

2 Phase Behavior and Polymer-Polymer Interface

2.1 General Consideration

In this chapter, the theoretical methods which are used to study the phase behavior of polymer mixtures and interface properties of two different types of polymer systems will be discussed briefly.

All the theoretical methods that are used to study polymer interfaces can be categorized as being either an analytical or a simulation technique. The analytical techniques can be further classified as being either microscopic or phenomenological. The examples of microscopic approaches are lattice mean-field theories, self-consistent field (SCF) theory, and certain scaling and renormalization group theories. Similarly, the examples of phenomenological approaches include Landau theories of phase transitions [48] and Cahn-Hilliard theory [49]. A big advantage of working with polymeric liquids, as well as other types of mesoscopic systems in which the phenomena of interest occur at length scales that greatly exceed the fundamental molecular dimensions (e.g. monomer size), is that it is often possible to explicitly “coarse-grain” a microscopic description into a phenomenological one, thus providing microscopic expressions for the phenomenological coefficients. Simulation methods for studying polymer interfaces are almost always based on microscopic models, but vary widely in the level of detail ascribed to the monomers, the intermolecular potentials, and the realism of the molecular dynamics. Simulations can be performed on lattices of various symmetries, or in continuous space. The techniques most commonly used for polymer simulations are Monte Carlo, Molecular Dynamics and Brownian Dynamics. Simulation methods will be discussed briefly in section 2.4.

The complicated polymeric systems partly simplify the physics. For example, the very fruitful approach to the study of the system near its critical point is based on the mean-field Flory-Huggins free energy [12] and the de Gennes random phase approximation (RPA) [13] for the scattering intensity. de Gennes showed that the mean-field theory is rather good for high molecular mass mixtures, in contrast to the low molecular mass mixtures, for which the mean-field theory breaks down close to the critical point. Due to the chain connectivity, the effective range of interactions between polymers, which

is roughly the extension of the chains, becomes very large for high molecular weights and according to the Ginzburg criterion, the critical region in which critical fluctuations become important is very small as a result. The mean-field approach is qualitatively correct if the correlation length $\xi \sim (\frac{T}{T_c} - 1)$ comparable or smaller than the typical length scale in the system i.e. the radius of gyration $\sim \sqrt{N}$. When we compare two length scales for large N , we find that the mean-field theory breaks down very close to the critical point, i.e. for $\frac{|T-T_c|}{T_c} \sim \frac{1}{N}$ [3].

The phase behavior of binary and ternary polymer mixtures is of long standing interest. For large molecular weight, the configurational entropy of mixing contribution to the Gibbs free energy is strongly reduced in comparison with mixtures of small molecules, therefore, many polymer mixtures are strongly incompatible. We are interested in such strongly segregated systems i.e., far from critical region to study interface properties. The systems in weak segregation limit will be studied to understand the phase behavior of flexible-semiflexible polymer blends.

2.2 Phase Behaviour in Polymer Mixtures

2.2.1 Flory-Huggins Theory

Flory-Huggins theory [12] provides the reference framework for considering polymer blend problems. Flory and Huggins [12] formulated a lattice model which captures the essential features of the competition between configurational entropy of mixing and enthalpy contributions. Based on the Flory-Huggins (FH) lattice theory, the free energy of mixing ΔF_{mix} for an asymmetrical system (in which two types of monomers have different sizes) is given by [50];

$$\frac{\Delta F_{mix}}{k_B T} = \frac{\phi_A \ln \phi_A}{z_A N_A v_0} + \frac{(1 - \phi_A) \ln(1 - \phi_A)}{z_B N_B v_0} + \frac{\chi_{AB} \phi_A (1 - \phi_A)}{v_0} \quad (2.1)$$

where $z_A = \frac{v_A}{v_0}$, $z_B = \frac{v_B}{v_0}$ and v_0 is any reference volume, v_i ($i=A, B$) is the volume of i th type of a monomer, ϕ_A denotes the volume fraction of component A and incompressibility is assumed. k_B is Boltzmann constant and T is temperature. N_A and N_B are the degree of polymerization of the A and B components respectively. Furthermore, the parameter, χ_{AB} , denotes the degree of interaction between two types of segments, A and B, and is a quantitative measure of the miscibility. Knowing the free energy, one can easily find the binodal and spinodal curve [12, 13]. Further the critical value of χ_{AB} i.e., χ_c can be obtained by third derivative of right hand side of 2.1 with respect to ϕ_A and it is given by (for a system in which two types of monomers have equal size but different number of monomers per chain);

$$\chi_c = \frac{1}{2} \left(\frac{1}{\sqrt{N_A}} + \frac{1}{\sqrt{N_B}} \right)^2 \quad (2.2)$$

If the value of χ_{AB} is less than χ_c , the two components A and B mix. For a symmetrical system ($N_A = N_B$), this expression reduces to,

$$N\chi_c = 2 \tag{2.3}$$

To derive Flory-Huggins free energy functional 2.1, they used several approximations. Therefore, from a theoretical point of view, one can see following sources of errors.

- Flory-Huggins theory is a mean-field theory and so neglects those large composition fluctuations that occur close to the critical point. It neglects any local composition fluctuations also.
- In Flory-Huggins theory it is assumed that there is no change of volume on mixing the two species and no extra space is created when the two polymers are mixed.
- The local structure of monomers may lead to difficulties in packing.

A huge amount of effort has gone into making a more refined theory of polymer mixtures. Although many of the resulting methods have had their successes, no single improved method has achieved universal applicability. Dudowicz and Freed [51] (see below) have studied the local structure and packing effects whereas Schweizer and Curro [52] (see below) has attempted to adapt methods to deal with small-molecule liquids. Despite all its shortcomings, Flory-Huggins theory provides the reference framework for considering polymer blend problems.

The critical behavior of binary polymer mixtures is itself a very interesting research subject. Analyzing the critical behavior enables us to discuss the universality class of the polymer mixture, and hence, one can investigate to what extent the mean field approximation, which was first introduced to polymer systems by Flory, is correct. Therefore, knowledge of the critical behavior characteristic of polymer mixtures is important from a technical point of view when a precise determination of the critical temperature is required.

2.2.2 Lattice Cluster Theory

Lattice cluster theory (LCT) is an extension of the Flory-Huggins lattice model. It is able to distinguish polymer structural detail [53]. In LCT, a branched polymer can be distinguished from a linear polymer, distinction that is not possible in the original Flory-Huggins (F-H) formulation of the lattice model. Further, it is possible to include contributions to thermodynamic properties from packing and induced local correlations. As a result, χ which is strictly energetic in origin in the F-H model, also has an entropic component in LCT. The model can be developed in a compressible (vacancies allowed) or incompressible form. The LCT provides a solution to the lattice model beyond the traditional F-H calculation by expanding the free energy in a double power series in $\frac{1}{z}$ and $\frac{\epsilon_{ij}}{k_B T}$ where z is the lattice coordination number and ϵ_{ij} is the interaction energy between

monomers i and j . In the interaction energies, terms in the expansion are retained to the second order. The LCT free-energy expression contains corrections to the FH lattice energy expression that are in the form of a polynomial expression in the site fractions. The coefficients in polynomial contain information that depend on polymer structure. In this model, chain stiffness can also be incorporated by using a bend or flex energy. It captures the detail effects of structure on polymer blend.

The standard lattice models consider the equal volumes for a monomer, a solvent molecule and a void. Therefore, in blends also both types of monomers occupy the volume of a single lattice site. This deficiency has led in both the lattice and ‘equation of state’ models to the introduction of a phenomenological unit volume and of a variety of different composition dependent combining rules for describing this unit volume in mixtures. But Nemirovsky and coworkers [54] have considered more general lattice models of polymer solutions in which different monomers can occupy different number of lattice sites.

Nemirovsky *et al.* have considered calculations to a level of sophistication that exceeds that of Flory’s theory in order to describe the architecture dependence of thermodynamical properties of polymer melts, blends and solutions. The fact that different sizes of monomers of two different types of polymers, say A and B, is believed to influence many thermodynamic and interfacial properties of these systems [55].

Pesci and Freed [41] have provided the theoretical description of the computation of the corrections to the F-H approximation, heats of mixing for lattice models of flexible polymer blends where the monomers may cover several lattice sites and therefore have different sizes and shapes. They have obtained the corrections as an expansion in inverse powers of the lattice coordination number z and the Van der Waals interaction energies ϵ_{ij} (in units of $k_B T$) using the convenient ordering recipe that $z \sim \epsilon_{ij}$ and considering terms through order z^{-2} .

2.2.3 PRISM

Schweizer and co-workers [56, 57, 58] have studied polymer melts and blends using polymer reference interaction site model (PRISM) theory. PRISM theory is the polymeric generalization of the RISM theory of Chandler and co-workers. The PRISM model allows certain structural features of polymers to be incorporated. Each polymer structure has a unique structure factor that, in principle, can be calculated. PRISM is unique among the models used in study of polymers because it is able to incorporate details of the polymer’s structure. The radial distribution function for all possible site-site pairs is calculated using a series of coupled integral equations. To solve these integral equations, some closure relations are necessary. These closure relations generally deal only with repulsive interactions, as these interactions are thought to be the controlling factor for polymer structure. The attractive forces between sites on the chain can be handled in a perturbation theory and are first order corrections to the theory. Using this theory one

can calculate structure factors which can be used to see how blend miscibility is affected by subtle structural differences. The only other model capable of distinguishing small structural differences is the lattice cluster model of Freed and coworkers (see previous subsection). PRISM can be used on any level of detail for polymer chain, from representing each atom in the chain to treating the chain as a Gaussian thread. An equation of state can be obtained directly from the radial distribution functions calculated from the PRISM formulation. Equation of state determined from the PRISM formalism are far from inferior to those obtained by other methods [59, 60]. PRISM has ability to deal with polymer blends. Solubility parameters for polymers can be calculated directly from the radial distribution functions, by integrating the pair-pair energy function times the radial distribution function. Subtle structural effects on blend miscibility can be investigated systematically using PRISM. PRISM can also be applied to polymers with gross differences in architectures. Block copolymers, star polymers, and ring polymers can also be described with PRISM. PRISM can describe the structure of polymers with varying stiffness also. Coarse-grained models can be used as first predictions of structure. It also fits simulation data (structure factors) of particular models quite well.

Singh and Schweizer [11] have studied the possibility of nonlocal entropy-driven ‘athermal phase separation’ in binary polymer blends. For the idealized gaussian thread model, PRISM predicts no entropy driven phase separation [61, 62, 63]. Contrary to PRISM predictions, Singh and Schweizer [11] have shown that for the more realistic, finite thickness semiflexible chain model athermal phase separation is observed under certain conditions. This arises from spatially nonlocal, nonrandom packing correlations induced by local chain rigidity present in any realistic non-Gaussian model of polymer structure. The entropy packing effects display many nonuniversal features including a sensitive dependence on chain length, blend composition, monomer volume difference, and both the mean and relative aspect ratios of the polymers. So, they have carried out study of athermal spinodal phase diagrams and structural correlations for various values of ratio of hard core diameters.

Weinhold *et al.* [19] have estimated quantitatively the excess entropic contributions to the free energy of mixing of binary blends of two tangent hard sphere polymers of different stiffnesses by performing computer simulations and compressible PRISM calculations under constant density conditions. Their results show that the stiffer component in the mixture is stabilized on blending while the flexible component is destabilized on blending. It should be noted that the PRISM theory considers length scales of monomer levels. To compare the analytical results with simulations they have used off-lattice model. The Monte Carlo simulation method used standard reptation, crankshaft moves, and chain identity exchanges [42]. In their study they do not consider very high stiffness disparity.

2.2.4 Landau-de Gennes Free Energy Functional

Liu and Fredrickson [21] have calculated a free energy functional that depends on two order parameters, namely the concentration and orientational density of polymer segments. The phase behavior of flexible polymers is described in terms of a single order parameter (see above), which is composition of one type of polymers. However, due to the fact that individual monomers may have a rigid, anisotropic character, a description of stiff polymers must include the orientational density as a second order parameter. To describe both the isotropic-nematic transition and ordinary phase separation, they have expanded to arbitrary order in concentration and up to fourth order in orientation density, by combining a density functional theory with a Landau-de Gennes theory for the orientational order parameter. They have used a microscopic model of wormlike chains rather than Gaussian chains to calculate the expansion coefficients. They have explicitly computed the coefficients of the terms in the free energy expansion, so they are not unknown parameters. The nonlocal terms in both the concentration and the orientational density are included. The expression for the free energy functional obtained by Liu and Fredrickson is the following;

$$F = F_{FH} + F_{LdG} \quad (2.4)$$

where F_{FH} is the usual Flory-Huggins free energy density (see equation, 2.1) and,

$$F_{LdG} = \frac{1}{2} (B - w) \bar{S}^2 - \frac{C}{3} \bar{S}^3 + \frac{D}{4} \bar{S}^4 \quad (2.5)$$

where \bar{S} is the orientational order parameter, w is the Maier-Saupe parameter and the coefficients B , C , D represent the entropic cost of orienting chains and depend up on the flexibility parameter, κ (the ratio of elastic bending constant to the thermal energy), and ϕ , composition of polymers. κ defines the flexibility of the polymers and it gives the persistence length in units of bond length.

Using above free energy functional one can study phase behaviors of flexible and semi-flexible polymers. Lee et al. [64] have studied the phase behavior of liquid crystalline polymer/model compound mixtures using this free energy functional. Their experimental data agree very well with that obtained from the expression 2.4.

2.3 Polymer-Polymer Interfaces

2.3.1 Overview of Square Gradient Theory

To predict the width and interfacial tension of polymer-polymer interfaces in detail we need to go beyond a description of the thermodynamics of spatially uniform mixtures to include the effect on the free energy of concentration gradients. A detailed derivation of the square gradient term relies on the use of the random phase approximation (RPA) [13]. If one is considering polymer-polymer interface such that two types of monomers

not only have different segment lengths, b_A and b_B but also different volumes (v_A and v_B , for type A and type B monomers respectively), then free energy functional takes the form [50];

$$\frac{\Delta F}{k_B T} = \int d\vec{r} \frac{1}{v_o} [f[\phi(\vec{r})] + \frac{1}{36} \left[\frac{b_A^2}{z_A \phi(r)} + \frac{b_B^2}{z_B (1 - \phi(r))} \right] |\nabla(\phi)|^2] \quad (2.6)$$

where

$$f[\phi(\vec{r})] = \frac{\phi \ln \phi}{z_A N_A} + \frac{(1 - \phi) \ln(1 - \phi)}{z_B N_B} + \chi \phi(1 - \phi) \quad (2.7)$$

is the Flory-Huggins free energy density, $z_A = \frac{v_A}{v_o}$, $z_B = \frac{v_B}{v_o}$ and v_o is any reference volume.

For a symmetric polymer-polymer interface (when $b_A = b_B$, $z_A = z_B$ and $N_A = N_B$) above free energy functional gives the following expressions for interfacial width and tension near the critical point. The interfacial width ‘ w ’ and tension ‘ σ ’ are given by [1],

$$w = \frac{b\sqrt{N}}{3} \left(\frac{\chi}{\chi_c} - 1 \right)^{-\frac{1}{2}} \quad (2.8)$$

and

$$\frac{\sigma}{k_B T} = \frac{9}{b^2 \sqrt{N}} \left(1 - \frac{\chi_c}{\chi} \right)^{\frac{3}{2}} \quad (2.9)$$

for $\chi \rightarrow \chi_c$ respectively. In equations 2.8 and 2.9, b is statistical segment length k_B is the Boltzmann constant, T is the temperature and N is degree of polymerization. From equation (2.8) and (2.9), we find that the interfacial tension vanishes and the interfacial width becomes indefinitely wide as the two phases merge into one.

All of the square gradient theory is derived on the assumption that concentration gradients were small compared with the overall size of the chain. But in the non-critical regime (in the strong segregation limit) interfacial widths are already smaller than the overall size of the polymer. Therefore, the square gradient theory valids only near to the critical region [1, 6]. But square gradient theory gives corect qualitative conclusions even for the strong segregation regime.

To obtain more accurate results, particularly for situations in which composition gradients are steep on the scale of the polymer radius of gyration, we need to keep track of the polymer configurations in more detail. This way is provided by self-consistent field (SCF) methods. Helfand and Tagami [65] have studied symmetric polymer-polymer interfaces following SCF methods, Helfand and Sapse [20] have studied unsymmetric polymer-polymer interfaes by applying SCF methods. Using SCF methods they have obtained analytic expressions for interfacial tensions and interfacial width.

2.3.2 Self-Consistent Field (SCF) Theory

Helfand and Tagami [65] have studied the internal polymer-polymer melt interface. They adopted the self-consistent field formalism of Edwards to the case of a symmetrical, flat interface between two molten, flexible homopolymers. Apart from the energetic contacts between type A and type B monomers, described by a Flory χ parameter, they recognized the importance of cohesive forces that maintain nearly uniform density in polymer melts. After prescribing the form of the interactions, they followed the Edward's procedure of generating statistical weights for the two types of chains via the solution of modified diffusion equations. After framing the problem, they recognized that a full solution to the nonlinear diffusion equations was not required; rather, only the steady state (ground state approximation) solution was needed to capture the interfacial thermodynamics in the limit of infinite molecular weight. In the incompressible limit, the form of the interfacial composition profile is 'tangent hyperbolic'. The interfacial width ' w ' and tension ' σ ' are given by following expressions;

$$w = \frac{b}{\sqrt{6\chi}} \quad (2.10)$$

and,

$$\frac{\sigma}{k_B T} = \rho_o b \sqrt{\frac{\chi}{6}} \quad (2.11)$$

respectively, where ' b ' is the statistical segment length, ρ_o is the uniform number density of monomers, k_B is the Boltzmann constant, T is the temperature and χ is the Flory-Huggins interaction parameter. A follow-up paper by Helfand and Sapse [20] extended above approach to asymmetric melt interfaces in which the two pure polymer components differ in statistical segment lengths, b_i , and/or segment volumes, v_i ($i = A$ or B). In their contribution, Helfand and Sapse have defined a parameter,

$$\beta_i^2 \equiv \frac{1}{6} \rho_{0i} b_i^2 \quad (2.12)$$

for both types of chains and difference in β_i 's measures the asymmetry between different types of polymers. They solved the diffusion equation

$$\frac{\partial q_i(\vec{r}, N)}{\partial t} = \left(\frac{b_i^2}{6} \nabla^2 - \frac{U_i(\vec{r})}{k_B T} \right) q_i(\vec{r}, N) \quad (2.13)$$

where $q_i(\vec{r}, N)$ is proportional to the probability density that the end of a molecule of type i ($i = A, B$) and degree of polymerization N is at \vec{r} , $U_i(\vec{r})$ is the external field which is replaced by $\Delta\mu_i^*(\vec{r})$ i.e., the work of bringing a unit of i from bulk i to the point \vec{r} . It is given by,

$$\Delta\mu_A^*(\vec{r}) = \left(\frac{\partial \Delta f^*[\tilde{\rho}_A(\vec{r}), \tilde{\rho}_B(\vec{r})]}{\partial \rho_A} \right)_{\rho_B} \quad (2.14)$$

where Δf^* is the free energy density of a hypothetical mixture of densities ρ_A, ρ_B , less the free energy density of the material in bulk. The density of species i at \vec{r} can be

written,

$$\rho_i(\vec{r}) = \frac{\rho_{0i}}{Z_i} \int_0^{Z_i} dN q_i(\vec{r}, Z - N) q_i(\vec{r}, N) \quad (2.15)$$

where prefactor on right hand side slightly modified for Z finite. Equations 2.13, 2.14 and 2.15 form a closed set of SCF. They solved the SCF equations employing following assumptions;

- random mixing,
- no volume change on mixing,
- small compressibility, κ , and
- κ independent of composition.

Considering zeroth order in compressibility, they have obtained analytic expressions for interfacial tension (' σ ') and width (' w ') which are given by;

$$\frac{\sigma}{k_B T} = \frac{2}{3} (\chi \sqrt{\rho_{0A} \rho_{0B}})^{\frac{1}{2}} \left(\frac{\beta_A^3 - \beta_B^3}{\beta_A^2 - \beta_B^2} \right) \quad (2.16)$$

and,

$$w = \left(\frac{\beta_A^2 + \beta_B^2}{2\chi \sqrt{\rho_{0A} \rho_{0B}}} \right)^{\frac{1}{2}} \quad (2.17)$$

We compare the simulation data with data obtained from these expressions. But in their study, to obtain these expressions they did not consider the orientation of chains near the interface. For the chains which are very stiff the orientational effect is important as the chains orient parallel to the interface.

Schmid and Mueller [66] have compared self-consistent field (SCF) theories for polymers near interfaces with Monte Carlo simulations quantitatively. These authors have considered a planar interface between immiscible phases in a symmetric polymer blend in self-consistent field for flexible (Gaussian) and semiflexible chains. Within the framework of SCF theory, they have defined the end-segment distribution functions,

$$Q_i(\vec{r}_o, s) = \int \hat{D}(\vec{r}(\cdot)) \exp \left[- \int_0^s ds' W_i(\vec{r}(s')) \right] \delta(\vec{r}_o - \vec{r}(s)) \quad (2.18)$$

(for Gaussian chains) and,

$$Q_i(\vec{r}_o, \vec{u}, s) = \int \hat{D}(\vec{r}(\cdot)) \exp \left[- \int_0^s ds' W_i(\vec{r}(s')) \right] \delta(\vec{r}_o - \vec{r}(s)) \delta(\vec{u}_o - \vec{u}(s)) \quad (2.19)$$

(for semiflexible chains).

Where $Q_i(\vec{r}_o, s)$ is end distribution for flexible chains, s varies from 0 to 1 and the functional integral $\hat{D}(\vec{r}(\cdot))$ depends upon the assigned statistical weights which depend upon

stiffness. $W_i(\vec{r})$ is the external field acting on the chain and depends upon coarse-grained free energy functional which can be obtained from monomer density $\phi_i(\vec{r})$. $\vec{u} = \frac{d\vec{r}/ds}{Na}$ is a dimensionless tangent vector constrained to unity. The end distribution functions obey the diffusion equations,

$$\left(\frac{1}{N} \frac{\partial}{\partial s} - \frac{1}{6} b^2 \nabla_{\vec{r}}^2 + W_i \right) Q_i(\vec{r}, s) = 0 \quad (2.20)$$

(for Gaussian chains) and,

$$\left(\frac{1}{N} \frac{\partial}{\partial s} + a\vec{u}\nabla_{\vec{r}}^2 - \frac{1}{2\eta} \nabla_{\vec{u}}^2 + W_i \right) Q_i(\vec{r}, \vec{u}, s) = 0 \quad (2.21)$$

(for semiflexible chains)

with initial condition $Q_i(\vec{r}, 0) \equiv 1$ ($Q_i(\vec{r}, \vec{u}, 0) \equiv 1$), the laplacian on the unit sphere $\nabla_{\vec{u}}^2$, η is the dimensionless stiffness parameter given by, $\eta = \frac{b^2}{2a^2}$, a is monomer length, b is statistical segment length and N is the number of monomers per chain. The average density of type i is given by,

$$\phi_i(\vec{r}) = \int_0^1 ds Q_i(\vec{r}, s) Q_i(\vec{r}, 1-s) \quad (2.22)$$

(for Gaussian chains) and,

$$\phi_i(\vec{r}, \vec{u}) = \int_0^1 ds Q_i(\vec{r}, \vec{u}, s) Q_i(\vec{r}, \vec{u}, 1-s) \quad (2.23)$$

for semiflexible chains. The equations 2.18(2.19), 2.20(2.21) and 2.22(2.23) complete the cycle of self-consistent equations. After solving these equations they have calculated the distribution of chain ends and other interfacial properties for example, monomer density profile, interfacial width, interfacial tension, distribtuion of bond vectors and orientation of chains. They have compared their results of self-consistent field theory with Monte Carlo data. Their results show that interfacial width decreases with the increase in stiffness of semiflexible chains, the interfacial tension (in simulation) at large χN is higher than would have been expected in an incompressible system of Gaussian polymers. The concentration profile resembles a simple tangent hyperbolic profile. For the chain orientation self-consistent field theory predicts a slightly too strong alignment. The depth of the dip in concentration profile for semiflexible chains of low stiffness ($\eta \leq 4$) from SCF theory agrees very well with that of simulation results.

2.3.3 Landau - de Gennes Free Energy Functional

Liu and Fredrickson [67] have studied interfaces between polymers of different flexibilities. By adding a gradient term in the free energy functional (2.4) they have obtained free energy functional for the system with interfaces. The expression for the free energy functional by Liu and Fredrickson is the following;

$$F = F_{FH} + F_{LdG} + F_{grad} \quad (2.24)$$

where F_{FH} and F_{LdG} are already defined (equation 2.1 and 2.5) and F_{grad} is given by;

$$F_{grad} = \frac{1}{2}L_1(\phi)(\partial_k S^{ij})^2 + \frac{1}{2}L_2(\phi)\partial_i S^{ik}\partial_j S^{jk} - L_0(\phi)\partial_i\phi\partial_j S^{ij} + \frac{1}{2}M_0(\phi)(\nabla\phi)^2 \quad (2.25)$$

where \bar{S} is the orientational order parameter and the coefficients in the expansion depend up on κ 's (the ratio of elastic bending constant to the thermal energy) and ϕ .

Using above free energy functional these authors have studied interface properties of isotropic semiflexible blends [67]. For asymmetric interfaces their expressions for interface width (' w ') and tension (' σ ') are given by;

$$w = \frac{\sqrt{2}}{3} \left(\frac{(\kappa_A + \kappa_B)a_0^2}{\chi} \right)^{\frac{1}{2}} \quad (2.26)$$

and

$$\frac{\sigma}{k_B T} = \frac{4}{9a_0^2} \sqrt{\chi} \frac{\kappa_A^{\frac{3}{2}} - \kappa_B^{\frac{3}{2}}}{\kappa_A - \kappa_B} \quad (2.27)$$

where a_0 is the monomer length.

2.4 Study of Polymer Blends by Simulation

2.4.1 Models

Phase behavior for mixtures of simple fluids can be simulated taking into account full atomistic detail with chemically realistic forces. It is sufficient to simulate small boxes containing atoms or molecules in the order of 10^3 [42], except from the region near a critical point in Monte Carlo or Molecular Dynamics methods. These methods work because fluids off critical points are already essentially homogeneous on a length scale of 10 \AA and staying away from the glass transition region. However, the situation is fundamentally different for mixtures of polymers. This is due to varying length scales for example, a single chain exhibits structure in the length of a chemical bond ($\approx 1 \text{ \AA}$) to the persistence length ($\approx 10 \text{ \AA}$) to the coil radius ($\approx 100 \text{ \AA}$) to the correlation length, ξ , which has lower bound ($\approx 100 \text{ \AA}$) of concentration fluctuations [42].

In this chapter we briefly discuss about various simplified models used in computer simulation of polymers. There is no unique way to construct coarse-grained models of polymer systems. The choice of model very much depends on the physical problems that one may wish to address and also many details are fixed from the desire to construct computationally efficient simulation algorithms. All the models used in computer simulations are either off-lattice models (which are performed in continuous space) or lattice models (which are performed in various symmetries of lattices).

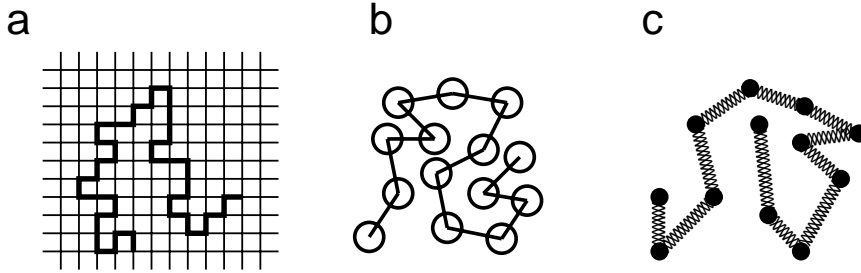


Figure 2.1: Models used to study polymers. (a) is a two dimensional lattice model, (b) is perl necklace, off-lattice model and (c) is the bead spring, off-lattice model.

The simplest lattice model considers a regular lattice where each effective bead of the polymer takes a single lattice site, and bond connecting two beads is just a nearest neighbor link on the lattice. Figure 2.1(a) shows a two dimensional square lattice model. Since each lattice site can at most be occupied by one bead, the walk cannot intersect itself and thus an excluded volume interaction is automatically included. The lattice algorithm that is now most widely used for the simulation of many-chain systems is the bond fluctuation model [39, 42] (not shown in the figure). This model is in an intermediate between lattice (self avoiding walk) model and the off-lattice models, because the vector that connects two monomers can take 108 values in three dimensions.

Figure 2.1(b),(c) show off-lattice models for polymer chains. The perl necklace model in figure 2.1(b) is an athermal model. In this model, by a proper choice of the ratio $\frac{d}{l}$ (where d is diameter of a bead and l is bond length), one can ensure automatically that chains cannot cross each other if they respect excluded volume restrictions. The chain consists of hard spheres of diameter d and fixed length l . The bead-spring model shown in figure 2.1(c), can be used not only for Monte Carlo but also for Molecular dynamics and Brownian dynamics simulations. It often is advantageous not to use a simple harmonic potential for the bond lengths but rather allow only a finite extensibility of the chains.

2.4.2 Simulation Methodology

In the simulation of polymer blends mainly used methods are Monte Carlo (MC), Molecular dynamics (MD) and Brownian dynamics (BD). The MC method is a stochastic strategy that relies on probabilities. In MC simulations of polymer blends there could be several interacting potentials (for example see chapter 3, for our model) like excluded volume, connectivity between two consecutive beads, interaction between different types of beads and potential controlling the angle between subsequent bonds along a chain (in semiflexible polymers), etc. These potentials then enter the transition prob-

ability $W(\phi) = \text{Min}\left(1, \exp\left(-\frac{\delta E}{k_B T}\right)\right)$ where δE is the energy change produced by the change of configuration. According to standard Metropolis sampling (which is used in the present work), the trial move is only carried out if $W(\phi)$ exceeds a random number ζ distributed uniformly in the interval from zero to one, since then one generates an ensemble of configurations (when equilibrium is reached) distributed according to the canonical Boltzmann weights. In the MD simulation each monomer i of the system moves according to Newton's equations of motion. In contrast to MC, chances plays no part in MD. BD is nothing but the numerical solution of the Smoluchowski equation [68]. The method exploits the mathematical equivalence between Fokker-Planck type of equation and the corresponding Langevin equation [69].

In a simulation of polymer blends there are two distinct aspects: one is the generation of equilibrium configurations of dense polymer melts and the relaxation of the configurations of individual chains. For lattice model, dynamic Monte Carlo methods such as combinations of 'kink jump' and 'crankshaft rotation' algorithms [42] or simple hops of effective monomers in randomly chosen lattice directions (in the case of bond fluctuation model [39]) or the 'slithering snake' technique are used for the equilibration of the configurations. These algorithms need a nonzero concentration of vacancies. However, for off-lattice model, the most widely used algorithm is random hopping. Watching the decay of the component of the end-to-end vector in the direction of the initial state, as disorder diffuses in from the ends of the chains into their interior as time passes, one can make sure that all 'memory' of the initial nonrandom state is lost. The second aspect is relaxation of the long wavelength degrees of freedom related to phase transitions occurring in the studied system, for the unmixing of polymer blends, these are long wavelength Fourier components of the volume fractions of species A, B in the system. If the total numbers of both A-chains and B-chains are kept fixed, the conservation law of the concentration leads to "hydrodynamic slowing down" [42] of these Fourier components, i.e., extremely slow relaxation. The situation is worse near the critical point. It is due to an anomalous growth of relaxation times which is called "critical slowing down" and in addition there are severe finite size effects on the transition [42, 70].

The problem of 'hydrodynamic slowing down' can be avoided for symmetrical (as well as weakly asymmetrical) polymer mixtures by carrying out the simulation in the semi-grand-canonical ensemble rather than the canonical ensemble: only the total number of chains $n = n_A + n_B$ is fixed, while the ratio $\frac{\phi_A}{(1-\phi_v)}$, ϕ_A = number density of A types of monomers and ϕ_v = number density of vacancies, fluctuates in equilibrium with a given chemical potential difference $\Delta\mu = \mu_A - \mu_B$ between the chains with $\phi_A + \phi_B = 1 - \phi_v = \text{constant}$. Thus in addition to the moves necessary to equilibrate the coil configuration, one allows for moves where an A-chain is taken out of the system and replaced by B-chain or vice-versa. The transition probability for the "semigrandcanonical" moves where one goes from an old configuration (c) to a new configuration (c') via an "identity switch" of a chain ($A \rightleftharpoons B$), is given by;

$$W(c \rightarrow c') = \text{Min}\left(1, \exp\left[\frac{\Delta\mu(M' - M)Nn}{2k_B T}\right] \exp\left[\frac{-(E - E')}{k_B T}\right]\right) \quad (2.28)$$

where E , M are energy and order parameter of the old configuration and E' , M' refer to the new configuration, k_B is the Boltzmann constant, T is the temperature and N is the number of polymerization.

In principle, this semigrandcanonical ensemble procedure could be generalized to the asymmetric case ($N_A \neq N_B$ or $b_A \neq b_B$ or $V_A \neq V_B$ or combination of these, where N_i ($i=A,B$) are the number of monomers per chain, b_i are the statistical segment lengths and V_i are the volumes of monomers), but such moves would almost always fail in a dense system due to excluded volume constraints. In the thermodynamic limit, where $n_A, n_B \rightarrow \infty$, the different ensembles of statistical mechanics yield completely equivalent results, and for such equilibrium properties it then does not matter whether one computes them in the grand-canonical ensemble (both μ_A and μ_B are given separately, n_A and n_B can fluctuate independently from each other), the semi-grand-canonical ensemble, or the canonical ensemble (where both n_A and n_B would be fixed, while μ_A and μ_B would both be fluctuating). Since experiments are done in canonical ensemble only, and chain “identity switches” do not occur but due to this equivalence between the statistical ensembles that distinction does not matter, in the thermodynamic limit.

Now we discuss methods to study the phase behavior in equilibrium. One approach is the generalization of techniques for the estimation of chemical potentials in dense polymer systems to chemical potential differences. However, this approach is hampered by the slow relaxation effects (hydrodynamic as well as critical slowing down). Another technique is based on the calculation of the structure factor $S(q)$. As shown first by Sariban and Binder [71], in the framework of a semigrandcanonical simulation, one can estimate the spinodal curve from a linear extrapolation of $S^{-1}(q \rightarrow 0)$ versus $\frac{\epsilon}{k_B T}$ and then estimating the temperature T where $S^{-1}(q \rightarrow 0) = 0$ for various concentrations yields an estimate of the spinodal curve.

However, for a strong asymmetry between two different types of monomers and limited computing facilities no method described above can be applied. We have studied the phase behavior of flexible-semiflexible polymer systems by studying the interfacial properties. As described in the previous section, from equation 2.27 and 2.26, one can estimate the critical value of Flory-huggins parameter, χ by analyzing the interface properties in weak segregation limit. When the value of χ decreases the interfacial tension decreases and finally it vanishes for $\chi = \chi_c$. Similarly, when the value of χ decreases the interfacial width increases and finally it diverges for $\chi = \chi_c$. By comparing the simulation data with equation 2.27, we can estimate the critical value of χ . In the present work this method is followed.

The study of polymer-polymer interfaces by computer simulation also is not free of difficulties. For example, very large system sizes are required to investigate, e.g. the effect of capillary wave broadening. Inhomogeneous system of long flexible polymer melts (with $\chi \ll 1$) can be described by two parameters; χN and Rg (or Re), where N

is the number of monomers per chain, Rg is the radius of gyration and Re is the end to end distance of the chain [4]. However, for a polymer system of highly stiff chains [22] or two types of polymers have large value of χ , i.e., the system is in strong segregation limit [38] another length, l_p (persistence length, see page 27) which characterizes the length of the chain over which the monomers are still strongly correlated, also should be taken into account.