperscript{17}. However, imposing “ideal” behavior by setting $C_o = 0$ and $g(r)$ to unity on all length scales while employing an $N$– independent value of $R$ does not alter the predicted scaling behavior of the critical density with rod length. This finding agrees with a computer simulation study of overlapping prolate ellipsoids of large aspect ratios\textsuperscript{7}, as well as with prior numerical PRISM studies on athermal rods in which end-site effects were explicitly accounted for\textsuperscript{6(b)}. 

Figure II.2 The logarithm of the volume fraction at the percolation threshold \( \eta_P \), defined as the site density at the percolation threshold normalized by the maximum permissible site density, as a function of the logarithm of the number of sites \( N \) per rod-like molecule. Filled squares: thread model for athermal rods with \( \lambda \equiv R/d = 1.25 \); Open squares: string model for rods, with \( \lambda = 1.25 \); Filled triangles: thread model for rods, with \( \lambda = L / (2d) \); Crosses: thread model for “ideal” rods, i.e., with \( C_0 = 0 \), and with \( \lambda = 1.25 \). The broken lines are drawn with slopes of \(-1\) and \(-2\). (The broken line with slope \(-2\) is nearly indistinguishable from the filled triangles.) The smoothed lines are visual guides.
Results for $g(r)$ and $h_1(r)$ for both rod-like and coil-like molecules within the thread-like approximation at site densities close to their respective percolation thresholds are shown in Fig. II.3. The functions $g(r)$ and $h_1(r)$ approach asymptotic limits of unity and zero, respectively, as $r \to \infty$. As expected based on the discussion following Eq. (10), these functions are not equal in a pointwise sense even within the range $R$ defining direct connectivity. However, in all cases, the integrated number of intermolecular contacts within this range of separations is equal when calculated from either $g(r)$ or $h_1(r)$, which is the physical meaning of the approximation introduced in the second line of Eq. (10).
Figure II.3  (a) The solid and broken lines show \( g(r) \) and \( h_1(r) \), respectively, for rod-like and coil-like macromolecules within the thread-like approximation. In each case, the volume fraction \( \eta = 0.95 \eta_p \). The number of sites per molecule, \( N \), takes values of \( N = 160 \) and \( N = 25600 \) for the rod-like and coil-like polymers, respectively. In each case, \( \lambda \equiv R/d = 1.25 \); for the coil-like molecules, \( \Gamma = 1.0 \). (b) Same as (a), showing the asymptotic behavior of \( g(r) \) and \( h_1(r) \).
Figure II.4 shows the average number of direct *interchain* contacts per molecule at the percolation threshold, calculated from:

\[ N_c = 4 \pi \rho_m N \int_0^R dr \, r^2 g(r), \]  

(24)

within the thread-like approximation. This number is approximately constant, and independent of \( N \), for the case of rod-like particles, but increases \( \propto \sqrt{N} \) in the case of flexible coils obeying ideal random walk statistics. The greater number of contacts per chain in the case of flexible polymers reflects the higher site density required to achieve percolation. For rods of length \( L \), and coils of radius of gyration \( R_g \), the number of such direct interchain contacts per unit volume at the threshold scales as \( 1/L^2 \) and \( 1/\sqrt{R_g} \), respectively. While these are decreasing functions of macromolecular size in both instances, the significantly fewer number of close contacts necessary in the case of rod-like particles may partially explain their substantial impact on mechanical properties of composites even at very low volume fractions\(^{14(a)}\). For rod and coil-like molecules, if \( R \) is equated to \( L/2 \) or \( R_g \), respectively, \( N_c \) increases as \( N_c \propto N^2 \) in both cases, reflecting the fact that on length scales comparable to the molecular dimensions, the “correlation hole” disappears\(^{9(b),15}\) and the pair correlation function approaches unity.
Figure II.4  The logarithm of the number of sites directly connected to a given molecule at the percolation threshold, calculated from Eq. (24) within thread-like approximation, as a function of the molecular dimensions. The variable ‘X’ represents one-half the rod length for rod-like molecules, and the radius of gyration for coil-like molecules. Filled and open symbols represent results for coil-like and rod-like molecules, respectively. In each case, the symbols have the following meanings: Squares: \( \lambda \equiv R/d = 1.25 \), athermal systems; Triangles: \( \lambda = X/d \), athermal systems. The smoothed lines are visual guides.
II.4.2. Flexible Coils with Attractive Interactions

Within the analytical thread-like approximation, results for the percolation threshold obtained from numerical solution of Eq. (16) are shown in Fig. II.5, together with the corresponding spinodal boundaries. Including the attractive branch of the site-site interaction leads to a dramatic, temperature-dependent, reduction in the percolation threshold. Similar effects of attractive interactions on the percolation threshold have been reported in previous work on spherical particles\(^2\). In all cases, the static percolation line meets the spinodal boundary at concentrations below the critical concentration. Results for the dependence of the percolation threshold on chain length within the thread approximation are shown in Fig. II.6, for both athermal and thermal conditions. Figure II.6 reveals that the behavior at the \(N \to \infty\) theta temperature differs qualitatively as well as quantitatively from the athermal prediction. Calculations performed at the theta temperature (Fig. II.6) find that the percolation threshold varies as \(\rho_m^P \propto N^{-1/2}\), similar to the semidilute overlap threshold for ideal chains. A similar conclusion was reached in the case of athermal coils based on the thread-like model, in which chain ideality was enforced in a less careful manner by equating the regular direct correlation parameter to zero. The present work shows that this result, namely the coincidence of the semidilute crossover with the percolation threshold for short-range direct connectedness in ideal solutions of flexible coils, remains valid within a more detailed treatment of both the repulsive and attractive contributions to the direct correlation function.
Figure II.5  The solid lines and open diamonds show, respectively, the spinodal boundaries and percolation thresholds, calculated within the thread-like analytical model. In all cases, $R = a = \sigma$. The temperature is in units of the $N \to \infty$ limiting value of the theta temperature, and the dimensionless site density is defined as $\Phi = \rho_m \sigma^3$. For the solid lines, $N = 100, 1000, \text{and} 10000$, from bottom to top, and for the percolation lines, $N = 100, 1000, \text{and} 10000$, from right to left.
Figure II.6  The uppermost and lowermost solid curves show the dependence on $N$ of the percolation thresholds calculated from the thread-like model under athermal conditions and at the theta temperature, respectively. The dimensionless site density is defined as $\Phi = \rho_m\sigma^3$. The intermediate solid line shows the $N$ dependence of the critical site density at the liquid-vapor transition. In all cases, $R = a = \sigma$. From top to bottom, the broken lines indicate slopes of $-1/4$, $-1/3$, and $-1/2$, respectively.
Numerical PRISM calculations for the percolation thresholds and spinodal boundaries for flexible chains modeled by the Koyama distribution are shown in Fig. II.7. These results are broadly consistent with those obtained within the thread-like approximation, and suggest that the delta function representation for $c(r)$ does not lead to radically different predictions from those obtained through a more painstaking computation. Numerical calculations under fixed temperature conditions have been performed which suggest that under near-theta conditions, the percolation threshold scales with the semidilute overlap concentration, in agreement with the thread-model based finding. These results are presented in the following section together with numerical calculations of the chain length dependence of the percolation threshold for finite thickness polymers under athermal conditions.
Figure II.7  The filled and open diamonds show, respectively, the spinodal boundaries and percolation thresholds of finite thickness, flexible, tangent bead coils, calculated using purely numerical techniques. In all cases, \( R = a = 2d \). Dimensionless temperatures and site densities are defined as \( T^* = k_B T / \varepsilon \) and \( \Phi \equiv \rho_m d^3 \), respectively. The connecting lines are visual guides. For the solid lines, \( N = 50, 100, 200, \) and \( 500, \) from bottom to top, and for the broken lines, \( N = 50, 100, 200, \) and \( 500, \) from right to left.
II.4.3 Results from Numerical Calculations

In our numerical calculations, the mean cluster sizes are calculated from Eq.(8) as functions of the site density. Percolation thresholds are determined either from (i) the divergence of the mean cluster size, or, (ii) by fitting the mean cluster size and the corresponding site density to the relation \( S_1 \approx \left( \rho_m^p - \rho_m \right)^{-\gamma} \). The critical exponent \( \gamma \) characterizing the divergent mean cluster size \( S_1 \) at the percolation threshold equals \( \gamma = 2 \) for both rod-like and coil-like molecules based on the thread like polymer models and PY-like closure approximation employed.\(^{6,11}\) A log-log plot of the numerically obtained mean cluster size versus the difference of the site density from its value at the threshold is shown in Figure II.8. The percolation threshold is treated as an adjustable parameter to obtain the best fit to the relation \( S_1 \approx \left( \rho_m^p - \rho_m \right)^{-\gamma} \) while keeping the exponent \( \gamma \) as close to the value of 2 as possible. The discrepancies between the values of the percolation thresholds obtained from this fitting procedure and from the mean cluster size divergence criterion are less than 4.5\% in all cases.

Results for the critical percolation thresholds for (i) athermal rod-like molecules, (ii) athermal flexible coil-like molecules, and (iii) for coil-like molecules interacting through a hard core + square well potential, are shown in Fig. II.9 as functions of the molecular dimensions. Our numerical results for rod-like molecules are consistent with the prediction of the thread model for the percolation threshold, and with Monte Carlo computer simulations on ellipsoids\(^7\) as well as recent
experiments on rod-like boehmite clay particles\textsuperscript{29} and arguments based on excluded-volume concepts\textsuperscript{30}.
Figure II.8a  The mean cluster size as a function of the difference of the site density from its value at the threshold for flexible coil-like polymers. $\delta \rho$ is defined as $\delta \rho = \rho_m^p - \rho_m$. The open triangle, diamond and square correspond to $N = 800, 3200, 12800$, respectively. The solid line is of slope 2.
Figure II.8b  The mean cluster size as a function of the difference of the site density from its value at the threshold for rod-like polymers. \( \delta \rho \) is defined as \( \delta \rho = \rho_m^p - \rho_m \). The open triangle, diamond and square correspond to \( N = 20, 40, 160 \), respectively. The solid line is of slope 2.
Figure II.9  The dependence on chain dimensions of the percolation thresholds calculated using purely numerical methods for finite thickness chain models. The filled diamonds, filled squares, and open diamonds correspond to athermal flexible coils, athermal rigid rods, and flexible coil-like molecules interacting through a hard core + square well potential at constant reduced temperature $T^* = k_B T/\varepsilon = 25$, respectively. The dimensionless site density is defined as $\Phi \equiv \rho_m d^3$. The variable representing chain major dimension is defined as $X / d$, where $X$ is the radius of gyration $R_g$ and half-length $L / 2$ for coils and rods, respectively. From top to bottom, the broken lines indicates slopes of -0.37, -1.0, and -1.0.
The athermal numerical PRISM results in Fig. II.9 show that, as suggested by the thread-like model, percolation thresholds for flexible molecules significantly exceed those for rod-like polymers. However, the dependence of percolation threshold on chain length for the case of flexible polymers in Fig. II.9 shows significant finite-$N$ effects for short chains, and it is difficult to identify a power-law exponent with complete unambiguity. If we confine attention to our results for chains with $N \geq 500$ beads, the observed behavior is approximately consistent with $\rho_p m \propto N^{-0.18}$, somewhat weaker than predicted by the athermal thread model. Given that these polymer concentrations are well into the semidilute regime, we believe that shortcomings of the coarse-grained thread-like approximation at high polymer volume fractions are responsible for the observed discrepancy.

The constant temperature numerical calculations which include the attractive square well potential were restricted to chain lengths $N$ ranging from 50 to 500. In each case, these calculations were performed at a fixed reduced temperature $T^* = 25.0$, corresponding to the critical temperature of the largest ($N = 500$) chains investigated (see Fig. II.7). Admittedly this value does not represent the long chain limiting value of the theta temperature, which must be determined from an extrapolation of results from still larger model chains. However, these calculations should approximately mimic the effect of being close to theta conditions. The numerically obtained results at this fixed value of the reduced temperature are in close agreement with the thread model prediction of $\rho_p m \propto N^{-1/2}$ behavior for the range of chain lengths ($500 \geq N \geq 50$) which was studied.
Numerically obtained results for the number of “direct” contacts per macromolecule at the percolation threshold are shown in Fig. II.10. The number of direct contacts is calculated from Equation (24) and results for this quantity obtained from the athermal thread-like approximation are shown in Fig. II.4. The results shown in Fig. II.10 are consistent with the power law behavior $N_c \propto N^{1/2}$ for flexible coils, in agreement with the findings of the analytical model. A weak decrease of $N_c$ with increasing length is found for rod-like molecules (from $N_c = 17.4$ for rods with $N = 10$ to $N_c = 12.4$ for rods with $N = 160$), which is probably a finite-size effect as was the case for the corresponding analytical model (Fig. 5 of Ref. 11). The impact of molecular architecture is clearly reflected in the significantly lower number of direct contacts required to mediate the formation of an infinite cluster for more extended, rod-like polymers.
Figure II.10  The dependence on chain dimensions of the number of direct contacts [Eq. (24)] per macromolecule at the athermal percolation thresholds obtained from purely numerical calculations. Symbols and axis variables have the same meanings as in Fig. II.9. The broken lines indicate slopes of 1.0 and -0.13.
Numerically obtained results for pair and connectedness correlation functions at the percolation thresholds for athermal, finite diameter, flexible and rigid rod-like chain models are shown in Figs. II.11a, II.11b, and II.11c. These correlation functions are identical within the range of direct connectivity, i.e., for \( r < R = 2d \). For flexible coil-like molecules, the pair correlation function \( g(r) \) increases monotonically to unity on the length scale of the radius of gyration \( R_g \). Owing to the greater stiffness of rigid rod-like molecules, additional short range structure and more pronounced “solvation shells” are seen in the corresponding \( g(r) \). The chain length dependence of correlation functions on local length scales is significantly reduced in the case of rigid rod-like molecules, a phenomenon reflected in the weak dependence on chain length of the number of direct contacts at the threshold (Fig. II.10). Figure II.11c shows correlation functions for both coils and rods of similar major dimensions for purposes of comparison. The contact values of \( g(r) \) and \( h_1(r) \) increase significantly for the case of rigid rods, even though the site densities at the percolation threshold are much lower than for the case of coils. Physically, greater stiffness permits increased interpenetration and better molecular “packing” of rod-like molecules at small length scales.
Figure II.11a Solid and broken lines show, respectively, the radial distribution function $g(r)$ and connectedness correlation function $h_1(r)$ for athermal, finite thickness flexible coils from numerical calculations at the percolation threshold. For each set of curves, $N = 800, 3200,$ and $12800$, from top to bottom.
Figure II.11b The radial distribution function $g(r)$ and connectedness correlation function $h_1(r)$ for athermal rigid rods from numerical calculations at the percolation threshold. Symbols and lines have the same interpretations as in Fig. II.11a. For both sets of curves, $N = 40, 80,$ and $160$, from top to bottom.
Figure II.11c The radial distribution function $g(r)$ and connectedness correlation function $h_1(r)$ for flexible coils and rigid rods with similar molecular dimensions from numerical calculations at the percolation thresholds. Symbols and lines have the same interpretations as in Figs. II.11a and II.11b. For the rod-like and coil-like molecules, $N = 40$ and 1600, respectively, corresponding to rods of half-length $L/2 = 20 \, d$, and coils with radii of gyration $R_g = 21.07 \, d$. 
II.5 Concluding Remarks and Future Directions

Analytically tractable, approximate treatments for the PRISM equation based on the thread-like chain model and the string-like approximation to the connectedness Ornstein-Zernike equation have been developed and applied to calculate percolation thresholds for athermal one-component systems of flexible coil-like and rigid rod-like macromolecules. Numerical PRISM calculations in which the hard-core excluded volume constraint is explicitly enforced have been performed which yield results consistent with those from the simpler, coarse-grained, analytically tractable theoretical framework. The string-like approximation for the C-OZ equation has been extended to include attractive interactions within a molecular closure approximation used successfully in prior work \cite{15(b),21}. Corresponding numerical calculations using finite thickness chain models suggest that the heuristic approximations involved in this theoretical approach lead to qualitatively accurate results. A strong dependence on the molecular geometry of both the percolation threshold and the number of direct contacts necessary for percolation is described satisfactorily by the simplified model. The present work has focused attention on the simplest, linear, homopolymeric, one-component models in an effort to evaluate the approximate treatment under consideration.

Our findings suggest that similar, relatively simple, approximate treatments could be useful in understanding percolation in more complex macromolecular systems. The theoretical methodology developed in this work can be readily extended to study multiblock architectures as well as multicomponent systems. Situations of
particular interest to the present investigators include mixtures of flexible and rigid polymers, relevant to nanocomposite materials\textsuperscript{13,14}, which are the subject of the next chapter on two-component macromolecular systems. Generalizations to treat anisotropic molecules can be made by suitable modification of the form factor\textsuperscript{20}, and will permit a study of connectivity in systems oriented by either flow or external fields\textsuperscript{31}.

\section*{II.6 References}


CHAPTER III: 

Connectedness Percolation in Athermal Two-Component Mixtures of Flexible and Rigid Macromolecules
III.1 Abstract

A semi-analytic theory is developed for calculating percolation thresholds for rod-like nanoparticles dispersed in a flexible polymeric matrix. Methods of macromolecular integral equation theory are combined with the Connectedness Ornstein-Zernike equation and an explicitly two-component model in which both the molecules constituting the matrix as well as the filler species are accounted for. Numerical calculations in which the hard-core excluded volume constraint is explicitly enforced have been performed. Results for the rod percolation thresholds obtained from the analytical treatment are qualitatively similar to those from numerical calculations. In numerical calculations, results are also presented for a one-component model of identical rod-like particles in the absence of a matrix. The effects on the percolation threshold of explicitly including the matrix species are examined and compared with predictions based on an analogous approach which restricts attention to the rod-rod second virial coefficient. Explicit inclusion of the polymeric matrix does not alter the qualitative dependence of the percolation threshold on rod aspect ratio. However, accounting explicitly for the molecules constituting the matrix leads to a quantitative reduction of the critical volume fraction by a factor independent of the rod length. Although the present work focuses on the athermal situation (excluded volume interactions alone), the methodology developed in this account can be readily extended to model matrix-filler specific interactions as well.
III.2 Introduction

Nanoscopic rod-like\textsuperscript{1,2}, as well as disc-like\textsuperscript{3}, filler particles have been widely investigated for their role in enhancing the toughness\textsuperscript{2(a)} and shear modulus\textsuperscript{1,2(b)} of polymeric materials. Nanocomposites based on clay particles\textsuperscript{4}, functionalized silica\textsuperscript{5,6}, and cellulose nanocrystals\textsuperscript{1,2} have, among others, been the subject of recent experimental interest. The formation of percolating networks of reinforcing filler nanoparticles has been suggested as a probable mechanism for large enhancements in the shear modulus as a function of the filler volume fraction\textsuperscript{1,7,8}. Recent experiments\textsuperscript{9}, as well as molecular dynamics computer simulations\textsuperscript{10}, indicate that the nature of the interaction potential between the molecules constituting the matrix and the filler particle surface also affects the efficacy of filler-induced reinforcement. Experimental observations of the dependence of the composite shear modulus on filler particle volume fraction have frequently been interpreted in terms of effective medium theories\textsuperscript{8,11}, and of concepts drawn from percolation theory\textsuperscript{1,8,12}. A significant body of theoretical work has studied connectedness percolation in mixtures of penetrable and adhesive spheres\textsuperscript{13}, and one-component models of rod-like\textsuperscript{14} and flexible polymers\textsuperscript{15}. However, relatively few efforts have addressed more realistic, two-component descriptions in which the matrix polymers and filler particles are both accounted for. A preliminary study of the steric/entropic effects operative in such two-component systems, and how they affect the percolation thresholds of dispersed rod-like nanoparticles, is the subject of this investigation.
This study generalizes our previous work described in Chapter II to treat athermal two-component mixtures of rigid rod-like filler particles dispersed in a matrix of flexible coil-like molecules. The choice of appropriate form factors allows both matrix molecules and filler nanoparticles to be explicitly represented as nonspherical entities. A semi-analytic treatment of the two-component Polymer Reference Interaction Site Model (PRISM)\textsuperscript{16} and the Connectedness Ornstein-Zernike (COZ) formalism\textsuperscript{17,18} within the string-like approximation\textsuperscript{16,19} is developed in the present study. Numerical calculations in which the hard-core excluded volume constraint is explicitly enforced at all points interior to the hard-core diameter have been performed. The impact of matrix-filler specific interactions on the percolation threshold can be treated within the same framework and is the subject of an ongoing investigation. The theory developed in this account will permit more realistic modeling of the percolation threshold as a function of the filler particle geometry and surface chemistry, and the stiffness and architecture of the matrix molecules.

The remainder of this chapter is organized as follows. Section III.3.1 describes our application of analytic PRISM theory to calculating pair correlation functions in athermal mixtures of rod-like and flexible macromolecules. The COZ formalism, together with our approximate methods for determining the percolation threshold, are also discussed in Section III.3.1. Issues relevant to the chain models investigated using purely numerical techniques are discussed in Section III.3.2. Results from our analytic calculations for the percolation thresholds and contact values for the rod-coil and rod-rod pair correlation functions are presented in Section III.4.1, along with a
study of how these depend on the number density of coil-like molecules. Results from numerical calculations of the percolation thresholds and correlation functions are presented in Section III.4.2. Our account concludes with a summary and directions for ongoing and future investigations in Section III.5.

III.3 Models and Methods

III.3.1 Analytical Methods for Athermal Mixtures

III.3.1.1 Athermal String Polymer Reference Interaction Site Model (PRISM) Theory for Two-Component Systems

The present investigation employs the Polymer Reference Interaction Site Model (PRISM) to calculate correlation functions within an interaction site representation of macromolecules. Within this formalism, the site-averaged Ornstein-Zernike (OZ) equation for a mixture of homopolymers is\(^{16}\):

\[
\hat{h}_{MM'}(k) = \hat{\omega}_M(k) \left[ \hat{C}_{MM'}(k) \hat{\phi}_M(k) + \sum_{M''} \hat{C}_{MM''}(k) \rho_{M''} \hat{h}_{MM''}(k) \right] \tag{1}
\]

where the equivalent site approximation has been employed. In Eq. (1), \(\hat{h}_{MM'}\) and \(\hat{C}_{MM'}\) are Fourier transforms of the pair and direct correlation functions, respectively, and \(\rho_M\) and \(\hat{\omega}_M\) represent the site number density and intramolecular structure factors corresponding to species \(M\), respectively. Dimensionless site densities will be denoted by the symbols \(\Phi_{i,2}\), defined as: \(\Phi_i = \rho_i d_i^3\). In the present study, the intramolecular structure factors will be assumed known \textit{a priori}, as opposed to being...
calculated in a self-consistent fashion. We focus on two-component mixtures of flexible, Gaussian homopolymers (designated component “1”), and rigid rod-like filler nanoparticles (designated component “2”). Eq. (1) for two-component mixtures represents a set of three coupled equations. The present work focuses on the athermal situation, in which the only interactions between sites on distinct molecules are of the purely repulsive, excluded volume, type. The impact of attractive interactions on the percolation threshold is being investigated presently.

In view of our use of a coarse-grained, semi-analytical, procedure for calculating the pair and direct correlation functions, we adopt the following approximations for the molecular form factors:

\[
\hat{\omega}_1(k) = \frac{N_1}{N_1 \Gamma^2 k^2 d_{11}^2} + \frac{12}{1+\frac{12}{N_1 \Gamma^2 k^2 d_{11}^2}}, \text{ for all } k, \\
\hat{\omega}_2(k) = \frac{N_2}{N_2 \Gamma^2 k^2 d_{22}^2} + \frac{24}{1+\frac{24}{N_2 \Gamma^2 k^2 d_{22}^2}}, \text{ for } 0 < k < \frac{1}{N_2 \Gamma^2 d_{22}^2}, \\
= \frac{24}{25 k d_{22}^2}, \text{ for } \frac{1}{N_2 \Gamma^2 d_{22}^2} < k.
\]

In Eq. (2), \(N_{1,2}\) represent the number of interaction sites per polymer molecule (proportional to the contour length), \(d_{11,22}\) represent effective site diameters, and the statistical segment length \(\sigma\) of the flexible molecules is given in units of the site diameter by: \(\sigma = \Gamma d_{11}\). For all the calculations described in this account, we set \(\Gamma = 1\), i.e., \(\sigma = d_{11}\). The form factors for flexible coils and rigid rods expressed in Eq. (2)
have been used to investigate percolation in one-component systems which have been discussed in Chapter II.

In keeping with our interest in developing a semi-analytic theoretical treatment, this work adopts the athermal string closure\textsuperscript{16,19} for solving the two-component PRISM OZ equations. The closure approximation which defines the string-like model corresponds to a coarse-grained, spatially averaged, implementation of the widely used Percus-Yevick (PY) closure\textsuperscript{20}, which stipulates that: (i) $h_{ij}(r) = -1$ for $r < d_{ij}$, and (ii) $C_{ij}(r) = 0$ for $r > d_{ij}$ for athermal systems. Within the string-like model, the direct correlation functions are approximated as Dirac delta functions in position space with a cutoff at large wave vectors:

$$
\hat{C}_{ij}(k) = C_{ij}, \quad k < \frac{2\pi}{d_{11}},
$$

$$
= 0, \quad k > \frac{2\pi}{d_{11}}
$$

(3)

The strength parameters $\{C_{ij}\}$ are determined by imposing the repulsive excluded volume condition in the following coarse-grained manner:

$$
\int_{0}^{d_{ij}} dr r^2 \left[ 1 + h_{ij}(r) \right] = 0
$$

(4)

The approximations in Eqs. (3) and (4) have been employed in prior investigations of percolation in one-component systems of flexible, persistent, and rod-like molecules\textsuperscript{21,22}. The upper cutoff on the range of wave vectors is a technical approximation employed to ensure the convergence of integrals involving the form factor for rod-like particles. Our choice of the cutoff in Eq. (3) reflects the fact that the diameter of an individual site representing a monomer belonging to a flexible
molecule is the smallest length scale we can expect to model accurately in a coarse-grained manner. Results for the percolation threshold obtained from this approach as applied to one-component systems are in qualitative agreement with prior theoretical findings \(^{14(b),23}\), as well as with computer simulation experiments \(^{24}\) and have been presented and discussed in Chapter II of this thesis. In addition, the string-like model applied (within the compressibility route \(^{20}\)) to a system of flexible macromolecules alone provides an accurate semi-quantitative description of the thermodynamics of polymer solutions over the entire range of concentrations \(^{19}\). Additivity of the effective site diameters is assumed throughout \(^{20}\) this chapter, i.e., \(d_{ij} = (d_{ii} + d_{jj})/2\). Equations (1-4) provide a complete framework for determining the site-site pair correlation functions, which is the first step in our calculation of percolation thresholds. For a system composed exclusively of coil-like molecules with the form factors given by Eq. (2) and the closure approximation of Eqs. (3) and (4), the maximum site density corresponding to the incompressible limit (disappearance of the isothermal compressibility) occurs at (Ref.22 or Chapter II): \(\Phi_{1}^{\text{max}} = 1.438 / \Gamma^2\), within the compressibility route \(^{20}\).

The second virial coefficient is frequently a convenient measure of the effective two-body interactions between macromolecules. In this work, we investigate the effect of matrix-mediated interactions on the second virial coefficient between rod-like particles. The second virial coefficient, denoted \(B_2\), follows from McMillan-Mayer solution theory as \(^{25}\):
Eq. (5) has been employed in prior work\textsuperscript{26,27} to investigate the interaction between hard spheres induced by macromolecules.

For rod-like particles with large aspect ratios, the percolation threshold is anticipated to occur at relatively low volume fractions, comparable to those which characterize the nematic-isotropic transition calculated within Onsager theory\textsuperscript{23,28}. For sufficiently low rod concentrations, the rod-rod pair correlation function \( h_{22} (r) \) is expected to deviate little from its form in the limit of vanishing rod concentration.

With this circumstance in mind, the PRISM OZ equations are solved to determine the set of direct correlation parameters \( \{C_{ij}\} \) within three distinct schemes of approximation, reflecting the manner in which the concentration \( \rho_2 \) of sites representing the rod-like particles is accounted for:

(i) In the “zeroth-order” approximation, we evaluate the direct and pair correlation functions in the limit \( \rho_2 \rightarrow 0 \). The values of \( \{C_{ij}\} \) and \( h_{22} (r) \) obtained for a system of infinitely dilute rods are subsequently used to determine percolation thresholds even at finite, non-zero, rod concentrations. This approach corresponds to the Onsager approximation in the theory of liquid crystallinity\textsuperscript{28}, as it restricts attention to the rod-rod (and rod-coil) second virial coefficients.

(ii) In the “first-order” treatment, the \( \{C_{ij}\} \) and \( h_{22} (r) \) are determined through terms linear in the rod concentration for fixed values of the density of sites
representing coil-like molecules. The coefficients of the linear terms in an expansion of the \( \{C_{ij}\} \) in powers of \( \rho_2 \) for a fixed value of \( \rho_1 \) can be obtained from Eqs. (1-4) by way of numerical quadrature. This approximation goes beyond the Onsager treatment in that the rod-rod third virial coefficient is included explicitly, without introducing the necessity for an iterative solution of the coupled, nonlinear, PRISM OZ equations. Expressions for the zeroth and first-order terms in an expansion of the \( \{C_{ij}\} \) in powers of \( \rho_2 \) have been developed which reduce the problem to numerical quadrature, and these are presented in the appendix to this chapter.

(iii) In the “complete/full” calculation, multidimensional iterative Newton-Raphson methods are employed to solve for the \( \{C_{ij}\} \) numerically at the desired values of coil and rod site densities. These results are then used as inputs for calculating percolation thresholds. In the interests of brevity, this procedure will be referred to in following sections as our “full” method of calculation. A comparison of findings from this method with those obtained following procedures (i) and (ii) above will reveal the impact of accounting for third and higher-order rod-rod virial coefficients. The foregoing approximate treatments (i) and (ii) are significantly less cumbersome and time-consuming to implement, as only a single step of numerical integration is required. Consequently, if proven accurate in the athermal situation, these simpler procedures may provide convenient
starting points for subsequent work in which the attractive branch of the pair potential is included.

**III.3.1.2 Connectedness Ornstein-Zernike Equation**

For determining the percolation thresholds of rod-like particles, we employ a generalization of the usual Ornstein-Zernike equation which has been used in previous studies of hard and adhesive spheres, as well as macromolecular fluids. The connectedness Ornstein-Zernike (COZ) equation requires as inputs (i) the pair correlation functions for the liquid mixture, and, (ii) a geometric criterion for when two sites belonging to distinct molecules are assigned to the same physical cluster. The present work focuses on the percolation of rod-like particles dispersed in a matrix of flexible molecules, and hence we define connected clusters to include only sites belonging to molecules of species “2”. Specifically, we adopt the definition that a pair of sites belonging to distinct rod-like molecules is considered to be “directly” connected within the same cluster if and only if their center-to-center separation does not exceed a pre-assigned distance $R \equiv \lambda d_{22}$. Pairs of sites on different rods which are not “directly” connected may nevertheless be connected “indirectly” through the mediation of other sites, to which each member of such a pair is individually connected directly (see, e.g., Fig. 2 of Ref. 13(a)). The connectedness analog of the usual pair correlation function satisfies the COZ equation:

$$\hat{h}_1 (k) = \frac{\hat{\varphi}_2^2 (k) \hat{C}_1 (k)}{1 - \rho_2 \hat{\varphi}_2 (k) \hat{C}_1 (k)}$$  \hspace{1cm} (6)
where the subscripts “1” of $\hat{h}_1(k)$ and $\hat{C}_1(k)$ indicate that the pair and direct correlation functions are those appropriate to the connectedness problem. Equation (6) is identical in form to Eq. (7) of Chapter II. Note that the usual pair and direct correlation functions are denoted as $\hat{h}_g(k)$ and $\hat{C}_g(k)$, respectively. In Eq. (6), $h_1(r)$ represents the intermolecular pair correlation function for sites on distinct rods which are connected, either directly or indirectly, to the same physical cluster. In keeping both with preceding analytic work using the C-OZ formalism (see Ref. 22 or Chapter II), as well as the spirit of the approximation introduced in Eq. (3), the connectedness direct correlation function $\hat{C}_1(k)$ is approximated as:

$$
\hat{C}_1(k) = C_1, \quad k < 2\pi / d_{11}, \\
= 0, \quad k > 2\pi / d_{11}.
$$

(7)

The connectedness analog of the usual PY closure approximation, when combined with our criterion for identifying directly connected sites, stipulates that$^{14(b),31}$ (i) $h_1(r) = 1 + h_{22}(r) = g_{22}(r)$ for $R \geq r$, and (ii) $C_1(r) = 0$ for $r \geq R$. In this work, given the approximation for $\hat{C}_1(k)$ introduced in Eq. (7), and in view of our treatment of the direct correlation functions in Eq. (3), we do not enforce the connectedness PY closure in a pointwise manner. Instead, we determine the parameter $C_1$ by requiring that, on average, the regular and connectedness pair correlation functions yield the same number of directly connected sites located within the region $R \geq r$:
\[
\int_0^R r \, r^2 \left[ 1 + h_{22} (r) \right] = \int_0^R r \, r^2 \, h_1 (r). \tag{8}
\]

The above closure approximation for the COZ equation bears the same relationship to the connectedness analog of the PY closure as the string-like approximation [Eq. (4)] bears to the requirements imposed by the usual PY theory. The condition in Eq. (8), together with knowledge of the pair correlation function \( h_{22} (r) \), determines \( C_1 \) and \( h_1 (r) \). The percolation threshold is determined from the divergence of the mean connected cluster size, \( i.e., \) by the condition that \( \rho_2 N_2 C_1 = 1 \), as can be seen by inspecting the denominator of the right-hand-side of Eq. (6). The procedure followed in this context is precisely analogous to previous work (described in Chapter II) which investigated one-component fluids\(^{21,22}\). The novelty of the present study resides in the consideration of an explicitly two-component system, in which neither species is represented by spherical particles. Our use of the string-like model [Eq. (4)] for calculating \( h_{22} (r) \) implies that percolation by the rods is impossible unless \( R \) exceeds \( d_{22} \), as, for \( R = d_{22} \), Eqs. (4), (6), and (8) are satisfied trivially by setting \( C_1 = h_1 = 0 \).

It should be noted that our criterion for direct connectedness between sites on distinct molecules is based on purely structural, \( i.e., \) static, considerations, and the thresholds we calculate are those describing geometric percolation. This is to be contrasted with criteria which explicitly incorporate dynamics and trajectory information in the assignment of particles to a “connected cluster”\(^{32}\). Additionally, our condition that only sites representing rods participate in the formation of connected clusters is by no means the only choice possible. In principle, sites
representing the flexible coils (the matrix) can also be allowed to participate in cluster formation. Generalization of the present approach to account for clustering inclusive of rod-coil and coil-coil site proximity would require (i) specifying three range parameters $R_{ij}$ over which direct connectedness is established for rod-rod, rod-coil, and coil-coil site pairs, and, (ii) subsequent calculation of three sets of connectedness correlation functions. Such an extension of the criterion for when sites are considered to be directly connected will be relevant to modeling situations characterized by strong matrix-filler specific interactions.

### III.3.2 Numerical PRISM Calculations

In our numerical PRISM calculations, the methods used are similar to those in the one-component systems described in Chapter II, except that the PRISM OZ relations involve three coupled equations for two-component mixtures in contrast to a single equation for one-component systems.

The semiflexible coil-like molecules (species 1) considered in the present numerical work are modeled as overlapping bead chains whose form factor is specified by a bond length and bond bending energy. The bond length $l_1$ is chosen to be one-half of the species 1 site diameter $d_{11}$, and the bending energy is chosen such that the statistical segment length and species 1 site diameter are equal. The form factor is calculated from the Koyama distribution$^{33}$, which interpolates smoothly between Gaussian coil-like and rigid rod-like limits. These parameters have been previously shown to be approximately representative of polyethylene chains$^{34}$. The
rod-like molecules are likewise modeled as linear arrays of overlapping spherical beads, with a bond length $l_2 = 0.1 \; d_{22}$. The use of such an overlapping bead model corresponds to a less corrugated surface more closely representative of a cylindrical nanofiber. In those calculations which employ the two-component model, the site diameters are assigned the ratio: $d_{22} = 10 \; d_{11}$. This choice reflects frequently observed ratios between the segment lengths of flexible polymers and the typical diameter of cellulose nanofibers obtained by acid hydrolysis of woody materials\textsuperscript{1,2(a),12}. The number density of species 1 type monomers representing the semiflexible matrix is held fixed at $\rho_1 \; d_{11}^3 = 1.375$, which reproduces a value of the isothermal compressibility corresponding to an experimental melt-like density\textsuperscript{34}.

In all cases, the range of direct connectedness $R$ in our numerical calculations is chosen to be $R = 1.1d_{22}$. The present numerical calculations study percolation of rod-like particles both with and without an embedding medium of flexible polymers for purposes of comparison.

### III.4 Results and Discussion

#### II.4.1 Results from Analytical Methods

Results for the percolation thresholds for rods dispersed among flexible coils obtained from the zeroth order, first order, and full calculations are shown in Figures III.1 and III.2. In all cases, we have chosen the range parameter $R \equiv d_{22} + d_{11}$; two rods are considered directly connected if their surfaces are separated by a distance no
greater than the diameter of a coil monomer. The ratio of diameters of rod versus coil monomers, $d_{22}/d_{11}$, was arbitrarily chosen to be either 1 or 5 for the purpose of these illustrative calculations. The corresponding values of $\lambda$ ($\lambda \equiv R / d_{22}$) are 2 and 1.2, respectively. Our interest in rods with diameters greater than the thickness of the matrix coils arises from the typical dimensions of cellulose nanocrystals, which are frequently $\approx 10$ nm in width with lengths of up to $\approx 1 \mu$m$^{35}$. For all our calculations, the flexible matrix polymer consists of chains with $N_1 = 10^4$, for which the radius of gyration $R_g = (N_1/6)^{1/2} \Gamma d_{11} = 40.82 d_{11}$, corresponding to a semidilute crossover concentration$^{28} \Phi_1^* = 3 N_1 d_{11}^3 / (4 \pi R_g^3) = 0.035$.

Figures III.1 and III.2 show results for situations in which (i) the coils are at effectively infinite dilution, with concentrations $\Phi_1 << \Phi_1^*$, and, (ii) the coil site density is representative of that describing melt conditions, $\Phi_1 = 1.0 \approx 0.7 \Phi_1^{\text{max}}$. Our numerical procedure employing the full calculations (containing contributions to all orders in the rod concentration) with a matrix site density $\Phi_1 = 1.0$ for rods with $L < 25 d_{22}$ and $d_{22} = 5 d_{11}$ indicate that the percolation threshold $\Phi_2$ is such that the total volume fraction ($\Phi_1 + \Phi_2$) exceeds the “incompressible limit” for the two-component system (corresponding to vanishing isothermal compressibility). Vanishing of the isothermal compressibility is linked to divergences in the $\{ C_{ij} \}^{36}$, and thus our zeroth and first-order calculations do not exhibit this phenomenon for finite rod densities (see Appendix). Thus, our results for thick rods with aspect ratios < 25 for the case of a melt-like coil site density are drawn exclusively from the zeroth and first order approaches. Including the first order correction to the rod-rod pair correlation
function in powers of the rod concentration leads to markedly improved agreement with results from the full calculations. In all cases, increasing the concentration of coil-like molecules representing the matrix reduces the rod percolation threshold without significantly altering the dependence on rod length. This finding is consistent with the numerical PRISM calculations (discussed in the following section) in which the excluded volume constraint was implemented in a more literal manner, and reflects a “depletion attraction” between the rods induced by the molecules in the matrix. As might have been expected, the percolation threshold is lower for the case of rods with smaller diameters, which also exhibit stronger finite-size effects in the dependence of the percolation threshold on rod length.
Figure III.1  The diamonds, circles and triangles show, respectively, the percolation threshold $\Phi_{2,p}$ for rods dispersed in a matrix of flexible coils as a function of the rod length $L/d_{22}$ from full, first-order, and zeroth-order calculations. The connecting dotted lines are visual guides. Open and solid symbols indicate coil site densities $\Phi_1 = 10^{-5}$ and $\Phi_1 = 1.0$, respectively. The crosses show the percolation thresholds of a one-component system of rods alone. The solid line indicates a slope of $-1$. In all cases, $d_{22} = 5.0 \, d_{11}$ and $R = 1.2 \, d_{22}$. 

$$\text{Log}(\Phi_{2,p})$$

$$\text{Log}(L/d_{22})$$
Figure III.2  All symbols and lines have the same significance as in Figure III.1. In all cases, \( d_{22} = d_{11} \) and \( R = 2.0 \ d_{22} \).
The impact of coil concentration on the rod percolation threshold, and on the contact values of the pair correlation functions $g_{12}(d_{12})$ and $g_{22}(d_{22})$, is shown in Figs. III.3, III.4, and III.5. Explicit inclusion of the matrix has little effect on either the percolation thresholds or contact values at coil concentrations below the semidilute crossover\textsuperscript{38}. However, at coil concentrations above the semidilute crossover, the percolation threshold exhibits a monotonic decline with rising coil site number density. This trend is reflected in simultaneous increases in the contact values at the thresholds, regardless of the precise calculation procedure adopted. With increasing coil concentrations, sites forced into closer proximity adopt a more ordered, locally structured, arrangement, as found from numerical PRISM calculations (discussed in the following section) on finite diameter rod-coil mixtures. Results from similar calculations, showing the contact values at the percolation thresholds as functions of the rod length, are shown in Figs. III.6 and III.7. Increasing the concentration of coil-like molecules leads to enhanced clustering of both rod-rod and rod-coil site pairs. The contact value $g_{22}(d_{22})$ at the threshold is nearly independent of the rod length, consistent with the viewpoint that an infinite network is formed when there occur a fixed number of rod-rod contacts, irrespective of the aspect ratio of the filler species\textsuperscript{38}. 
Figure III.3  The diamonds, circles and triangles show, respectively, the percolation thresholds $\Phi_{2,p}$ of rods as a function of the coil site density $\Phi_1$, based on our full, first-order and zeroth-order calculations. The connecting dotted lines are visual guides. Open and solid symbols indicate results for $d_{22}=5.0 \ d_{11}$ and $R=1.2 \ d_{22}$, and for $d_{22}=d_{11}$ and $R=2.0 \ d_{22}$, respectively. In all cases, the rods are of aspect ratio $L/d_{22}=100$. The semidilute crossover concentration $\Phi_1^*=0.035$ is indicated by the arrow.
Figure III.4  The dependence on coil site densities of the radial distribution function $g_{12}$ at contact at the rod percolation thresholds based on the full, first-order, and zeroth-order calculations. Symbols and lines have the same interpretations as in Figure III.3.
Figure III.5  The dependence on coil site densities of the radial distribution function $g_{22}$ at contact at the rod percolation thresholds based on the full, first-order, and zeroth-order calculations. Symbols and lines have the same interpretations as in Figure III.4.
Figure III.6  The diamonds, circles and triangles show, respectively, the dependence on rod aspect ratio of the radial distribution function $g_{12}$ at contact at the rod percolation thresholds from full, first-order, and zeroth-order calculations. The connecting dotted lines are visual guides. Open and solid symbols correspond to coil site densities $\Phi_1 = 10^{-5}$ and 1.0, respectively. In all cases, $d_{22}=5.0$ $d_{11}$ and $R=1.2$ $d_{22}$. 
Figure III.7  The dependence on rod aspect ratio of the radial distribution function \( g_{22} \) at contact at the rod percolation thresholds from full, first-order, and zeroth-order calculations. All symbols and lines have the same meanings as in Figure III.6. In all cases, \( d_{22} = 5.0 \ d_{11} \) and \( R = 1.2 \ d_{22} \).
The rod-rod second virial coefficients at fixed rod length $L = 100d_{22}$ are shown in Fig. III.8 as a function of the coil density. For each choice of rod-coil diameter ratio, a minimum is observed near the coil semidilute crossover concentration, corresponding to the turning point on the curve of rod percolation threshold as function of $B_2$ (Fig. III.9). Similar results have been found in prior investigations of the polymer-induced interactions between hard spheres. $B_2$ is calculated from rod-rod pair correlation functions at zero wave vector and it involves contributions to $h_{22}(r)$ on all length scales, hence both the strength and range of the interactions play important roles in determining the behaviors of $B_2$. The minimum found in Fig. III.8 arises from a competition between two effects, (i) the coil-induced depletion attraction becomes stronger with increasing coil concentration as anticipated based on excluded-volume arguments, (ii) however, the range of the attraction is simultaneously diminished due to the decrease of the screening length with increasing coil concentration.
Figure III.8  Squares and diamonds show the rod-rod second virial coefficient as a function of coil density for the cases $d_{22}=5d_{11}$ and $d_{22}=d_{11}$, respectively. The values of $B_2$ are normalized with respect to the $B_2$ at zero coil density. In all cases, $N_1=10000$ and $N_2=100$. Solid lines are visual guides.
Figure III.9  Squares and diamonds show rod percolation thresholds as functions of rod-rod second virial coefficients for the cases $d_{22}=5d_{11}$ and $d_{22}=d_{11}$, respectively. The values of $B_2$ are normalized with respect to the $B_2$ at zero coil density. In all cases, $N_1=10000$ and $N_2=100$. Solid lines are visual guides.
### III.4.2 Results from Numerical Calculations

Results for the percolation thresholds of rod-like particles are shown in Fig. III.10 as a function of the rod aspect ratio. Rod-like particles with 100, 200, 400, 800, 1600, and 3200 beads per rod are investigated, corresponding to aspect ratios ranging from 10 to 320. The surfaces of sites belonging to different rods must approach to within a distance equal to the thickness of the matrix chains to be considered directly connected, a separation intended to mimic the length scales representing direct chemical interaction. The volume of a rod-like particle is calculated by treating it as a right circular cylinder with hemispherical ends. The semiflexible matrix molecules are modeled as having $N = 100$ beads per chain, a large enough degree of polymerization that finite-size effects in the coil-coil pair correlation functions are largely irrelevant at melt-like volume fractions. The explicit inclusion of semiflexible matrix molecules induces greater clustering, and thus lower percolation thresholds, for the rod-like particles. However, the dependence of this critical volume fraction on rod aspect ratio is nearly unaltered. The inverse dependence of critical volume fraction on rod length is consistent with prior results based on the analytical thread model (see Ref. 22 or Chapter II), and with Monte Carlo simulations on ellipsoidal particles$^{24(a)}$. Also shown in Fig. III.10 are the volume fractions at the dilute-semidilute crossover and isotropic-nematic transition as predicted by Onsager theory$^{28}$. Interpolation of our results for rods with an aspect ratio of 70 yields a critical volume fraction of approximately 1.4 %, within a factor of 2 of the value 1 % suggested in recent experiments on cellulose whisker reinforced matrices of
polystyrene-co-butyl acrylate$^{1,12}$. Deviations from the experimentally observed value could arise from our neglect of (i) specific interactions, particularly hydrogen bonds, and, (ii) polydispersity in the distribution of rod lengths, and, (iii) our very crude overlapping bead model for the matrix molecules.
Figure III.10 The volume fraction of rod-like particles at the percolation threshold as a function of the particle aspect ratio from numerical calculations. Diamonds and triangles show results from one-component and two-component (semiflexible matrix included) calculations, respectively. The broken lines are drawn with a slope of –1. The upper and lower solid lines indicate the rod volume fractions at the isotropic-nematic transition as predicted by Onsager theory, and at the semidilute crossover concentration, respectively.
The rod-rod, rod-coil, and coil-coil pair correlation functions, and rod-rod connectedness correlation functions calculated in the vicinity of the percolation threshold are shown in Figs. III.11 and III.12. The coil-coil correlation functions appear virtually identical for rods of large aspect ratio, for which the critical volume fractions are small. Additional structure is seen in the case of the shortest rods (aspect ratio 10), for which the rod volume fraction is large enough to affect the ordering of monomers belonging to the matrix. Similar remarks apply to the rod-coil pair correlations, which in all cases approach unity from below. The existence of such a “correlation hole” in the rod-coil distribution is consistent with the existence of a coil-mediated attraction between the rods which results in a reduced rod percolation threshold when compared to the one-component model. The 1-2 correlation hole has a range of a couple of monomer diameters, i.e., it is independent of and much smaller than the rod length, which explains why the observed impact on the rod percolation threshold does not alter the dependence on aspect ratio. The coil-induced attractive interactions also impact the rod-rod correlation functions, as evidenced by the significantly enhanced contact values found from the two-component model (Figs. III.11 and III.13). Noteworthy also is the oscillatory local solvation-shell structure found in the rod-rod correlation functions (Fig. III.11), reflecting ordering on the length scale of the monomers making up the matrix chains. Such ordering is completely absent from the analogous one-component model (Fig. III.13) at the relatively low volume fractions associated with the rod percolation threshold.
Figure III.11  The rod-rod pair and connectedness correlation functions for rod-like particles at the percolation threshold from the two-component model numerical calculations. For each set of correlation functions, the curves from top to bottom correspond to particles with aspect ratios of 10, 80, and 320.
Figure III.12  The coil-coil (broken lines) and rod-coil (solid lines) pair correlation functions from two-component model calculations at the rod percolation threshold. For each set of curves, from top to bottom, the rod aspect ratio equals 10, 80, and 320. The correlation functions for rods with aspect ratios of 80 and 320 are nearly identical in appearance.
Figure III.13  Curves have the same significance as in Fig. III.11, for calculations within the one-component model.
III.5 Concluding Remarks and Future Directions

An analytically tractable model has been developed for connectedness percolation in multicomponent macromolecular systems, and applied to athermal mixtures of rod-like and flexible polymers. Numerical PRISM calculations in which the hard-core excluded volume constraint is explicitly enforced have been performed for rod-like particles dispersed in a matrix of semiflexible linear homopolymers. Results for the percolation thresholds obtained from the analytical treatment are qualitatively similar to those derived from the more computationally intensive, literal enforcement of the PY closure approximation. The primary effect of including the matrix in the full, two-component, description is a reduction in the rod percolation thresholds in a manner which does not strongly alter the dependence on particle aspect ratio. This finding is consistent with a matrix-induced depletion attraction which operates on the length scale of the matrix segmental size. The present work creates a framework for studying polymer-particle nanocomposites which explicitly includes both the matrix and filler species.

The methodology developed in this account can be generalized in a number of directions, and provides a starting point for a detailed picture of geometric network formation in mixtures of non-spherical molecules. The impact on the percolation threshold of altering the stiffness of the matrix, which can be modeled by modifying the form factors in Eq. (2) to include variations in the persistence length, will be investigated, as also of accounting for specific interactions between matrix and filler sites. That the impact of accounting for specific interactions on the percolation
threshold can be complex and non-monotonic, and dependent on the range parameter $R$ as well as global phase behavior, has been demonstrated in a previous study of spherical particles\textsuperscript{39}. The relative efficacies of rod-rod versus rod-coil attractive interactions in promoting percolation at lower rod volume fractions are being studied presently. Results of such investigations bear on optimal strategies for the chemical modification of filler particle surfaces to achieve effective reinforcement at the lowest possible weight of added material. Though the present investigation has employed a purely equilibrium description of the fluid structure, future work will use the replica OZ formalism\textsuperscript{40} to investigate the role of truly equilibrated, versus quenched, matrix organization. Percolation by disc-like filler particles, which can model clay-based nanocomposites\textsuperscript{41}, as opposed to the rod-like particles representing fiber-based reinforcement studied in this account, can also be examined within the present approach. Systems in which the filler species have anisotropic orientational distributions have been studied previously within excluded volume models\textsuperscript{42}, and will be treated within the present approach by suitable generalizations of the form factor\textsuperscript{43}.

III.6 Appendix: Virial Expansion of the Pair and Direct Correlation Functions:

We define the sets of parameters $\{a_{ij}\}, \{b_{ij}\}$ in terms of the expansion of the direct correlation functions $\{C_{ij}\}$ in the following manner:

$$
\frac{C_{ij}}{d_{ij}} = a_{ij} + b_{ij} \Phi_2 + \ldots ,
$$

(A.1)
to first order in the rod site density. The Taylor expansions in Eq. (A.1) are used with the PRISM-OZ Eq. (1) to express the \( \{ \hat{h}_{ij}(k) \} \) through first order in \( \Phi \):

\[
\frac{\hat{h}_{11}}{d_{11}^3} = \frac{\hat{\omega}^2_1 a_{11}}{[1 - \Phi_1 \hat{\omega}_1 a_{11}]} + \Phi_2 \left[ \frac{\hat{\omega}^2_1 b_{11}}{1 - \Phi_1 \hat{\omega}_1 a_{11}} + \frac{a_{11} \Phi_1 \hat{\omega}^3_1 b_{11}}{(1 - \Phi_1 \hat{\omega}_1 a_{11})^2} + \alpha a_{12} \hat{\omega}^2_1 \hat{\omega}_2 + \frac{\alpha}{(1 - \Phi_1 \hat{\omega}_1 a_{11})^2} \right] + \ldots, \tag{A.2}
\]

\[
\frac{\hat{h}_{12}}{d_{12}^3} = \frac{\hat{\omega}_1 \hat{\omega}_2 a_{12}}{1 - \Phi_1 \hat{\omega}_1 a_{11}} + \Phi_2 \left[ \frac{b_{12} \hat{\omega}_1 \hat{\omega}_2}{1 - \Phi_1 \hat{\omega}_1 a_{11}} + \frac{a_{12} \hat{\omega}_1 \hat{\omega}_2 (a_{12} - \Phi_1 \hat{\omega}_1 (a_{11} a_{22} - \alpha a_{12}))}{(1 - \Phi_1 \hat{\omega}_1 a_{11})^2} \right] + \ldots, \tag{A.3}
\]

and:

\[
\frac{\hat{h}_{22}}{d_{22}^3} = \hat{\omega}^2_2 \left[ \frac{a_{22} - \Phi_1 \hat{\omega}_1 (a_{11} a_{22} - \alpha a_{12})}{1 - \Phi_1 \hat{\omega}_1 a_{11}} \right] + \Phi_2 \hat{\omega}^2_2 \left[ \frac{1}{(1 - \Phi_1 \hat{\omega}_1 a_{11})^2} \right] + \ldots, \tag{A.4}
\]

where \( \alpha \equiv d_{12}^6 / (d_{11}^3 d_{22}^3) \). The string-like closure conditions [Eq. (4)] are then used to determine the \( \{ a_i \} \) and \( \{ b_i \} \), and thereby the \( \{ C_{ij} \} \) to first order in \( \Phi_2 \). After Fourier transforms have been taken, Eq. (4) takes the form:
\[
1 + \frac{3}{2 \pi^2} \int_{0}^{2\pi} d k_1 \left[ \hat{h}_{ij}(k_1) \right] \left[ \sin\left( k_1 d_{ij} / d_{11} \right) - \left( \frac{k_1 d_{ij}}{d_{11}} \right) \cos\left( k_1 d_{ij} / d_{11} \right) \right] = 0,
\]

(A.5)

where \( k_1 \equiv k d_{11} \). Substitution of Eqs. (A.2-4) into Eq. (A.5) shows that the \( \{a_{ij}\} \) and \( \{b_{ij}\} \) can be determined sequentially through numerical integration, by imposing the condition that Eq. (A.5) is satisfied to each order in \( \Phi_2 \) for each of the correlation functions \( \hat{h}_{ij} \).

### III.7 References


CHAPTER IV:

Chain Orientation and Extension in Steady Shear Flow
IV.1 Abstract

A generalization of the linear bead-spring model for the dynamics of flowing homopolymer solutions is presented, in which finite chain extensibility effects are accounted for through a self-consistent determination of the coil dimensions under shear. Hydrodynamic interactions are included within the pre-averaged Zimm approximation. Results are presented for the chain orientation angle and extension ratio under shear. Inclusion of the hydrodynamic interaction leads to semi-quantitative agreement with experimental measurements of the coil deformation factor for polystyrene (PS) in dioctyl phthalate (DOP).
IV.2 Introduction

Flexible polymer chains under steady shear flow undergo deformation and orientation owing to hydrodynamic forces. The spherical symmetry of the radius of gyration tensor of an isolated flexible macromolecule under quiescent (shear-free) conditions is distorted into an approximately ellipsoidal structure when subject to shear flow\(^1\). Knowledge of the stretching and orientation of linear polymer chains under shear is essential to understanding the macroscopic flow behavior of polymeric liquids. The process of chain deformation has been studied extensively within the Rouse (free draining) and Zimm (non-draining) models\(^2,3\) for polymer dynamics, as well as in experiments using flow light scattering techniques\(^4-6\). Models incorporating finite extensibility, which recognize the upper limit imposed by the chain contour length, have been investigated using analytical theory\(^7\) and computer simulations\(^8\). Inclusion of finite-extensibility effects\(^7\) within the free-draining Rouse model for chain dynamics\(^9\) has been shown to permit semi-quantitative agreement with measurements on fluorescently-labelled DNA molecules\(^10\). The present work quantifies the deformation of flexible polymer chains in a sheared solution through modified bead-spring models which incorporate finite-extensibility effects both with and without pre-averaged hydrodynamic interactions. Our results are compared with light scattering measurements\(^4,5,6\) on polystyrene (PS) in dioctyl phthalate (DOP).

Information on the extension and orientation of polymer chains predicted from the present work is a necessary preliminary step for the investigation of shear induced effects on the miscibility of polymer solutions and blends, which are discussed in
Chapter V and VI. Our theoretical model is described in Section IV.3, results obtained from model calculations are presented and compared with experiments in Sec. IV.4.

### IV.3 Theory

We incorporate finite extensibility in our bead-spring model through a self-consistent determination\(^7\) of the effective spring constant \(k\). The effective spring constant is determined by enforcing an upper bound on the degree of possible coil extension\(^7\). Though there is no unique method for constructing such a description, and the present treatment does not lay claim to rigor, the essential results from different implementations of this idea are similar and the model provides a vehicle for quantifying this important physical phenomenon. The effective spring constant \(k\) is related to a shear-rate and chain conformation-independent spring constant \(k_0\) through the function \(b\), defined as:

\[
b = \frac{1 - \alpha}{1 - z} = \frac{k}{k_0},
\]

where \(\alpha\) and \(z\) are, respectively:

\[
\alpha \equiv \frac{\langle R^2 \rangle_0}{\langle R^2 \rangle_m}, \quad \text{and} \quad z \equiv \frac{\langle R^2 \rangle}{\langle R^2 \rangle_m}.
\]

In Eq. (2), \(\langle R^2 \rangle\) is the mean square end-to-end distance of the chain at a given shear rate, \(\langle R^2 \rangle_0\) is the mean square end-to-end distance in the absence of shear, and \(\langle R^2 \rangle_m\) is the maximal value of the mean square end-to-end distance at high shear.
rates. The ansatz in Eqs. (1) and (2) is motivated by recent work within the Rouse model\(^7\), which reported semi-quantitative agreement with experimental results\(^{10}\) for sheared solutions of DNA. Theta conditions are assumed throughout this work, \textit{i.e.}, ideal chain statistics describe the shear-free state. This functional form for the effective spring constant is motivated by the finitely extensible nonlinear elastic (FENE) model\(^7, 11\) for linear polymers. Equations (1) and (2) relate the effective spring constant \(k\) self-consistently to the chain extension ratio under shear. The effective segment length, \(\sigma\), is related to the segment length, \(\sigma_0\), in the absence of shear by: \(\sigma^2 = \sigma_0^2 / b\). \(N\) denotes the number of beads per chain, proportional to the contour length or degree of polymerization. The parameter \(\alpha\) introduced in Eq. (2) specifies the ratio of quiescent to maximal observed values of the mean square end-to-end distance. In the spirit of earlier work\(^7\), we treat \(\alpha\) as an empirically adjusted fitting parameter, as opposed to calculating it directly from the contour length\(^3\). (Light-scattering experiments for extensional flows\(^{12}\) suggest that, even at high shear rates, individual chains may not undergo full stretching up to the limit imposed by the contour length). The usual, strictly harmonic, formulations of the Rouse and Zimm models are recovered by equating \(b\) to unity.

The overdamped Langevin equations describing the chain dynamics written in terms of the Rouse normal modes\(^2, 7, 9\), defined as:

\[
X_p(t) = \frac{1}{N} \int_0^N dn \cos \left( \frac{pn}{N} \pi \right) R_n(t), \quad p = 0, 1, 2, \ldots, (N-1),
\]  

(3)
where \( R_n(t) \) are the instantaneous bead co-ordinates and \( p \) indexes the normal modes, take the form:

\[
\dot{X}_p + \frac{k_p}{\zeta_p} X_p - \hat{\kappa} \cdot X_p = \frac{1}{\zeta_p} f_p ,
\]

(4)

where \( \hat{\kappa} \) is the velocity gradient tensor, \( f_p \) a random force, and \( k_p \) and \( \zeta_p \) are force and friction constants associated with the \( p^{th} \) normal mode, respectively. We employ the notation of Ref (2). For steady shear flow, where \( \hat{\kappa}_{ij} = \dot{\gamma} \delta_{ij} \), the steady-state normal mode correlations satisfy:

\[
\langle X_{pa}^2 \rangle = \frac{k_B T}{k_p} + \frac{1}{2} \left( \frac{k_B \dot{\gamma}}{k_p} \right)^2 \delta_{axx} \quad \text{and} \quad \langle X_{ax} X_{px} \rangle = \frac{k_B k_p \dot{\gamma}}{2k_p^2},
\]

(5)

where \( k_p = 2k_0 \frac{\pi^2 p^2}{N} \), and \( k_0 = \frac{3k_B T}{\sigma_0^2} \).

In the present model, the shear-rate independent spring constant \( k_0 \) is replaced by the effective spring constant \( k \) as described above. Consequently, \( k_p \) becomes:

\[
k_p = \frac{6k_B T b \pi^2 p^2}{\sigma_0^2 N} .
\]

(6)

For the free-draining Rouse model, the transformed friction coefficient \( \zeta_p \) is:

\[
\zeta_p = 2N\zeta ,
\]

(7)

where \( \zeta \) is the friction coefficient for a single bead. For the Zimm model, in which hydrodynamic interactions are accounted for in a pre-averaged sense, \( \zeta_p \) is:

\[
\zeta_p = \eta_s \sqrt{12\pi^3 N \sigma_0^2 p} ,
\]

(8)
where $\eta_s$ is the solvent viscosity. The components of the mean-square end-to-end vector and mean-square radius-of-gyration tensors are, respectively:

$$\langle R\beta R\beta \rangle = 16 \sum_{p=1,3,5} \langle X_{p\alpha} X_{p\beta} \rangle, \quad \text{and} \quad \langle S\alpha S\beta \rangle = 2 \sum_{p=1}^{\infty} \langle X_{p\alpha} X_{p\beta} \rangle. \quad (9)$$

We express our results in terms of the dimensionless shear rate $\beta$, defined as:

$$\beta \equiv \left[ \frac{\eta_s M \dot{\gamma}}{N_A k_B T} \right], \quad (10)$$

where $[\eta]$ is the intrinsic viscosity, $M$ the polymer molecular weight, and $N_A$ is Avogadro’s number. Within the present linear bead-spring model, the intrinsic viscosity is:

$$[\eta]^{\text{Rouse}} = \frac{N_A N^2 \zeta \sigma_0^2}{36 M \eta_s b}, \quad \text{and} \quad [\eta]^{\text{Zimm}} = \frac{0.425 N_A \left( N \sigma_0^2 b \right)^{3/2}}{M}, \quad (11)$$

where the factor $b$ modifying the effective spring constant is yet to be determined.

Equation (11) reveals the following relationships between the values of the dimensionless shear-rate variable $\beta$ and $\beta_0$, calculated respectively with and without the present adjustment for finite chain extensibility:

$$\beta^{\text{Rouse}} = \beta_0 b^{-1} \quad \text{and} \quad \beta^{\text{Zimm}} = \beta_0 b^{-3/2}. \quad (12)$$

Self-consistent determination of the factor $b$ modifying the effective spring constant follows from Eqs.(1), (2), (5), and (9), and leads to the following equations for determining $b$ in terms of the dimensionless shear rate variable $\beta_0$ and the extensibility parameter $\alpha$:

$$b^3 - b^2 - 0.2 \beta_0^2 \alpha = 0, \quad \text{Rouse Model},$$
and:

\[ b^4 - b^3 - 0.0797 \beta_0^2 \alpha = 0, \quad \text{Zimm model.} \quad (13) \]

**IV.4 Results and Discussion**

We define the chain extension ratio, \( e \), as:

\[
e = \sqrt{\frac{\left\langle R_g^2 \right\rangle_\beta}{\left\langle R_g^2 \right\rangle_0}},
\]

(14)

where \( \left\langle R_g^2 \right\rangle_\beta \) is the mean-square radius of gyration under shear flow. Recent flow light scattering experiments\(^4,5,6\) on solutions of PS in DOP have shown that the simple Rouse and Zimm models without correction for finite chain extensibility significantly over-predict the degree of chain extension. Equations (1), (2), (5), (9), (13), and (14) show that the chain extension is given by:

\[
e_{\text{Rouse}}^2 = \frac{1}{b} \left[ 1 + 0.152 \left( \frac{\beta_0}{b} \right)^2 \right]
\]

and:

\[
e_{\text{Zimm}}^2 = \frac{1}{b} \left[ 1 + 0.0617 \left( \frac{\beta_0^2}{b^3} \right) \right],
\]

(15)

where \( b \) is determined from Eq.(13) as a function of shear-rate and the parameter \( \alpha \). Existing results\(^2,13\) are recovered by equating \( b \) to unity in Eqs.(11) and (15).

Results based on the present treatment of the chain extension ratio calculated using both the Rouse and Zimm hydrodynamic models are compared with experimental measurements\(^4,5,6\) on PS in DOP in Fig. IV.1. The extensibility
parameter $\alpha$ has been treated as an adjustable fitting parameter for the purpose of these calculations. The dimensionless shear rate variable $\beta_0$ used as the horizontal axis variable has been calculated using the intrinsic viscosity at zero shear rate, when $b \to 1$. Predictions based on the usual formulation of the strictly harmonic Rouse and Zimm models\textsuperscript{2, 9} substantially over-predict the chain deformation, consistent with previous findings\textsuperscript{4,5, 6}. However, accounting for the finite chain extensibility leads to improved agreement with the experiments, particularly when the hydrodynamic interactions are accounted for, albeit within the pre-averaging approximation. It is believed that, at higher shear rates, the impact of hydrodynamic interactions is weakened\textsuperscript{14} and the chain dynamics become more closely “Rouse-like”. Such a crossover from Zimm to Rouse model-like dynamics may partially explain remaining discrepancies in the comparison shown in Fig. IV.1, and is under current investigation.
Figure IV.1 The coil extension ratio under shear, $e$ [Eq.(14)], as a function of dimensionless shear rate $\beta_0$. The broken and solid lines show results from the Rouse and Zimm hydrodynamic models, respectively, with and without the finite chain extensibility accounted for. Calculations within the Rouse model employ the strictly harmonic (“conventional”) model, and $\alpha = 0.45$ and 0.6. Calculations within the Zimm model likewise employ the strictly harmonic (“conventional”) model, and $\alpha = 0.3$ and 0.55. The filled triangles and squares represent flow light scattering measurements$^{4,5,6}$ on solutions of PS of molecular weights $3 \times 10^6$ and $10^7$, respectively, in DOP.
In the present work, $\alpha$ has been treated as an adjustable parameter to obtain the best fit to experimental data for PS in DOP at relatively low shear rates. Our values for $\alpha$ are about 3-6 times larger (corresponding to weaker maximal chain distortion) than those found appropriate in an earlier work\(^7\) which examined the stretching of DNA molecules at higher dimensionless shear rates. It is conceivable that extension of our results to treat experiments over a wider range of $\beta_0$ could lead to a fitted value for $\alpha$ which would correspond more closely to full extension towards the contour length under high shear conditions.

The orientation angle $\chi$ of the coils under flow is calculated from\(^{13}\):

$$\tan 2\chi = \frac{2G_{21}}{G_{11} - G_{22}},$$

where $G_{ij}$ are elements of the mean-squared radius-of-gyration tensor. Equations (5), (9), (13), and (16) lead to the following expressions for the orientation angle $\chi$:

$$\chi = \frac{\pi}{4} + \frac{1}{2} \arctan \left( \frac{\beta}{1.7454} \right),$$

Rouse model, and:

$$\chi = \frac{\pi}{4} + \frac{1}{2} \arctan \left( \frac{\beta_0}{1.7454b} \right),$$

Zimm model,

where $b$ is determined from Eq. (13). Calculations of the orientation angle as a function of applied shear-rate from Eqs. (13) and (17) are compared with experimental measurements\(^4,5,6\) on PS in DOP in Fig. IV.2. The values of the parameter $\alpha$ used in these calculations are the same as those employed for the chain extension ratio calculations shown in Fig. IV.1. This comparison reveals that the improved description of the coil extension ratio which is made possible by accounting for finite
chain extensibility comes at the expense of a less accurate, though still qualitatively correct, prediction for the coil orientation. Nevertheless, a more accurate, semi-quantitative description of the coil extension under shear is of interest in understanding the thermodynamics of flowing polymer solutions and blends, as the number of near-neighbor contacts and cohesive energy are intimately related to the coil geometry.
Figure IV.2  The coil orientation angle $\chi$ as a function of dimensionless shear rate $\beta_0$. All symbols have the same significance as in Fig. IV.1.
IV.5 References


CHAPTER V:

Shear-Induced Effects on Miscibility in Polymer Solutions
V.1 Abstract

Methods of macromolecular integral equation theory are employed to calculate the correlation functions of flexible linear homopolymers deformed by shear flow. The extent of coil deformation is calculated from bead-spring models which include corrections for finite chain extensibility and pre-averaged hydrodynamic interactions. The spinodal boundaries for sheared polymer solutions are obtained from the compressibility route under conditions of constant strain rate. It is shown that accounting for changes in the cohesive energy arising from flow-induced coil deformation may lead to non-monotonic shifts in the cloud point as a function of strain rate, even in the absence of nonlinear viscoelastic response. Our model calculations are compared with recent experimental measurements of the cloud point for sheared solutions of polystyrene (PS) in dioctyl phthalate (DOP).
V.2 Introduction

It has been known for a number of years that subjecting polymer solutions to shear or extensional flow regimes can have significant effects on their miscibility\textsuperscript{1-8}. Substantial shifts in the cloud point have been reported for sheared polymer solutions\textsuperscript{1-4} and blends\textsuperscript{5-8}. In some instances, the direction of the change is reported to be a non-monotonic function of the rate of strain\textsuperscript{2, 5, 8}. Complex, butterfly-like scattering patterns observed under flow\textsuperscript{9} have been related to the coupling of thermodynamic fluctuations to hydrodynamic modes of the fluid\textsuperscript{10}. The deformation of individual macromolecules under flow has been investigated in recent light-scattering experiments\textsuperscript{11,12}, and related to predictions for linear bead-spring models with and without hydrodynamic interactions or corrections for finite chain extensibility (Chapter IV or Ref.[13]). An understanding of flow-induced demixing (or mixing) is relevant to polymer processing applications, in order to forestall undesirable phase separation within pipelines. A substantial body of extant work has addressed this phenomenon from the standpoints of both thermodynamics\textsuperscript{2, 14-17} and kinetic mode-coupling theories\textsuperscript{10, 18-21}. The present account examines flow-induced miscibility changes in polymer solutions from a microscopic thermodynamic approach, which accounts for factors neglected in previous work within similar frameworks.

A widely used starting point in previous work on flowing polymer solutions within the thermodynamic approach has been the classical Flory-Huggins calculation of the free energy of mixing\textsuperscript{22}. This free energy of mixing, representing the quiescent,
shear-free, condition, has been augmented by an additional term representing the work involved in molecular deformation due to flow\textsuperscript{23}. The precise formulation of the flow-induced contribution to the free energy has been motivated by (i) calculations on harmonic chain models, and (ii) general arguments based on the thermodynamics of irreversible processes\textsuperscript{23}. Similar research using bead-spring models has investigated the storage of energy in different chain normal modes\textsuperscript{24}, in an effort to understand the preferred loci for shear-induced chain scission. Such an approach fails to include the impact of coil deformation on the cohesive energy, \textit{i.e.}, the fact that deformed molecules organize differently and the altered spatial correlations may affect the $\chi$-parameter irrespective of effects explicitly linked to the flow field. The present work employs methods of macromolecular integral equation theory\textsuperscript{25} to calculate correlation functions associated with flexible polymers under flow, and thereby estimates the strength of such “coupling” effects in modifying the phase behaviour. The deformation of flexible linear polymers is described within a generalization of the Rouse model which incorporates the constraint of finite extensibility (Chapter IV or Ref.[13]).

It should be emphasized at the outset that quantitative explanation of the complex, lobed scattering patterns exhibited by polymer solutions at high shear rates likely requires a non-equilibrium kinetic as opposed to thermodynamic approach\textsuperscript{10}. Nevertheless, an investigation of the purely thermodynamic treatment remains a complementary avenue which is not without interest. Our primary focus is the potential role of changes in the cohesive energy density induced by chain deformation.
under flow. For this reason, only the simplest models for the solution viscosity will be employed. In particular, the solution viscosity is treated as a linear function of the polymer concentration, and the concentration dependence of hydrodynamic screening$^{23}$ is not included in our model for the intrinsic viscosity.

The remainder of this chapter is organized as follows. Section V.3 describes the theoretical methods and models employed in this investigation. In Section V.3.1, the deformation of flexible, linear, polymer chains subject to shear flow is treated within the bead-spring Rouse and Zimm models adjusted for finite chain extensibility. The Polymer Reference Interaction Site Model (PRISM)$^{25}$ is employed in Section V.3.2 to calculate the free energy density of ellipsoidally deformed polymer chains interacting through a square well potential. All model calculations are performed within the coarse-grained thread-like chain approximation, which permits an analytic treatment for the present problem. Section V.4 presents predictions from our model examining the impact of hydrodynamic interactions and finite chain extensibility, and also a comparison to an experimental study of the flow-induced miscibility changes$^4$ for solutions of polystyrene (PS) in dioctyl phthalate (DOP). Generalizations to treat polymer blends are the subject of Chapter VI.

**V.3 Theories and Models**

**V.3.1 Chain Extension Under Shear Flow**

The results for shear-induced chain extension and orientation from Rouse and Zimm models with and without finite chain extensibility accounted for have been
discussed in Chapter IV, and only a brief summary is included in the present account for completeness. Finite extensibility is incorporated in the conventional bead-spring Rouse and pre-averaged Zimm models through the self-consistent determination of an effective spring constant \( k \). The effective spring constant \( k \) is related to a shear-rate and chain conformation-independent spring constant \( k_0 \) through the function \( b \), defined as (Chapter IV or Ref. [13,26]):

\[
b = \frac{1 - \alpha}{1 - z} = \frac{k}{k_0},
\]

where \( \alpha \) and \( z \) are, respectively:

\[
\alpha = \frac{\langle R^2 \rangle_0}{\langle R^2 \rangle_m}, \quad \text{and} \quad z = \frac{\langle R^2 \rangle_0}{\langle R^2 \rangle_m}.
\]

\( \langle R^2 \rangle \) is the mean square end-to-end distance of the chain at a given shear rate, \( \langle R^2 \rangle_0 \) is the mean square end-to-end distance in the absence of shear, and \( \langle R^2 \rangle_m \) is the maximal value of the mean square end-to-end distance in the limit of high shear rates. The extent of chain deformation is determined by the shear rate, polymer molecular weight, and solvent viscosity. These factors are included in a dimensionless shear rate defined by:

\[
\beta = \frac{[\eta] \eta \gamma}{N_A k_B T},
\]

where \([\eta]\) is the intrinsic viscosity, \( M \) the polymer molecular weight, and \( N_A \) Avogadro’s number. Our results are throughout expressed in terms of this dimensionless shear rate, which is a product of the rate of strain and longest intramolecular relaxation time. Values of the dimensionless shear rate \( \beta \) and \( \beta_0 \)
calculated respectively with and without the finite chain extensibility adjustment are related as follows:

\[ \beta_{\text{Rouse}} = \beta_0 b^{-1} \quad \text{and} \quad \beta_{\text{Zimm}} = \beta_0 b^{-3/2} \tag{4} \]

Results for the conventional Rouse and Zimm models are recovered when either \( b = 1 \) or, equivalently, \( \alpha = 0 \). The parameter \( \alpha \) governs the extent of coil deformation for a given strain rate, and can be reasonably expected to depend upon microscopic details of the chain chemistry and its hydrodynamic interaction with the solvent. As in the previous study (Chapter IV or Ref.[13]), this work treats \( \alpha \) as an empirically adjustable parameter.

Within such a linear bead-spring model, planar shear flow distorts the radius of gyration tensor into an ellipsoidal distribution with three unequal semi-axes. We define the statistical segment length under shear-free conditions, denoted \( \sigma_0 \), through the relationship: \( \langle R_g^2 \rangle_0 = N\sigma_0^2 / 6 \). Under planar shear flow, the principal axes of the distorted ellipsoidal radius of gyration tensor are described by the following effective segment lengths parallel and perpendicular to the direction of maximal extension (Chapter IV or Ref. [13]):

Rouse: \( \sigma_z = \sigma_0 \left\{ 1 + 0.228 \beta^2 + \left( 0.1593 \beta^2 + 0.052 \beta^4 \right)^{1/2} \right\}^{1/2} b^{-1/2} \)

\[ \sigma_\perp = \sigma_0 \left\{ 1 + 0.228 \beta^2 - \left( 0.1593 \beta^2 + 0.052 \beta^4 \right)^{1/2} \right\}^{1/2} b^{-1/2} \]

Zimm: \( \sigma_z = \sigma_0 \left\{ 1 + 0.0926 \beta^2 + \left( 0.0689 \beta^2 + 0.008556 \beta^4 \right)^{1/2} \right\}^{1/2} b^{-1/2} \)
In Eq. (5), $\sigma_\perp$ is the geometric mean of the segment lengths in the transverse plane, i.e., $\sigma_\perp = \sqrt{\sigma_x \sigma_y}$. This choice allows us to model the deformed chains as ellipsoids of revolution, while the volume of an individual coil remains that predicted from the model with three unequal principal moments of inertia. It should be noted that this model based on an ellipsoid of revolution represents an additional approximation. Flow light scattering experiments indicate that, while one of the three semi-axes is indeed deformed to a much greater extent than the other two, the three semi-axes are in fact all unequal. For brevity, we refer to the Rouse and Zimm models with the present finite extensibility adjustments as the Rouse-FE and Zimm-FE models, respectively.

**V.3.2 Thread PRISM Theory for Anisotropic Polymer Solutions**

Our starting point is the athermal thread Polymer Reference Interaction Site Model (PRISM) for polymer solutions. An attractive pair potential of the square well type is employed in our calculation of the phase diagram. Within this approach, the site-averaged Ornstein-Zernike equation for a one-component homopolymer fluid is:

$$\hat{h}(k) = \hat{\omega}(k)\hat{C}(k)\left[\hat{\omega}(k) + \rho_m \hat{h}(k)\right] = \hat{\omega}(k)\hat{C}(k)\hat{S}(k)$$

(6)
where \( \hat{h}(k) \) and \( \hat{C}(k) \) represent the Fourier-transformed site-site intermolecular total and direct correlation functions, respectively, \( g(r) = 1 + h(r) \) is the corresponding intermolecular radial distribution function, \( \rho_m \) the site number density, and \( \hat{\omega}(k) \) the single-chain structure factor normalized such that \( \hat{\omega}(k = 0) = N \), where \( N \) is the number of interaction sites per polymer chain. The present work employs an effective one-component model, in which the solvent molecules are not represented explicitly. For describing polymer solutions in which individual molecules are deformed by flow, we adopt an analytic approximation for \( \hat{\omega}(k) \), appropriate for anisotropic, ellipsoidally distorted Gaussian chains:

\[
\hat{\omega}(k) = \frac{N}{1 + \frac{N\sigma_z^2 k_z^2}{12} + \frac{N\sigma_i^2 k_i^2}{12}}. 
\]  

(7)

Such an approximation has been employed in previous investigations of nematic ordering in polymer fluids\(^{27}\), and permits an analytic treatment. In the coarse-grained thread approximation, the athermal direct correlation function is represented by a \( \delta \)-function at the origin in position space with an amplitude parameter \( C_0^{\text{ath}} \), i.e. \( C^{\text{ath}}(r) = C_0^{\text{ath}} \delta(r) \). Fourier transformation yields: \( \hat{C}^{\text{ath}}(k) = C_0^{\text{ath}} \). Athermal conditions are denoted by the superscript “\( \text{ath} \)” throughout this account. The parameter \( C_0^{\text{ath}} \) is chosen to satisfy the core condition:

\[
\frac{1}{(2\pi)^3} \int d\vec{k} \, \hat{h}(\vec{k}) = -1, 
\]  

(8)
corresponding to the requirement that \( g( r = 0 ) = 0 \). The hard core excluded volume constraint is thus implemented in a point-wise fashion. For the \( \hat{\rho}(k) \) in Eq. (7), the reference thread total and direct correlation function are given respectively by:

\[
g^{\text{ath}}(r) = 1 + \frac{3}{\pi \rho_m \sigma^2 \sigma_z} \left( \frac{\sigma_0}{r'} \right) \left( e^{-r' / \sigma_x} - e^{-r' / \sigma_z} \right)
\]

(9)

\[
\hat{C}^{\text{ath}}(k) = C_0^{\text{ath}} = -\frac{\pi \sigma^2 \sigma_z}{3 \sqrt{3} N} - \frac{\pi^2 \rho_m \left( \sigma^2 \sigma_z \right)^2}{108},
\]

(10)

where \( r' \) is defined as:

\[
r' = \sigma_0 \sqrt{\frac{x^2 + y^2}{\sigma^2_{\perp}} + \frac{z^2}{\sigma^2_z}}, \text{ with } x, y \text{ and } z \text{ Cartesian coordinates in the principal axis representation.}
\]

The length scales \( \xi_c \) and \( \xi_\rho \) are given by:

\[
\xi_c = \sqrt{\frac{N}{12 \sigma_0}}, \quad \xi_\rho = \frac{\sigma_0}{\xi_c} + \frac{\pi \rho_m \sigma^2 \sigma_z}{3}.
\]

(11)

The attractive branch of the pair potential is incorporated within the successful linearized Reference Molecular Percus-Yevick (High Temperature Approximation) (RMPY/HTA) closure. This procedure, when applied to the zero-thickness thread model, modifies the direct correlation parameter in the following way:

\[
\hat{C}(0) = C_0^{\text{ath}} - \frac{1}{k_B T} \int d \vec{r} \ V(\vec{r}) \ g^{\text{ath}}(\vec{r}).
\]

(12)

In Eq. (12), \( k_B \) is the Boltzmann constant, \( T \) the temperature, and \( \hat{C}(0) \) the direct correlation function at zero wave vector. The present work assumes \( V(r) \) to be an attractive square well with spherical symmetry, of amplitude \( -\varepsilon \) and range \( a \). The range \( a \) in the present work is chosen to be unity in units of \( \sigma_0 \). To eliminate the need
for a fully numerical determination of the attraction-modified direct correlation function, we refrain from using the analytical form of $g_{\text{nth}}(r)$ given by Eq. (9). Instead, we adopt the following Pade approximant for $g_{\text{nth}}(r)$:

$$g_{\text{nth}}(r) = \frac{r' \left( \frac{1}{2\zeta_p} + \frac{1}{2\zeta_x} \right)}{1 + r' \left( \frac{1}{2\zeta_p} + \frac{1}{2\zeta_x} \right)} = \frac{p(r'/\zeta_p)}{1 + p(r'/\zeta_p)}, \quad p = \frac{1}{2} \left( 1 + \frac{\zeta_p}{\zeta_e} \right),$$  

(13)

where $r'$ has the same meaning as in Eq. (9), and $p$ is a number which depends on the site number density and extent of chain deformation. This approximation agrees with the linear term in the Taylor expansion of $g_{\text{nth}}(r)$, and has the correct limiting values as $r \to 0$ and $r \to \infty$. We have verified that use of the approximation in Eq. (13) does not alter the predictions for the chain-length dependence of the critical temperature and concentration from those already obtained within the RMPY/HTA closure for the case of zero strain rate using Eq. (9). Interestingly enough, choice of a value of $p$ independent of the polymer concentration leads to the predictions of the Flory-Huggins theory for the critical temperature and concentration, a result captured by none of a variety of closure approximations (atomic or molecular) when implemented using Eq. (9)\textsuperscript{29}. The present model exhibits an upper critical solution temperature (UCST) for the quiescent system.

The spinodal boundary is determined from the condition that the second derivative of the Helmholtz free energy with respect to volume vanishes. The free energy is modified from its value under shear-free conditions by the coil deformation
under flow. Flow-induced coil deformation impacts the structure factor, leading to an anisotropic pair correlation function, with consequent changes in the cohesive energy. Accounting for such effects requires an explicit treatment of the deformed polymer conformation under flow, and cannot be addressed by extant approaches based on the Flory-Huggins model. We consider two separate, but closely related, additional contributions to the Helmholtz free energy. (i) Firstly, we account for the free energy including modifications arising from the deformed chain conformations, but without any explicit shear-induced component. This may be regarded as the free energy of a stationary polymer solution in which the coil conformations have nevertheless been deformed as they would under the flow conditions of interest. (ii) Contributions to the free energy explicitly due to the shear flow must be accounted for. Thus the spinodal condition becomes:

\[
\frac{\partial^2 f_{\text{eq}}^{\text{mon}}}{\partial V_m^2} + \frac{\partial^2 f_{\text{shear}}^{\text{mon}}}{\partial V_m^2} = 0,
\]

where \( f_{\text{eq}}^{\text{mon}} \) and \( f_{\text{shear}}^{\text{mon}} \) are the Helmholtz free energy contributions per monomer at equilibrium and due to explicit flow processes, respectively, and \( V_m \) is the volume per monomer. The quiescent-state, non-flowing, free energy contribution is obtained through the compressibility route. The isothermal compressibility \( \kappa_T \) follows from the zero-wavevector value of the direct correlation function, \( \hat{C}(0) \), or the static structure factor, \( \hat{S}(k = 0) \equiv S_0 \), as:

\[
\frac{1}{\rho_m k_B T \kappa_T} = \frac{1}{S_0} = \frac{1}{N} - \rho_m \hat{C}(0) .
\]
The Helmholtz free energy is related to the static structure factor as:

\[
\frac{\partial^2 f_{\text{mon}}^{\text{eq}}}{\partial \nu_m^2} = \rho_m^2 \frac{k_B T}{S_0} .
\]  

(16)

It is to be noted that this free energy explicitly includes effects due to flow-induced chain anisotropy, which determines the direct correlation parameter. Equations (14) and (16) yield:

\[
\frac{1}{S_0} + \rho_m^2 \frac{\partial^2 \left( f_{\text{mon}}^{\text{shear}} / k_B T \right)}{\partial \rho_m^2} \left|_T \right| + 2 \rho_m \frac{\partial \left( f_{\text{mon}}^{\text{shear}} / k_B T \right)}{\partial \rho_m} \left|_T \right| = 0 .
\]  

(17)

The free energy explicitly due to the work involved in stretching a harmonic chain is:

\[
f_{\text{mon}}^{\text{shear}} = \frac{k}{(2N)} \sum_i \delta \left( \frac{\bar{r}_{i,i+1}^2}{2} \right) ,
\]  

(18)

where \( k \) is the spring constant and \( \delta \left( \bar{r}_{i,i+1}^2 \right) \) is the extent of mean squared deformation of the \( i^{th} \) bond vector. Within the Rouse and Zimm models, this free energy becomes\(^{30}\):

\[
\frac{f_{\text{mon}}^{\text{shear}}}{k_B T} = \frac{a}{N} \beta^2 ,
\]  

(19)

where \( a \) is a number depending on the model and independent of polymer concentration. Thus, this contribution to the free energy does not affect our calculation of the spinodal, as we employ either Rouse or Zimm type dynamic models over the entire range of polymer concentrations studied. Inclusion of a crossover from Zimm (non-draining) to Rouse-like (free-draining) dynamics to reflect the screening...
of hydrodynamic interactions with increasing polymer concentration would introduce concentration dependence in this term. Such modifications have been considered in previous work based on the Flory-Huggins free energy of mixing\textsuperscript{23}, but are not central to the theme of the present investigation. The present choice corresponds to assuming a linear dependence of solution viscosity on polymer concentration through the intrinsic viscosity. Contributions from the Huggins coefficient and higher-order corrections\textsuperscript{30} are neglected.

As has been pointed out recently\textsuperscript{23}, experiments corresponding to fixed values of shear stress as opposed to strain rate represent very different physical situations, and must be considered distinctly. The present work focuses on the scenario in which the rate of strain is held at a constant value independent of polymer concentration. Given our present interest in the impact of shear-induced conformational changes, we employ the simplest, linear viscoelastic model for the solution viscosity and compliance. Nonlinear viscoelastic effects and contributions from the Huggins coefficient are undoubtedly relevant at large polymer concentrations or strain rates, but are not central to analyzing the importance of coil deformation in and of itself in modifying the phase diagram. If the strain rate is held constant, and a purely linear dependence of solution viscosity on polymer concentration is assumed, the free energy contributions per monomer explicitly due to shear flow are independent of polymer concentration. Within these assumptions, the spinodal condition becomes simply: $1 / S_0 = 0$. This condition can be expressed as a closed-form analytical equation, obtained from Eq.(15):
\[
\frac{1}{S_0} = \frac{1}{N} + \frac{\pi \rho \sigma_\gamma^2 \sigma_z^2}{3 \sqrt{3} N} + \left( \frac{\pi \rho \sigma_\gamma^2 \sigma_z^2}{108} \right)^2 - \frac{4 \pi}{\rho} \left( \frac{\sigma_\gamma}{\rho} \right) \rho_m I .
\] (20)

In Eq. (20), \( p \) has the same significance as in Eq. (13), \( t \) is the dimensionless temperature defined as \( t = k_B T / \varepsilon \), and \( I \) represents the following integral:

\[
I = -\frac{1}{4 \pi} \frac{\varepsilon}{\sigma_0} \int d \tilde{r} V(\tilde{r}) g^{\text{anh}}(\tilde{r}) .
\] (21)

The anisotropic nature of the pair correlation function is a crucial feature of our evaluation of Eq.(21). As the final results are quite unwieldy (despite a closed-form expression for the answer), we refrain from displaying them in detail in the interests of brevity. Note that within the present approximations, the usual treatment which neglects chain deformation would predict no flow-induced shift in the spinodal boundary whatsoever.

**V.4 Results and Discussion**

Spinodal boundaries calculated from Eqs. (20) and (21) for polymer chains with \( N=10^4 \) are shown in Figures V.1 and V.2. Each figure also shows the spinodal line in the absence of shear for purposes of comparison. Figures V.1(a) and V.1(b) show results at \( \alpha = 0.3 \) and different shear rates predicted by the Rouse and Zimm models, respectively. It should be pointed out this value of \( \alpha \) is chosen to highlight the potential non-monotonic phase behavior discussed later. This value (\( \alpha = 0.3 \)) differs from that used in previous work (Chapter IV or Ref.[13]) in which \( \alpha \) was treated as a fitting parameter for describing experimental measurements of flow-
induced coil deformation. Both the conventional Rouse and Zimm models predict a downward shift in the spinodal temperatures under shear flow, \textit{i.e.}, shear-induced mixing or dissolution.

Interestingly, predictions from these models change significantly when corrected for finite chain extensibility (Rouse-FE and Zimm-FE). At low shear rates the spinodal temperature is reduced (shear-induced mixing), whereas the opposite effect (shear-induced demixing) is observed at sufficiently large flow rates. Figure V.2 examines the impact of the parameter $\alpha$, which controls the adjustment for finite extensibility, at a fixed dimensionless shear rate $\beta_0 = 2$. Note that the spinodal temperatures predicted by the conventional Rouse and Zimm models are lower than those from the models corrected for finite chain extensibility. This is also the case for the calculations shown in figures V.1(a) and V.1(b). In the limit $\alpha \to 0$, the conventional Rouse and Zimm models are equivalent to the Rouse-FE and Zimm-FE models, respectively. Thus higher values of $\alpha$ (greater resistance to coil deformation) correlate with higher spinodal temperatures and reduced miscibility. The magnitudes of the shifts in spinodal temperatures are less within the Zimm-FE than within the Rouse-FE models for equal values of all model parameters. This finding is consistent with previous work\textsuperscript{14} which suggests that hydrodynamic interactions between macromolecules tend to minimize the shift in the spinodal lines.
Figure V.1(a) The liquid-vapor spinodal boundaries for chains with $N = 10^4$ predicted by conventional Rouse (solid lines) and Rouse-FE (broken lines) models. In the Rouse-FE case, $\alpha = 0.3$. The temperature is in units of the $N \to \infty$ limiting value of the theta temperature, and the dimensionless site density is defined as $Z = \rho_m / \rho^* = \rho_m \sqrt{N}$. $\rho^*$ is the semidilute crossover concentration. For the solid lines, $\beta_0 = 5, 1,$ and 0, from bottom to top, and for the broken lines, $\beta_0 = 1$ and 5, from bottom to top.
Figure V.1(b) The liquid-vapor spinodal boundaries predicted by conventional Zimm (solid lines) and Zimm-FE (broken lines) models for chains with $N = 10^4$, $\alpha = 0.3$. Symbols and axis variables have the same meanings as in Fig.V.1(a). For the solid lines, $\beta_0 = 6$, 1, and 0, from bottom to top, and for the broken lines, $\beta_0 = 1$ and 6, from bottom to top.
Figure V.2 The liquid-vapor spinodal boundaries for chains with $N = 10^4$ predicted by the Rouse (solid lines) and Zimm (broken lines) models. The crosses represent the quiescent situation, $\beta_0 = 0$. In all other cases, $\beta_0 = 2$. Axis variables have same meanings as in Fig. V.1(a). For each set of lines (solid and broken) $\alpha = 0$, 0.2, and 0.5, from bottom to top. $\alpha = 0$ in the Rouse-FE and Zimm-FE cases corresponds to the conventional Rouse and Zimm models, respectively.
The effects of varying the parameter $\alpha$ on the shear rate dependence of the critical temperature and density are shown in figures V.3 and V.4. In these calculations, the number of sites $N$ in the chain was fixed at $10^4$. In Figure V.3, the conventional Rouse and Zimm models show decreasing critical temperature with increasing shear rate. On the contrary, the Rouse-FE and Zimm-FE models with high values of $\alpha$ show the opposite behavior, i.e., shear-induced demixing. For intermediate values of $\alpha$, the critical temperature may first decrease and subsequently increase with increasing shear rate. As shown in Figure V.4, the critical concentration behaves similarly to the critical temperature, and can be a non-monotonic function of the shear rate for intermediate values of $\alpha$. Given that the value of $\alpha$ is expected to be non-universal and sensitive to the monomer chemistry and monomer-solvent specific interactions, the direction of shear-induced migration in the cloud point may depend on local chemical structural features as well.
Figure V.3  The dependence on the dimensionless shear rate $\beta_0$ of the critical temperature calculated for chains with $N = 10^4$ for different values of $\alpha$. The temperature is in units of the $N \to \infty$ limiting value of the theta temperature. The solid and broken lines correspond to Rouse and Zimm models, respectively. For each set of lines (solid and broken), $\alpha = 0, 0.2, 0.5,$ and $0.7$, from bottom to top.
Figure V.4 The dependence on the dimensionless shear rate $\beta_0$ of the critical density calculated for chains with $N = 10^4$ at different values of $\alpha$. The dimensionless density $Z_c$ is defined as $z_c = \rho_c / \rho^* = \rho_c \sqrt{N}$. The values of the parameters are the same as in Fig. V.3.
Figure V.5 compares our model calculations with experimental measurements\textsuperscript{4} of the apparent spinodal temperature for PS in DOP using neutron scattering. Polystyrene used in the experiment had molecular weight $M_w = 1.80 \times 10^6$. The crosses shown in Figure V.5 was calculated based on the empirical equation (3.3) of Ref.\textsuperscript{4}: $\Delta T_s = T_s(\dot{\gamma}) - T_s(\dot{\gamma} = 0) = 1.57 \times 10^{-3} \dot{\gamma}^{3/2}$, and represent a fit to the experimental results of these workers. The weight fraction of polystyrene $\phi_{ps} = 0.0281$ used in the experiments was converted to a dimensionless site number density by identifying an individual site with each styrene monomer. Solution of PS in DOP exhibit UCST behavior, with a cloud point at approximately 285K for the polymer concentration investigated under shear-free conditions\textsuperscript{4}. Shear rates $\dot{\gamma}$ of up to 350 s\textsuperscript{-1} were investigated in this experiment\textsuperscript{4}. These shear rates were converted into our dimensionless parameter $\beta_0$ (Eq. [3]) using the following information: (i) the solvent viscosity for DOP at 298 K is $61 \times 10^{-3}$ Pa s, and (ii) the Mark-Houwink\textsuperscript{22} constants $K$ and $a$ describing the intrinsic viscosity of PS in DOP are $K = 4.25 \times 10^{-8}$ m\textsuperscript{3} g\textsuperscript{-1}, and $a = 0.54$, respectively\textsuperscript{12}. For the molecular weight of PS investigated in this experiment ($M_w = 1.80 \times 10^6$), Eq. (3) shows that the appropriate range of $\beta_0$ is $0 \leq \beta_0 \leq 1.6$. The density of the solution was assumed equal to that of pure DOP\textsuperscript{31}, i.e. 0.98 g ml\textsuperscript{-1}. The extensibility parameter $\alpha$ was in each case adjusted to obtain the best fit to the experimentally determined cloud point. As expected from the discussion of figures V.1(a), V.1(b), and V.2, the conventional Rouse and Zimm models predict shear-induced dissolution. However, in the
experiment of A.I. Nakatani et al. (Ref.[4]), the apparent spinodal temperature shifted to higher values with increasing applied shear rates. Our results from the Rouse-FE and Zimm-FE models show reasonable agreement with the experimental measurements. Calculations based on the Zimm-FE model can describe the experimental data over a wider range of shear rates than those from the Rouse-FE model, which completely neglects hydrodynamic interactions.

Given the substantial number of approximations invoked in the present theory, the semi-quantitative agreement between calculated and experimental results shown in Figure V.5 must be viewed as fortuitous. Key approximations we have employed include: (i) a one-parameter description of the deformed chain conformations, which are still described by an ellipsoidal radius of gyration tensor; (ii) use of a square-well inter-site interaction potential; (iii) a coarse grained model for the polymer chain; and (iv) complete neglect of polymeric contributions to the solution moduli besides those given by the intrinsic viscosity. Previous research on quiescent polymer solutions suggests that the fourth of the assumptions enumerated above may be most likely to alter the qualitative nature of our conclusions. We have also neglected temperature dependence of the intrinsic viscosity in the vicinity of the theta point. Our use of these approximations is admittedly open to question in the context of the experiments described in Ref.[4], given that the polymer concentration corresponds to roughly 2.7 times the dilute-semidilute overlap crossover (estimated using data for the quiescent $R_g$ from Ref. [12], a Flory exponent of $\nu = 1/2$, and the usual definition of the semidilute crossover concentration). The interest of the present work lies less in our
ability to describe shear induced shifts in the spinodal with quantitative accuracy than
in the finding that predictions may be qualitatively altered if one accounts, however
crudely, for finite chain extensibility and the impact of coil deformation on the
cohesive energy.
Figure V.5  Spinodal temperature as a function of dimensionless shear rate $\beta_0$. The temperature shown is defined as $\delta T_s / \theta = (T_s - T_{s0}) / \theta$. $T_{s0}$ is the spinodal temperature at zero shear rate. The crosses represent neutron scattering measurements on solutions of PS of molecular weight $1.8 \times 10^6$ in DOP (Ref.[4]) at a polymer volume fraction of 0.0281. The solid and broken lines represent, respectively, results from Rouse and Zimm models. All model calculations correspond to the same concentration as in the experiment. The lower solid and broken lines correspond to the conventional Rouse and Zimm models, respectively. The upper solid and broken lines correspond to calculations within the Rouse-FE with $\alpha = 0.5$, and Zimm-FE with $\alpha = 0.58$, respectively.
Figures V.6(a) and V.6(b) reveal the mechanism underlying the non-monotonic behavior of the critical points predicted by the Rouse-FE and Zimm-FE models. In these figures, the critical temperatures are plotted against the parameter $\delta$ defined as $\delta = \sigma^2 / \zeta$ and proportional to the hydrodynamic volume of the deformed chains. The existence of such a simple correlation is linked to our use of a simple square well attractive potential. The cohesive energy density is thus directly related to the number of near-neighbor intermolecular segmental contacts. More realistic models for the attractive pair potential would enhance sensitivity to the slope, and not merely overall volume, of the correlation hole, and the close relationship shown in figures V.6(a) and V.6(b) would disappear. The present findings suggest that similar treatments could be relevant to understanding phase separation in more complex macromolecular systems under flow. A non-monotonic dependence of the critical temperature on rate of strain may potentially arise from flow-induced modifications to the cohesive energy, rather than nonlinear viscoelastic functions per se. The theoretical methodology developed in this work is extended to study multi-component systems, e.g., two component polymer blends, of macromolecules with differing degrees of flexibility, which is discussed in Chapter VI. The formalism adopted will allow for a calculation of the free energy for arbitrary extents of deformation of both species. The precise connection to imposed rate of strain, or applied electromagnetic fields, can be made either through independent, free-standing theoretical computations, or by appeal to direct experimental measurements.
Figure V.6(a) The dimensionless critical temperature calculated within Rouse model as a function of hydrodynamic volume. The dimensionless critical temperature is defined as $T_c^* = (T_c - T_{c0}) / T_{c0}$. $T_{c0}$ corresponds to the zero shear rate critical temperature. The x-axis variable $\delta^*$ is defined as $\delta^* = \delta - 1$, where $\delta \equiv \sigma_{z}^2 \sigma_{\perp}$. For each set of points, $\delta^*$ is calculated as a function of shear rate and $\alpha$, for values of $\alpha$ ranging from 0 to 1.0 in steps of 0.1. Short dashes represent results at $N=100$, $\beta_0 = 1$, open squares at $N=100$, $\beta_0 = 5$, open triangles at $N=100$, $\beta_0 = 10$, crosses at $N=10^4$, $\beta_0 = 1$, open diamonds at $N=10^4$, $\beta_0 = 5$, and open circles at $N=10^4$, $\beta_0 = 10$. 
Figure V.6(b) The dimensionless critical temperature calculated within Zimm model as a function of hydrodynamic volume. All symbols and axis variables have the same significance as in Fig. V.6(a).
V.5 References


CHAPTER VI:

Shear-Induced Effects on Miscibility in Blends of Flexible Polymers
VI.1 Abstract

This study employs macromolecular integral equation theory, together with
the bead-spring Rouse model for describing deformed chain conformations under
flow, to investigate the shifts in spinodal boundaries and critical temperatures and
concentrations in two-component polymer blends subject to shear flow. The direct
and pair correlation functions are calculated perturbatively in powers of the
eccentricity of the radius-of-gyration tensors. Molecular closure approximations were
employed to include the effects of inter-site interaction potentials, which for
simplicity were assumed to be of the square-well form. The spinodal boundaries were
calculated from the partial structure factors at zero wave vector within the
compressibility route to the thermodynamics. Inclusion of the free energy due to
chain extension, as well as modifications to the direct correlation functions to first
order in the coil eccentricities, were found in most instances to enhance the blend
miscibility, i.e., the domain of phase separation in the temperature-composition plane
was reduced. Additionally, remixing at low temperatures, i.e., a lower critical solution
temperature with an island-like immiscible region, is found even for model blends
which under quiescent conditions exhibit only an upper critical solution temperature.
VI.2 Introduction

Polymer blends subject to flow can exhibit miscibility behavior different from that observed under quiescent (stationary) conditions. Depending upon the specific system, shear flow has been reported to induce both enhanced as well as diminished miscibility for blends of linear homopolymers, even though most studies find that flow promotes mixing. Instances have been documented in which, for the same system, the nature of the shear-induced alteration of miscibility depends upon the magnitude of imposed shear rate. The phase behavior of polymer blends under shear flow is of both fundamental interest as well as technological importance, owing to the substantial shear rates characterizing polymer processing applications such as melt-mixing, and the fact that the brittleness temperature for polyolefin blends depends on the degree of microscopic homogeneity achieved in the blending process.

This study generalizes and extends our previous work described in Chapter V for one-component homopolymer solutions to the case of two-component mixtures of flexible, Gaussian homopolymers. The radius-of-gyration tensors for both polymeric species are assumed to have ellipsoidal symmetry under flow, and the bead-spring Rouse model is employed to describe the deformation of the polymer chains. A semi-analytical treatment of the two-component Polymer Reference Interaction Site Model (PRISM) within the thread-like approximation is developed to calculate the direct and pair correlation functions perturbatively in powers of the eccentricity of the radius-of-gyration tensor. The monomer friction coefficients, which are required for
estimating the extent of coil deformation, are calculated from a model which assumes that (i) the temperature dependence of the viscosity satisfies the WLF equation\textsuperscript{13}, and (ii) the composition dependence of the blend glass transition temperature is describable by the Fox equation\textsuperscript{14}. The spinodal boundaries were calculated from the partial structure factors at zero wave vector within the compressibility route to the thermodynamics. The quasi-thermodynamic analysis we employ is in the spirit of previous investigations of shear-induced shifts in the critical point based on the thermodynamics of non-equilibrium systems.

The remainder of this chapter is organized as follows. Section VI.3 describes the theoretical methods employed in this investigation. Section VI.3.1 summarizes earlier results for the deformation of flexible, linear, polymer chains subject to shear flow. The Polymer Reference Interaction Site Model (PRISM) is employed in Section VI.3.2 to calculate the correlation functions appropriate to a polymer blend whose molecules are deformed to ellipsoidal symmetry by shear flow. Square-well pair potentials are included through molecular closures to modify the athermal correlation functions. Methods for determining the spinodal boundaries and for calculating the stored free energy in polymers subject to shear flow are presented in Sections VI.3.3 and VI.3.4, respectively. Results for spinodal boundaries of polymer blends are discussed in Section VI.4. Expressions for the direct correlation functions and approximations for the pair correlation functions under athermal conditions are presented in the Appendix.
VI.3 Theories and Models

VI.3.1 Chain Extension Under Shear Flow

In the present investigation, shear-induced chain extension and orientation are treated within the bead-spring Rouse model\textsuperscript{15}. These results have been discussed in Chapters IV and V, and only a brief summary is included in the present account for completeness.

The extent of chain deformation and orientation are determined by the shear rate, polymer molecular weight, and solvent viscosity. The combined effect of these factors is included in a dimensionless shear rate defined by:

\[
\beta \equiv \frac{[\eta] \eta_s M \dot{\gamma}}{N_A k_B T},
\]

where $[\eta]$ and $\eta_s$ are the intrinsic viscosity and solvent viscosity, respectively, $\dot{\gamma}$ is the shear rate, $M$ the polymer molecular weight, and $N_A$ is Avogadro’s number. The results for shear-induced chain extension and orientation are expressed in terms of this dimensionless shear rate, which is a product of the rate of strain and the longest intramolecular relaxation time calculated within the Rouse model.

Within the Rouse model, planar shear flow distorts the radius-of-gyration tensor into an ellipsoidal distribution with three unequal semi-axes. We define the statistical segment length under shear-free conditions, denoted $\sigma_0$, through the relationship:

\[
\langle R_s^2 \rangle_0 = \frac{N \sigma_0^2}{6},
\]

where $N$ is the number of segments per chain. Under planar shear flow, the principal axes of the distorted ellipsoidal radius-of-gyration tensor are...
tensor are described by the following effective segment lengths parallel and perpendicular to the direction of maximal extension (Chapter IV or Ref. [16]):

\[
\sigma_z = \sigma_0 \sqrt{1 + 0.228\beta^2 + \sqrt{0.1593\beta^2 + 0.052\beta^4}}
\]

\[
\sigma_\perp = \sigma_0 \sqrt{1 + 0.228\beta^2 - \sqrt{0.1593\beta^2 + 0.052\beta^4}}.
\]  

(2)

In Eq. (2), \(\sigma_\perp\) is the geometric mean of the segment lengths in the transverse plane, \(i.e., \sigma_\perp = \sqrt{\sigma_x\sigma_y}\). This choice allows us to model the deformed chains as ellipsoids of revolution, while the volume of an individual coil remains that predicted from the model with three unequal principal moments of inertia. Since the primary focus of this work involves the effects of the coil deformation on the blend phase diagram, rather than the extent of the deformation itself, the finite extensibility correction employed in Chapters IV and V is not incorporated in the present model. This modification of our previous approach to treating sheared polymer solutions also makes for a simpler analytical treatment.

The orientation angle \(\chi\) of the coil is defined as the angle between the streamline directions and the major axis, \(i.e.\) Z-axis, of the ellipsoidal polymer coil. Within the Rouse model, the orientation angle is expressed as: (Chapter IV or Ref. [16])

\[
\chi = \frac{\pi}{4} + \frac{1}{2} \arctan\left(\frac{\beta}{1.7454}\right).
\]  

(3)

For a polymer blend of two or more components, each individual component will have a distinct value of \(\beta\) for a fixed strain rate. Thus, for a two-component blend, the
difference between orientation angles $\chi$ for each component equals the angular displacement between deformed coils of the two polymeric species.

**VI.3.2 Thread PRISM Theory for Anisotropic Polymer Blends**

**VI.3.2.1 Athermal Thread PRISM Theory**

Our starting point is the athermal thread Polymer Reference Interaction Site Model (PRISM) for polymer blends. Within this formalism, the site-averaged Ornstein-Zernike equation for a fluid mixture of homopolymers is\textsuperscript{11}:

$$
\hat{h}_{M,M'}(\tilde{k}) = \hat{\omega}_M(\tilde{k}) \left[ \hat{C}_{M,M'}(\tilde{k}) \hat{\omega}_{M'}(\tilde{k}) + \sum_{M''} \hat{C}_{M,M''}(\tilde{k}) \rho_{M''} \hat{h}_{M''M'}(\tilde{k}) \right],
$$

where the equivalent site approximation has been employed. In Eq. (3), $\hat{h}_{M,M'}$ and $\hat{C}_{M,M'}$ are Fourier transforms of the pair and direct correlation functions, respectively, $g_{M,M'}(\vec{r}) = 1 + h_{M,M'}(\vec{r})$ are the corresponding intermolecular radial distribution functions, and $\rho_M$ and $\hat{\omega}_M$ represent the site number density and intramolecular structure factors corresponding to species $M$, respectively. In the present study, we focus on two-component mixtures of flexible, Gaussian homopolymers, designated components “A” and “B”. The blend is treated as being composed of two chemically dissimilar, monodisperse components.

For describing polymer blends in which individual molecules are deformed by flow, we adopt the Debye approximation for the form factors, appropriate for anisotropic, ellipsoidally distorted Gaussian chains:
\[
\hat{\omega}_A(\vec{k}) = \frac{12}{(k_{Ax}\sigma_{Ax})^2 + (k_{Ay}\sigma_{Ay})^2 + (k_{Az}\sigma_{Az})^2},
\]
\[
\hat{\omega}_B(\vec{k}) = \frac{12}{(k_{Bx}\sigma_{Bx})^2 + (k_{By}\sigma_{By})^2 + (k_{Bz}\sigma_{Bz})^2}.
\]

(4)

A similar approximation for isotropic Gaussian chains has been employed in previous investigations\(^{17}\) of the miscibility of polymer blends. In Eq. (4), \(k_x, k_y\) and \(k_z\) are wave vector components, and \(\sigma_x, \sigma_y\) and \(\sigma_z\) are the effective segment lengths along the X, Y and Z coordinate axes. As shown in Figure VI.1, \(\sigma_z\) is chosen parallel to the direction of maximal extension for each component. Note that we have two sets of coordinates, corresponding to components \(A\) and \(B\). The X directions for components \(A\) and \(B\) are chosen to coincide. The angle between the Z directions for the two components corresponds to the relative orientation angle \(\alpha\) for chains of types \(A\) and \(B\) with respect to each other. As mentioned in Section VI.3.1, \(\alpha\) is defined as:

\[
\alpha = \chi_A - \chi_B.
\]

Our calculations are performed in a coordinate system chosen such that the Z-axis bisects the angle between the \(Z_A\) and \(Z_B\) axes, while the X-axis remains coincident with the \(X_A\) and \(X_B\) axes. The \((X_A, Y_A, Z_A)\) and \((X_B, Y_B, Z_B)\) coordinate directions are thus related to the \((X, Y, Z)\) directions by rotations through \(+\alpha/2\) or \(-\alpha/2\) around the common X-axis (Figure VI.1). Though the three semi-axes of the ellipsoid are all unequal, experiments\(^{18}\) show that one of the three semi-axes is deformed to a much greater extent than the other two and the difference between \(\sigma_x\) and \(\sigma_y\) is relatively minor. Based on this observation, \(\sigma_x\) and \(\sigma_y\) are set equal to \(\sigma_{\perp}\) in the present account.
Figure VI.1  Schematic diagram of the coordinate systems used in Chapter VI. Ellipsoids drawn with broken and dotted lines represent polymer coils of components $A$ and $B$, respectively. The $X_A$ and $X_B$ directions coincide with $X$, and $\alpha$ is the angle between the major axes of the two ellipsoids.
In the coarse-grained thread approximation, the athermal direct correlation function is represented by a δ-function at the origin in position space with an amplitude parameter $C_{MM'}$, i.e. $C_{MM'}(\vec{r}) = C_{MM'} \delta(\vec{r})$. Fourier transformation yields: $\hat{C}_{MM'}(\vec{k}) = C_{MM'}$. If not stated otherwise, all the direct correlation functions correspond to athermal conditions throughout this section. In Section VI.3.2.2, these direct correlation functions will be denoted with superscript ‘ath’, as opposed to the direct correlation functions modified to account for the attractive branch of the pair potential. The three parameters $C_{MM'}$ are chosen to satisfy the core conditions:

$$\frac{1}{(2\pi)^3} \int_0^\infty \hat{h}_{MM'}(\vec{k})^2 \, d\vec{k} = -1 ,$$

(5)

corresponding to the requirement that $g_{MM'}(r = 0) = 0$. The hard-core excluded volume constraint is thus implemented in a point-wise fashion. When the PRISM OZ equation [Eq. (3)] is used, the core conditions of Eq. (5) represent a set of three coupled nonlinear algebraic equations. For the isotropic case, the solutions to Eq. (5) have been shown in previous work to satisfy the simple “scaling” relation:

$$C_{AA}C_{BB} = C_{AB}^2 ,$$

$$C_{BB} = \gamma^4 C_{AA} ,$$

$$C_{AB} = \gamma^2 C_{AA} ,$$

(6)

where the relative segment length ratio $\gamma$, defined as: $\gamma \equiv \sigma_{b0} / \sigma_{a0} $, reflects local structural asymmetries between components A and B. Therefore, $\gamma$ is also referred to as the “asymmetry parameter”. The blend in which the two components have equal numbers of segments, i.e. $N_A = N_B$, is fully structurally symmetric if $\gamma$ equals 1.
We employ a perturbative method to solve Eq. (5) for the direct correlation functions associated with deformed polymer coils whose form factors are specified by Eq. (4). Our first step is to rescale the isotropic state where \( \sigma_{Ax} = \sigma_{Ay} = \sigma_{Az} = \sigma_{A0} \) and \( \sigma_{Bx} = \sigma_{By} = \sigma_{Bz} = \sigma_{B0} \), to another isotropic state where \( \sigma_{Ax} = \sigma_{Ay} = \sigma_{Az} = \sigma_{A0} \) and \( \sigma_{Bx} = \sigma_{By} = \sigma_{Bz} = \sigma_{B0} \). Note that the subscript “0” refers to the quiescent, undeformed, state characterized by spherical symmetry. The scaling relation in Eq. (6) remains valid for the second isotropic state if \( \gamma \) is redefined as: \( \gamma \equiv \sigma_{Bz} / \sigma_{Az} \). The next step is to perturb the second isotropic state to the anisotropic state of interest, for which \( \sigma_x = \sigma_y = \sigma_z \) and \( \sigma_z \) is kept unperturbed for both components \( A \) and \( B \). We now introduce two new parameters:

\[
\tau_A = \frac{\sigma_{A1}}{\sigma_{Az}} - 1
\]

and \( \tau_B = \frac{\sigma_{B1}}{\sigma_{Bz}} - 1 \),

which quantify the extent to which polymer coils are deformed from a state of spherical symmetry. These parameters form the basis for our perturbative calculations. The set of direct correlation parameters are expanded through second order in terms of these variables:

\[
C_{AA} = C_{AA0} + C_{A1A} \tau_A + C_{A2A} \tau_A^2 + C_{A3A} \tau_A^3 + C_{A4A} \tau_A^4 + C_{A5A} \tau_A^5 + \cdots
\]

\[
C_{BB} = C_{BB0} + C_{B1B} \tau_B + C_{B2B} \tau_B^2 + C_{B3B} \tau_B^3 + C_{B4B} \tau_B^4 + C_{B5B} \tau_B^5 + \cdots
\]

\[
C_{AB} = C_{AB0} + C_{A1B} \tau_A + C_{A2B} \tau_B + C_{A3B} \tau_A^2 + C_{A4B} \tau_B^2 + C_{A5B} \tau_A^3 + \cdots
\]
In Eq. (8), the direct correlation functions are determined in terms of three sets of coefficients, which we calculate perturbatively. With equations (3), (4), (6) and (8), Eq. (5) can be solved analytically to determine the coefficients \( \{C_{MM'}\} \). The results for the coefficients in Eq. (8) are presented in the Appendix to this chapter. Results appropriate to the isotropic situation, corresponding to stationary, flow-free, conditions, are recovered by setting \( \tau_A = \tau_B = 0 \).

### VI.3.2.2 Inclusion of Intermolecular Interactions

Our phase diagram calculations employ two distinct types of intermolecular pair potential, as described below:

(i) A repulsive square-well potential between the monomers of components \( A \) and \( B \), exclusively. This potential is assumed to be spherically symmetric and of amplitude \( \epsilon \) and range \( a \). For brevity, we refer to the two-component blend model with this type of interaction as the “AB model”:

\[
\begin{align*}
\epsilon_{AA} &= \epsilon_{BB} = 0; \\
\epsilon_{AB}(r) &= \epsilon, \quad r < a \\
&= 0, \quad r > a.
\end{align*}
\]  

(ii) Bertholet type pair potential:

\[
\begin{align*}
\epsilon_{AA}(r) &= \epsilon_{AA}, \quad r < a \\
&= 0, \quad r > a; \\
\epsilon_{AB} &= \lambda \epsilon_{AA} \\
\epsilon_{BB} &= \lambda^2 \epsilon_{AA}
\end{align*}
\]  

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where $\lambda$ is a positive constant. The blend model with the Bertholet potential is referred to as the Bertholet model. The range $a$ of these two types of potential in the present work is chosen to be unity in units of $\sigma_{A0}$.

The influence of the “thermal” interactions (i.e., the attractive branch of the pair potential) is studied within two molecular closure approximations: (i) the linearized Reference Molecular Percus-Yevick/High Temperature Approximation (RMPY/HTA) closure approximation, and (ii) the Reference Molecular Mean Spherical Approximation (RMMSA), which have both been used successfully in previous investigations\textsuperscript{19} of demixing transitions in polymer blends. Unlike the “atomic” closures which have been widely used in studies of simple liquids (e.g., the Mean Spherical Approximation, or MSA), molecular closure approximations yield the correct dependence of critical demixing temperature on molecular weight for polymer blends. These procedures, when applied to the zero-thickness thread model, modify the direct correlation parameters in the following way:

\[ \hat{C}_{\text{MM}}(0) = C_{\text{MM}}^{\text{ath}} - \frac{1}{k_B T} \int d\vec{r} \, e_{\text{MM}}(\vec{r}) \, g_{\text{MM}}^{\text{ath}}(\vec{r}) \quad \text{RMPY/HTA} , \]
\[ \hat{C}_{\text{MM}}(0) = C_{\text{MM}}^{\text{ath}} - \frac{1}{k_B T} \int d\vec{r} \, e_{\text{MM}}(\vec{r}) \quad \text{RMMSA} . \]  

In Eq. (11), $k_B$ is the Boltzmann constant, $T$ the temperature, and $\hat{C}_{\text{MM}}(0)$ is the direction correlation function at zero wave vector. The superscript ‘ath’ denotes athermal conditions. Use of the RMPY/HTA closure for the Bertholet blend requires knowledge of the radial distribution functions $g_{AA}^{\text{ath}}(\vec{r})$, $g_{BB}^{\text{ath}}(\vec{r})$ and $g_{AB}^{\text{ath}}(\vec{r})$. Given the
difficulty of obtaining perturbative solutions for the complete set of three radial distribution functions, our use of the RMPY/HTA closure is limited to the AB model blend, for which only $g_{AB}^{nth}(\bar{r})$ must be determined. $g_{AB}^{nth}(\bar{r})$ can be obtained by Fourier-transforming $\hat{h}_{AB}(\vec{k})$. Consistent with our perturbative method of calculation, $\hat{h}_{AB}(\vec{k})$ is Taylor expanded in terms of $\tau_A$ and $\tau_B$. For reasons of simplicity, only calculations to first order in the perturbation series have been performed within the RMPY/HTA closure. We define the Taylor coefficients of $\hat{h}_{AB}(\vec{k})$ as follows:

$$\hat{h}_{AB}(\vec{k}) = \hat{h}_{AB0}(k) + \hat{h}_{AB1}(\vec{k})\tau_A + \hat{h}_{AB2}(\vec{k})\tau_B$$

(12)

where

$$k^2 = k_x^2 + k_y^2 + k_z^2.$$  

Full expressions for the Taylor expansion coefficients defined in Eq. (12) are given in the Appendix (Section VI.5). We then Fourier transform $\hat{h}_{AB}(\vec{k})$ term by term into $h_{AB}(\vec{r})$, which takes the form:

$$h_{AB}(\vec{r}) = h_{AB0}(r) + h_{AB1}(\vec{r})\tau_A + h_{AB2}(\vec{r})\tau_B.$$  

(13)

An analytical result has been obtained for the first term in Eq. (13) in previous work\textsuperscript{17}:

$$\rho_A \sigma_{Az}^3 h_{AB0}(r) = \frac{-3}{\pi R(1 + \gamma^2 \rho_B / \rho_A)} \left[ 1 - \exp\left( - R / \xi \right) \right]$$

(14)

where

$$R \equiv r / \sigma_{Az}, \quad \xi^{-1} \equiv \frac{\pi}{3} \left( 1 + \gamma^2 \rho_B / \rho_A \right) \rho_A \sigma_{Az}^3.$$
For the function $\hat{h}_{AB1}(\vec{k})$ in Eq. (12), we integrate over $k_z$ analytically to yield $h_{AB1}(k_\perp, r_\perp, r_z)$. The variables $k_\perp$ and $r_\perp$ satisfy the relations, $k^2 = k^2_x + k^2_y$ and $r^2 = r^2_x + r^2_y$ respectively. $h_{AB1}(k_\perp, r_\perp, r_z)$ involves functions of $k_\perp$, exponentials and the $J_0$ Bessel function. The integral over $k_\perp$ to yield $h_{AB1}(r_\perp, r_z)$ cannot be done analytically for arbitrary values of $r_\perp$ and $r_z$. However, when we switch to spherical coordinates such that:

$$
\begin{align*}
   r_z &= r \cos \theta \\
   r_\perp &= r \sin \theta,
\end{align*}
$$

where $\theta$ is the angle between vector $r$ and the Z-axis, there are two special cases (i) $\theta = 0$ and (ii) $\theta = \pi/2$, for which the integral over $k_\perp$ can be performed analytically. The results for these two special angles are denoted $f_1_{AB1}(r)$ and $f_2_{AB1}(r)$, respectively. To eliminate the need for a fully numerical determination of $h_{AB1}(r)$, we adopt the following approximation:

$$
\begin{equation}
   h_{AB1}(r, \theta) = f_{2_{AB1}}(r) + [f_{1_{AB1}}(r) - f_{2_{AB1}}(r)] \cos^2 \theta
\end{equation}
$$

This approximation is consistent with the geometry of the system, has the correct limiting values as $r \to 0$ and $r \to \infty$, reduces to the correct functions for $\theta = 0$ and $\theta = \pi/2$, and allows the integration over $r$ required in Eq. (11) to be performed analytically. The function $h_{AB2}(r)$ is derived similarly, and explicit expressions for $f_1$ and $f_2$ are given in the Appendix.
In the next section, we use the modified direct correlation functions as inputs to determine the spinodal boundaries for the two-component polymer blend, when coil deformation induced by shear is accounted for.

**VI.3.3 Determination of Spinodal Conditions**

Our method for determining the spinodal boundary follows the work of X. S. Chen and F. Forstmann\textsuperscript{20}. This approach relies on the following relationship linking derivatives of the chemical potential to elements of the matrix of partial structure factors\textsuperscript{21}:

\[
[X^{-1}]_{ij} = \frac{1}{\kappa_g T} \left. \frac{\partial \mu_i}{\partial \rho_j} \right|_{r,\gamma,\rho_i} = \frac{1}{8 \pi^3} \left[ \hat{S}^{-1} (k = 0) \right]_{i,j},
\]

In Eq. (17), $\mu_i$ is the chemical potential of species “$i$”, \textit{i.e.}, the first derivative of the Helmholtz free energy with respect to the concentration of component “$i$”. We consider two separate, physically distinct, contributions to the Helmholtz free energy, as we did in our work on sheared solutions discussed in Chapter V:

(i) We account for free energy contributions arising from chain conformational deformation, but without any explicit chain-stretching related component. This may be regarded as the free energy of a quiescent polymer blend in which the coil conformations have nevertheless been deformed as they would be under the flow conditions of interest. Deformed, anisotropic, polymer molecules are characterized by modified radial distribution functions which reflect the impact of the
modified form factors, and this contribution to the free energy represents the sole
influence of these modifications on blend stability.

(ii) Contributions to the free energy explicitly due to chain stretching. This
contribution to the free energy represents the work performed in stretching the
harmonic chains to the deformed conformations relevant to the flow conditions of
interest.

The matrix $X^{-1}$ can thus be written in an additive format, when both flow-
induced contributions to the free energy are accounted for:

$$X^{-1} = X^{-1}_{eq} + X^{-1}_{shear},$$

(18)

where $X^{-1}_{eq}$ and $X^{-1}_{shear}$ are the matrices of the second derivatives of the Helmholtz
free energy in the quiescent-but-deformed state and due to chain stretching,
respectively. The quiescent-state free energy contributions are obtained from the
compressibility route\textsuperscript{11}. The elements of the 2x2 matrix of the partial structure factor
are related to the direct correlation functions by:

$$S_{AA} = \frac{N_A \rho_A (1 - N_B \rho_B C_{BB})}{\Lambda},$$

$$S_{AB} = \frac{N_A N_B \rho_A \rho_B C_{AB}}{\Lambda},$$

$$S_{BB} = \frac{N_B \rho_B (1 - N_A \rho_A C_{AA})}{\Lambda},$$

(19)

where the denominator in Eq. (19) is

$$\Lambda = 1 - N_A \rho_A C_{AA} - N_B \rho_B C_{BB} + N_A N_B \rho_A \rho_B (C_{AA} C_{BB} - C_{AB}^2).$$

(20)
Note that the direct correlation functions in Eqs. (19) and (20) are those modified with pair potentials through molecular closures. For all of the results we present in Sec.VI.4, the number of sites per chain is set to be \( N_A = N_B = 1000 \).

The free energy explicitly due to chain stretching will be discussed in Section VI.3.4. Equations (17) and (18) yield:

\[
\left[X^{-1}\right]_j = \left[\frac{1}{8\pi^3} \left[\hat{S}^{-1}(k = 0)\right]_j + \frac{1}{K_BT} \frac{\partial \mu_{i,shear}}{\partial \rho_j}\right].
\]  

(21)

The spinodal boundary is determined by the conditions under which an eigenvalue of the matrix \( X^{-1} \) goes to zero through positive values, corresponding to diverging concentration fluctuations. Our choices for the intermolecular pair potentials are always such that our model predicts demixing of the blend at temperatures below a molecular weight-dependent critical point under quiescent conditions, \( i.e. \), the phase diagram exhibits an Upper Critical Solution Temperature (UCST).

### VI.3.4 Stored Free Energy in Polymers Subject to Shear Flow

The total free energy of the polymer blend due to flow-induced chain stretching is assumed to be additive:

\[
F_{total}^{\text{shear}} = \sum_i n_i f_i^{\text{shear}},
\]

(22)

where \( n_i \) is the total number of monomers of species \( "i" \) and \( f_i^{\text{shear}} \) is the free energy per monomer. The definition of the chemical potential leads to the relation:
\[
\frac{\partial \mu_{i}^{\text{shear}}}{\partial \rho_{j}} = \frac{\partial f_{i}^{\text{shear}}}{\partial \rho_{j}} + \frac{\partial f_{j}^{\text{shear}}}{\partial \rho_{i}} + \sum_{k} \rho_{k} \frac{\partial f_{k}^{\text{shear}}}{\partial \rho_{j} \partial \rho_{i}}.
\] (23)

The free energy explicitly due to the work involved in stretching a harmonic chain is:

\[
f_{i}^{\text{shear}} = k_{i} / (2N_{i}) \sum_{j} \delta \langle r_{j,j+1}^2 \rangle,
\] (24)

where \(k_{i}\) is the effective spring constant of species \(i\) and \(\delta \langle r_{j,j+1}^2 \rangle\) is the extent of deformation of the \(j^{th}\) bond vector. Within the Rouse model, this free energy becomes\(^{22}\):

\[
\frac{f_{i}^{\text{shear}}}{k_{B}T} = \frac{2}{5N_{i}} \beta_{i}^2,
\] (25)

where the dimensionless shear rate \(\beta_{i}\) as defined in Eq. (1) can be expressed within the Rouse model by\(^{15}\):

\[
\beta_{i} = \frac{N_{i} \zeta_{i} \sigma_{i0}^2 \dot{\gamma}}{36k_{B}T},
\] (26)

where \(\zeta_{i}\), the monomer friction coefficient, is:

\[
\zeta_{i} = \frac{36 \eta_{i}}{\rho_{i} N_{i} \sigma_{i0}^2}.
\] (27)

It should be noted that the Rouse model is most appropriate for describing low molecular weight, unentangled, polymeric systems. The effects of entanglements and reptative dynamics, important in the viscoelasticity of high molecular weight polymers \([15,23]\), have been neglected in the present work. In Eq. (27), the viscosity \(\eta_{i}\) depends upon both temperature and composition. For the model calculations
presented in Section VI.4, we construct a very simple and skeletal model for the
dependence of viscosity on temperature and blend composition. The temperature
dependence is described in our model by the Williams-Landel-Ferry (WLF)
equation\textsuperscript{13}. The WLF equation for a pure component is:

\[ \eta(T) = \eta(T_0) e^{-C_1(T-T_0)/(C_2+(T-T_0))}, \]

(28)

where the reference temperature \( T_0 \) is usually chosen to be the glass transition
temperature. In extending our work to blends, we choose the glass temperature \( T_g \) of
the blend as the reference temperature in the WLF equation [Eq. (28)]. In the present
work, the “universal” values of coefficients \( C_1 \) and \( C_2 \) are used, \textit{i.e.} \( C_1 = 17.4 \) and \( C_2 = 51.6K \). The composition dependence of the viscosity is accounted for through the \( T_g \)
of the blend, which is described in our model by the Fox equation\textsuperscript{14}:

\[ \frac{1}{T_g} = \frac{\phi_A}{T_{gA}} + \frac{\phi_B}{T_{gB}}, \]

(29)

where \( \phi_A \) and \( \phi_B \) are the corresponding mole fractions of monomers of components \( A \)
and \( B \), respectively (\( \phi_i \equiv \rho_i / \rho_{\text{total}} \)). In terms of modeling the temperature and
composition dependence of the viscosity, a similar approach was used in a previous
work\textsuperscript{24} on the miscibility gaps in sheared polymer blends. Our work differs from the
model used in this earlier investigation\textsuperscript{24} in a number of important ways: (i) we do not
employ a phenomenological, temperature-dependent, Flory \( \chi \)-parameter, chosen so as
to generate heating-induced demixing under quiescent conditions in Ref. [24]; (ii) for
simplicity, we employ the “universal” values of the coefficients \( C_1 \) and \( C_2 \) in the
WLF equation for both components, as opposed to assigning different values to these
parameters for each component$^{24,25}$; and, (iii) we have assumed unentangled, Rouse-like, dynamics for the polymer chains, as opposed to the reptative, entangled, dynamical picture employed in Ref. [24]. Equations (2) and (7) reveal that the parameters $\tau_A$ and $\tau_B$ vary with the dimensionless shear rates $\beta_A$ and $\beta_B$, respectively. The temperature and composition dependences of the dimensionless shear rates give rise to temperature and composition dependent variations in the parameters $\tau_A$ and $\tau_B$.

In all of our calculations, the total density of the blend is set to be $\rho_{total} \sigma_{A0}^3 = 5.0$ in order for our systems to approximately mimic the isothermal compressibility characteristic of a dense liquid, and the viscosity at the glassy state is set to be $\eta(T_g) = 10^{12}$ Pa.S. The viscosity calculated from Eq. (28) is used in determining $\beta$ (Eqs. 26 and 27) for both components $A$ and $B$ at the temperatures and compositions of interest. Values for the energetic parameters $\{\varepsilon_{MM'}\}$ are chosen by calculating the dimensionless critical temperature $T_{c0}$ (defined below) under shear free conditions, and arbitrarily assigning to this the temperature $T_c = 350$K. This procedure corresponds to a choice of the temperature scale for our model. The dimensionless critical temperature is defined by:

$$T_{c0} = k_B T_c / \varepsilon$$

for the AB model blend, and

$$T_{c0} = k_B T_c / \varepsilon_{AA}$$

for the Bertholet model blend. (30)

The spinodal temperatures $T_s$ shown in all of our results are expressed in the dimensionless form $T_s^* = T_s / T_c$. 

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VI.4 Results and Discussion

Results from our calculations based on first and second order perturbation theories are closely similar, and hence we restrict our attention to results obtained from the first order calculations. These calculations are intended to illustrate the behavior found for two different types of intermolecular potential, rather than provide an exhaustive treatment of the entire range of possible relative interaction strengths. In order to separate the effects of the two distinct contributions to the free energy discussed previously, we have performed calculations for situations in which:

(i) only free energy contributions corresponding to the quiescent-but-deformed state are accounted for. The free energy explicitly due to chain stretching is ignored in this calculation, i.e. the second term in Eq. (21) is not included. The parameters $\tau_A$ and $\tau_B$ are either held constant at given fixed values or vary with the dimensionless shear rates $\beta_A$ and $\beta_B$, respectively. To ensure the validity of our perturbative methods, we restrict our calculations to relatively low shear rates so that the extremal values of $\tau_A$ and $\tau_B$ are no smaller than –0.2.

(ii) both contributions to the free energy are accounted for in Eq. (21) and the parameters $\tau_A$ and $\tau_B$ vary with the dimensionless shear rate. It is worth reminding our reader that the square-well pair potentials are included through either RMPY/HTA or the RMMSA closures for “AB” blends, while only the RMMSA closure is employed for Bertholet blends.

Spinodal boundaries calculated from Eq. (21) for “AB” blends are shown in Figures VI.2 and VI.3. These results were obtained without taking the stretching free
energy [Eq. (25)] into consideration, and three different values of the relative segment
length ratio $\gamma$ ($\gamma = 0.5, 1.0, 1.5$) were investigated. The values of $\tau_A$ and $\tau_B$ were fixed
at $\tau_A = -0.08$ and $\tau_B = -0.12$ or, $\tau_A = -0.12$ and $\tau_B = -0.08$. The spinodal boundaries in
the quiescent state ($\tau_A = \tau_B = 0$ or $\dot{\gamma} = 0$) are shown in each figure for purposes of
comparison. Figure VI.2 shows results obtained within the RMMSA closure. The
model employed corresponds to UCST phase separation under quiescent conditions.
At $\gamma = 1.0$, our model predicts that both downward and upward shifts in the spinodal
temperatures may occur for each set of fixed values of $\tau_A$ and $\tau_B$, with the direction of
the shift dependent on the blend composition. However, at asymmetry ratios of $\gamma =
0.5$ or $1.5$, the downward and upward shifts of the spinodal temperatures do not
depend on the blend composition but on the extent of the deformation of each
component, i.e. the (fixed) values of $\tau_A$ and $\tau_B$. The results shown in Fig.VI.3 were
calculated under the same conditions as those in Fig.VI.2, the difference being that
the RMPY/HTA closure was employed instead in Fig.VI.2. As shown in Fig.VI.3, the
RMPY/HTA closure predicts that the chain anisotropy enhances blend miscibility if
$\gamma \neq 1$. These results are different from those obtained within the RMMSA closure,
due to the emphasis of the RMPY/HTA closure on the local behavior of the radial
distribution functions.
Figure VI.2  Spinodal boundaries for “AB” blends. The RMMSA closure is employed. In all cases, Helmholtz free energy contributions explicitly due to chain deformation under shear are neglected. $\tau_A$ and $\tau_B$ do not vary with the dimensionless shear rate. For the three sets of curves, $\gamma = 0.5$, 1.0, 1.5 from left to right. Solid lines represent the quiescent situation, $\tau_A = \tau_B = 0$. Crosses are for case of $\tau_A = -0.08$ and $\tau_B = -0.12$, open diamonds for $\tau_A = -0.16$ and $\tau_B = -0.12$. 
Figure VI.3  Spinodal boundaries for “AB” blends. The RMPY/HTA closure is employed. In all cases, Helmholtz free energy contributions explicitly due to chain deformation under shear are neglected. $\tau_A$ and $\tau_B$ do not vary with the dimensionless shear rate. For the three sets of curves, $\gamma = 0.5, 1.0, 1.5$ from left to right. All symbols have the same significance as in Figure VI. 2.
The effects of the free energy contributions due to chain stretching on the spinodal temperatures of AB blends are shown in Figures VI.4 and VI.5, which show results from the RMMSA and RMPY/HTA closures, respectively. In these calculations, $\tau_A$ and $\tau_B$ vary with the dimensionless shear rate. We show results from calculations in which both types of shear free energy contributions are accounted for. Under these conditions, there are no dramatic differences between the results from the two molecular closures employed. If the stretching free energy contributions are excluded, the spinodal temperatures do not show noticeable changes at the shear rates $\dot{\gamma} = 0.01$ and $0.1$ s$^{-1}$. Compared with the results at fixed values of $\tau_A$ and $\tau_B$ shown in Fig.VI.2, the results obtained when $\tau_A$ and $\tau_B$ are allowed to vary with the dimensionless shear rate show that the effects of shear flow tend to counteract the effects of chain anisotropy. Interestingly, our results change significantly when chain stretching free energy contributions are included in these calculations. The spinodal temperatures are reduced (shear induced mixing), an effect which becomes more significant at higher shear rates. Moreover, LCST boundaries appear at low temperature, and the region of immiscibility shrinks to an island.
Figure VI.4 Spinodal boundaries for “AB” blends. The RMMSA closure is employed. In all cases, $T_{gA} = 0.5 T_c$ and $T_{gB} / T_{gA} = 0.8$. $\tau_A$ and $\tau_B$ vary with the dimensionless shear rate. For the two sets of curves, $\gamma = 0.5, 1.0$ from left to right. Solid lines represent the quiescent situation, $\dot{\gamma} = 0$. Symbols marked by “+” and “×” represent results at shear rate $\dot{\gamma} = 0.01$ s$^{-1}$ with and without free energy contributions explicitly due to chain stretching included, respectively. Open diamonds and triangles represent results at the shear rate $\dot{\gamma} = 0.1$ s$^{-1}$ with and without free energy contributions explicitly due to chain stretching included, respectively.
Figure VI.5  Spinodal boundaries for “AB” blends. The RMPY/HTA closure is employed. In all cases, $T_{gA} = 0.5T_c$ and $T_{gB} / T_{gA} = 0.8$. $\tau_A$ and $\tau_B$ vary with the dimensionless shear rate. For the two sets of curves, $\gamma = 0.5$, 1.0 from left to right. All symbols have the same significance as in Figure VI.4.
Figure VI.6 shows the spinodal temperatures of Bertholet blends for situations in which $\tau_A$ and $\tau_B$ are fixed at given values independent of the dimensionless shear rate, and free energy contributions due to chain stretching are not taken into account. The results shown correspond to $\gamma = 1.0$ and 0.5, and the Bertholet constant $\lambda$ is held fixed at either 0.8 or 1.2. For symmetric as well as asymmetric blends, anisotropy-induced mixing and demixing are both observed, depending on the choices of $\tau_A$ and $\tau_B$. For asymmetric blends, the value of the Bertholet constant $\lambda$ does not affect the results significantly, as opposed to the case of symmetric blends.
Figure VI.6  Spinodal boundaries for Bertholet blends. The RMMSA closure is employed. In all cases, Helmholtz free energy contributions explicitly due to chain stretching have been excluded. $\tau_A$ and $\tau_B$ are independent of the dimensionless shear rate. For the two sets of curves, $\gamma = 0.5$ and 1.0 from left to right. The solid lines represent the quiescent situation, $\tau_A = \tau_B = 0$. The two solid lines at $\lambda = 0.8, 1.2$, but with same value of $\gamma$ almost overlap. Open symbols represent results for $\lambda = 0.8$, and solid symbols for $\lambda = 1.2$. Diamonds and triangles represent results at $\tau_A = -0.05$, $\tau_B = -0.08$ and $\tau_A = -0.16$, $\tau_B = -0.12$, respectively.
Figures VI.7 and VI.8 reveal the effects of shear flow on spinodal boundaries for Bertholet blends. As for the “AB” blends considered earlier, the results shown in these two figures were calculated by allowing $\tau_A$ and $\tau_B$ to vary with the dimensionless shear rate. The results are similar to those obtained for the “AB” blends. However, for the case of $\gamma = 1.0$, LCST behavior is found even in the absence of free energy contributions explicitly due to chain stretching. If the value of $\lambda$ is changed from 0.8 as in Figure VI.7 to 1.2 as in Figure VI.8, the results show symmetric changes as expected.
Figure VI.7  Spinodal boundaries for Bertholet blends. The RMMSA closure is employed. In all cases, $T_{gA} = 0.5T_c$, $T_{gB}/T_{gA} = 0.8$ and $\lambda = 0.8$. $\tau_A$ and $\tau_B$ vary with the dimensionless shear rate. For the two sets of curves, $\gamma = 0.5$ and 1.0 from left to right. The solid lines represent the quiescent situation, $\tau_A = \tau_B = 0$. Solid and open symbols represent results with and without the free energy explicitly due to chain stretching accounted for, respectively. Diamonds and circles represent results at $\gamma = 1.0$ and shear rate $\dot{\gamma} = 0.01$, 0.1 s$^{-1}$, respectively. Squares and triangles represent results at $\gamma = 0.5$ and shear rate $\dot{\gamma} = 0.01$, 0.1 s$^{-1}$, respectively.
Figure VI.8  Spinodal boundaries for Bertholet blends. The RMMSA closure is employed. In all cases, $T_{gA} = 0.5T_c$, $T_{gB}/T_{gA} = 0.8$ and $\lambda = 1.2$. $\tau_A$ and $\tau_B$ vary with the dimensionless shear rate. For the two sets of curves, $\gamma = 0.5$ and 1.0 from left to right. The solid lines represent the quiescent situation, $\tau_A = \tau_B = 0$. All symbols have the same significance as in Figure VI. 7.
Figures VI.9 and VI.10 compare the effects of varying the glass transition temperature of each component for symmetric “AB” and Bertholet blends, respectively. Results at two glass transition temperature ratios, $T_{gB}/T_{gA} = 0.8$ and 1.2 are shown. For both “AB” and Bertholet blends, the spinodal boundaries are quite similar if the free energy contributions due to chain stretching are included. This again suggests that the free energy contribution explicitly due to chain stretching dominates the phase behavior. When chain stretching free energy contributions are excluded but the variations of $\tau_A$ and $\tau_B$ with the dimensionless shear rate are accounted for, the Bertholet blend shows LCST behavior for either choice of the glass transition temperature ratio.

In contrast to recent theoretical studies$^{24,26,27}$ of shear-induced shifts in the phase diagrams for polymer blends, our results find that the effects of including the free energies of chain stretching and deformation lead almost exclusively to greater miscibility for the blend, within the admittedly simplistic dynamical model we invoke. Experimental findings strongly suggest that both shear-induced mixing and demixing are observed$^{1-9}$. We believe that the primary shortcoming of this preliminary work is the focus on low molecular weight blends for which the dynamics are not entanglement-controlled, a subject which we plan to address in future efforts. Our findings in this work do suggest, however, that for unentangled systems, the primary effect of shear flow may be to enhance miscibility under a broad range of conditions. The approach we adopt makes it possible to consider different types of microscopic intermolecular interactions, which may all be consistent with the
same Flory $\chi$-parameter, and are therefore indistinguishable in approaches which treat this quantity as an empirically-chosen input for the model. In addition, a more realistic treatment of the friction factors for monomers of distinct species in a miscible blend would take into account the differing compositions in the local environments experienced by these monomers\textsuperscript{28}, an important issue which has not been addressed explicitly in extant discussions of this problem\textsuperscript{24,26,27}. 


Figure VI.9  Spinodal boundaries for “AB” blends. The RMMSA closure is employed. In all cases, $\gamma = 1.0$ and $\dot{\gamma} = 0.1$ s$^{-1}$. $\tau_A$ and $\tau_B$ vary with the dimensionless shear rate. The solid line represents the quiescent state. Solid and open symbols represent results with and without the free energy contributions explicitly due to chain stretching accounted for, respectively. Diamonds represent results at $T_{gA} = 0.4T_c$, $T_{gB} / T_{gA} = 1.2$, and circles at $T_{gA} = 0.5T_c$, $T_{gB} / T_{gA} = 0.8$. 

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Figure VI.10  Spinodal boundaries for Bertholet blends. The RMMSA closure is employed. In all cases, $\gamma = 1.0$, $\lambda = 0.8$ and $\dot{\gamma} = 0.1$ s$^{-1}$. $\tau_A$ and $\tau_B$ vary with the dimensionless shear rate. All symbols have the same significance as in Figure VI. 9.
VI.5 Appendix

VI.5.1 Perturbative Solutions for the Athermal Direct Correlation Functions

The results for the coefficients defined in Eq. (8) are given below:

\[ C_{A40} = -\frac{\sigma_4^6 \pi^2 \left( \rho_A + \gamma^2 \rho_B \right)}{108} \]

\[ C_{A41} = -\frac{\sigma_4^6 \pi^2 \left( 3 \rho_A + 2 \gamma^2 \rho_B \right)}{81} \]

\[ C_{A42} = -\frac{\sigma_4^6 \pi^2 \gamma^2 \rho_B}{81} \]

\[ C_{A43} = -\frac{\sigma_4^6 \pi^2 \left( 135 \rho_A^2 + 187 \gamma^2 \rho_A \rho_B + 54 \gamma^4 \rho_B^2 \right)}{2430 \left( \rho_A + \gamma^2 \rho_B \right)} \]

\[ C_{A44} = -\frac{\sigma_4^6 \pi^2 \gamma^2 \rho_B \left( 7 \rho_A + 9 \gamma^2 \rho_B \right)}{2430 \left( \rho_A + \gamma^2 \rho_B \right)} \]

\[ C_{A45} = -\frac{\sigma_4^6 \pi^2 \gamma^2 \rho_B \left( 79 \rho_A + 78 \gamma^2 \rho_B - 3 \left( \rho_A + 2 \gamma^2 \rho_B \right) \cos(2\alpha) \right)}{2430 \left( \rho_A + \gamma^2 \rho_B \right)} \]

\[ C_{B00} = \gamma^4 C_{A40} \]

\[ C_{B01} = -\frac{\sigma_4^6 \pi^2 \gamma^4 \left( 2 \rho_A + 3 \gamma^2 \rho_B \right)}{81} \]

\[ C_{B02} = -\frac{\sigma_4^6 \pi^2 \gamma^4 \rho_A}{81} \]

\[ C_{B03} = -\frac{\sigma_4^6 \pi^2 \gamma^4 \left( 54 \rho_A^2 + 187 \gamma^2 \rho_A \rho_B + 135 \gamma^4 \rho_B^2 \right)}{2430 \left( \rho_A + \gamma^2 \rho_B \right)} \]
\[ C_{BA4} = -\frac{\sigma^6 A_4 \pi^2 \gamma^4 \rho_A (9 \rho_A + 7 \gamma^2 \rho_B)}{2430 (\rho_A + \gamma^2 \rho_B)} \]

\[ C_{BA5} = -\frac{\sigma^6 A_4 \pi^2 \gamma^4 \rho_A (78 \rho_A + 79 \gamma^2 \rho_B - 3 (2 \rho_A + \gamma^2 \rho_B) \cos(2 \alpha))}{2430 (\rho_A + \gamma^2 \rho_B)} \]

\[ C_{AB0} = \gamma^2 C_{AA0} \]

\[ C_{AB1} = -\frac{\sigma^6 A_4 \pi^2 \gamma^2 (2 \rho_A + \gamma^2 \rho_B)}{81} \]

\[ C_{AB2} = -\frac{\sigma^6 A_4 \pi^2 \gamma^2 (\rho_A + 2 \gamma^2 \rho_B)}{81} \]

\[ C_{AB3} = -\frac{\sigma^6 A_4 \pi^2 \gamma^2 (52 \rho_A^2 + 57 \gamma^2 \rho_A \rho_B + 7 \gamma^4 \rho_B^2)}{2430 (\rho_A + \gamma^2 \rho_B)} \]

\[ C_{AB4} = -\frac{\sigma^6 A_4 \pi^2 \gamma^2 (7 \rho_A^2 + 57 \gamma^2 \rho_A \rho_B + 52 \gamma^4 \rho_B^2)}{2430 (\rho_A + \gamma^2 \rho_B)} \]

\[ C_{AB5} = -\frac{\sigma^6 A_4 \pi^2 \gamma^2 (79 \rho_A^2 + 159 \gamma^2 \rho_A \rho_B + 79 \gamma^4 \rho_B^2 - 3 (\rho_A^2 + \gamma^2 \rho_A \rho_B + \gamma^4 \rho_B^2) \cos(2 \alpha))}{2430 (\rho_A + \gamma^2 \rho_B)} \]

**VI.5.2 Taylor Expansion Coefficients for the Pair Correlation Function** \( h_{AB}(k) \)

The Taylor expansion coefficients for the pair correlation function \( \hat{h}_{AB}(k) \) defined in Eq. (12) are given below:

\[ \hat{h}_{AB0}(k) = -\frac{12 \sigma^2 A_4 \pi^2 (\rho_A + \gamma^2 \rho_B)}{k^2 \left(9 k^2 + \sigma^4 A_4 \pi^2 (\rho_A + \gamma^2 \rho_B)^2 \right)} \]
VI.5.3 Approximations for Taylor Expansion coefficients for the Pair Correlation Function \( h_{AB}(r) \)

In Sec. VI.3.2.2, we define the coefficients in the Taylor expansion of \( h_{AB}(r) \) in Eq. (13). The coefficients \( h_{AB1}(r) \) and \( h_{AB2}(r) \) take the approximate forms:

\[
h_{AB1}(r, \theta) = f_{2, AB1}(r) + \left[ f_{1, AB1}(r) - f_{2, AB1}(r) \right] \cos^2 \theta
\]

\[
h_{AB2}(r, \theta) = f_{2, AB2}(r) + \left[ f_{1, AB2}(r) - f_{2, AB2}(r) \right] \cos^2 \theta
\]

The functions \( f_{1}(r) \) and \( f_{2}(r) \) are:

\[
f_{1, AB1}(r) = 2\sigma_{A}^{2} \pi \gamma^2 \rho_{B} \left( \frac{Z^2 r^2 - 6}{9Z^4 r^3} \right) + \frac{2\rho_{A}(3 + Z^2 r^2)}{9Z^4 r^3}
\]

\[
-2\sigma_{A}^{2} \pi \rho_{A} \left( 6 + 6Zr + 5Z^2 r^2 + 3Z^3 r^3 \right) - 2\gamma^2 \rho_{B} \left( 3 + 3Zr + Z^2 r^2 \right) e^{-zr}
\]

\[
f_{2, AB1}(r) = \sigma_{A}^{2} \pi \gamma^2 \rho_{B} \left( 6 - Z^2 r^2 \right) + \frac{2\rho_{A}(2Z^2 r^2 - 3)}{9Z^4 r^3}
\]

\[
-\sigma_{A}^{2} \pi \rho_{A} \left( -6 - 6Zr + Z^2 r^2 + 3Z^3 r^3 \right) + 2\gamma^2 \rho_{B} \left( 3 + 3Zr + Z^2 r^2 \right) e^{-zr}
\]
\[ f_{1_{AB}}^2(r) = 2\sigma_{A,B}^2 \pi \rho_a \left( Z^2 r^2 - 6 \right) + 2\gamma^2 \rho_b \left( 3 + Z^2 r^2 \right) \]
\[ \quad - 2\sigma_{A,B}^2 \pi \gamma^2 \rho_b \left( 6 + 6Zr + 5Z^2 r^2 + 3Z^3 r^3 \right) - 2\rho_a \left( 3 + 3Zr + Z^2 r^2 \right) e^{-Zr} \]
\[ f_{2_{AB}}^2(r) = \sigma_{A,B}^2 \pi \rho_a \left( 6 - Z^2 r^2 \right) + 2\gamma^2 \rho_b \left( 2Z^2 r^2 - 3 \right) \]
\[ \quad - \sigma_{A,B}^2 \pi \gamma^2 \rho_b \left( -6 - 6Zr + Z^2 r^2 + 3Z^3 r^3 \right) + 2\rho_a \left( 3 + 3Zr + Z^2 r^2 \right) e^{-Zr} \]

where:
\[ Z = \frac{\sigma_{A,B}^2 \pi (\rho_a + \gamma^2 \rho_b)}{3} \]

**VI.6 References**


CHAPTER VII:

Conclusions
The conclusions from our investigation of geometric percolation in macromolecular systems are as follows:

1. Percolation thresholds and the number of direct interchain contacts necessary for percolation depend strongly on macromolecular architecture and dimensions. Analytical results within the thread treatment show that the percolation thresholds scale as $\rho_n^p \sigma^3 \propto R_g^{-0.5}$ for athermal, ideal, coils, as $\rho_m^p \sigma^3 \propto N^{-1}$ for athermal rods, and as $\rho_m^p \sigma^3 \propto R_g^{-1}$ for flexible coils near the $\theta$ temperature. Results from our numerical calculations are consistent with predictions from analytical methods both for athermal rods and for flexible coils near the $\theta$ temperature. The behavior of the percolation threshold for athermal coils ($\rho_m^p \sigma^3 \propto R_g^{-0.37}$) is, however, somewhat weaker than that predicted by the corresponding thread model. Results from both analytical and numerical approaches show that the average number of direct interchain contacts at the percolation threshold is approximately independent of $N$ for the case of rod-like particles, but increases $\propto \sqrt{N}$ for athermal flexible coils.

2. Attractive segmental interactions, when included in our treatment of one-component flexible polymers, lead to a dramatic, temperature-dependent, reduction in the percolation threshold.

3. The dependence of critical volume fraction on rod aspect ratio found in our two-component model (rods and coils both represented explicitly) is strikingly similar to that found for the analogous one component model which considered rods
alone. The primary effect of explicitly including the flexible matrix polymer molecules is a reduction of the critical volume fraction by a factor which depends only weakly on the particle aspect ratio.

4. Results from our fully numerical calculations are qualitatively consistent with those obtained from analytical approximations, and computer simulation studies of systems of rod-like and ellipsoidal particles.

5. A comparison of results from different methods suggests that our relatively simple analytical treatment could be useful for understanding percolation in more complex, multicomponent, macromolecular systems.

Conclusions drawn from our investigation of shear-induced effects on the miscibility of polymer solutions and blends are as follows:

1. Accounting for changes in the cohesive energy arising from flow-induced coil deformation may lead to non-monotonic shifts in the cloud point of polymer solutions as a function of strain rate, even in the absence of nonlinear viscoelastic response;

2. Our calculations from the Rouse-FE and Zimm-FE models show reasonable agreement with experimental measurements of the apparent spinodal temperature for sheared solutions of polystyrene (PS) in dioctyl phthalate (DOP);

3. Calculations for the spinodal temperatures of polymer solutions based on the Zimm-FE model can describe the experimental data over a wider range of shear
rates than those from the Rouse-FE model, which completely neglects hydrodynamic interactions;

4. Inclusion of the free energy due to chain extension, as well as modifications to the direct correlation functions to first order in the coil eccentricities, are found in most instances to enhance the blend miscibility, i.e., the domain of phase separation in the temperature-composition plane is reduced;

5. Shear-induced remixing at low temperatures, i.e., a lower critical solution temperature with an island-like immiscible region, is found even for model blends which under quiescent conditions exhibit only an upper critical solution temperature.
Vita

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Education:

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<tr>
<td>NUST</td>
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<td>1999 – 2001</td>
<td>Teaching Assistant</td>
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<tr>
<td>College of Environmental Science and Forestry</td>
<td>2002 – 2003</td>
<td>Research Assistant</td>
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<td>Syracuse, New York</td>
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Publications: