Interfacial Properties and Phase Behavior of Unsymmetric Polymer Blends



Dissertation

zur Erlangung des akademischen Grades

doctor rerum naturalium (Dr. rer. nat.)

vorgelegt der

Mathematisch-Naturwissenschaftlich-Technischen Fakultät (mathematisch-naturwissenschaftlicher Bereich) der Martin-Luther-Universität Halle-Wittenberg

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Halle (Saale), den 28.09.2001

ACKNOWLEDGEMENTS

I wish to express my indebtedness to Prof. Dr. Ekkehard Straube for suggesting the problem and his constant guidance throughout this work. His encouragement and assistance at all times has been of immense value.

I would like to express my gratitude to Dr. S. Stepanow for his lectures in Polymer Physics, encouragement and assistance. I am also very grateful to Dr. Rolf Auhl for his assistance especially in writing the computer code and for his help during this work. I wish to express my sincere thanks to Dr. U. Bauerschaefer and Dr. Z. Khattari for their kind hospitality.

I appreciate encouragement and cooperation given to me by my friends in Halle. The financial support from the "Graduiertenkolleg Polymerwissenschaften" is gratefully acknowledged.

Last but not least, all the love for my family for their continuous encouragement to me in all my studies.

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1 Introduction

1.1 General Consideration

The subject of phase behavior of polymer melts, polymer mixtures (or blends) and polymer interfaces [1, 2, 3, 4, 5, 6, 7] has attracted a great deal of attention because of intriguing physical properties and an essential role in polymer technology. The practical importance arises from the many **industrial applications** of these materials and scientific importance arises from the **complex behavior** they display, a molecular description of which is a challenging problem in statistical mechanics. Therefore, the study of phase behavior of polymer blends or alloys is very important for the design of new multiphase materials as well as to understand their complex behavior.

Polymers do not mix at a molecular level at equilibrium under a wide variety of circumstances because any slight incompatibility of monomers in enthalpic interactions and/or entropic packing effect is amplified by the number of monomers in the macromolecule and cannot be balanced by the entropy of mixing. If such a pair of polymers are dispersed mechanically, there will be domains of one polymer in the other. In such a situation, one is interested to know the nature of the interface between the two coexisting phases and determination of the interfacial energy. The morphology of the mixture will be greatly influenced by the interfacial energy [8], which will control the domain size, while the microscopic structure of this interface will determine the degree of adhesion between the phases. Thus the mechanical properties of the whole mixture will be largly controlled by properties of these interfaces. Further, interfacial properties of polymers play important role in kinetics of the phase separation. Moreover, one may be interested to know at what condition the two components mix. An important feature of polymeric interfaces is that they are often characterized by structure and correlations on scales significantly larger than the monomer size [5], resulting in a degree of universality of interfacial properties. Correlations between interfacial and bulk properties are present on various length scales. The mechanical stability of the alloy depends upon the local interfacial structure - the interfacial width, the conformation of polymers, enrichment of chain ends or the solvent at the interface.

Polymer interfaces play an important role in polymer technology of polymers including adhesives, blends, resists and coatings. Polymeric materials provide an exceptionally varied class of interfacial systems. Polymers can have interfaces with air or solid substrates (external interfaces or surfaces), but also can form internal interfaces, for example the interface between two incompatible homopolymers. The material properties of polymers depend sensitively on the structure and the properties of the interfaces between different phases. Therefore, key to applications of polymeric materials is the ability to control surface or interfacial properties. In polymer blends or filled polymer composites, for example, interfacial tension and adhesion are primary factors in establishing microstructure, strength, and mechanical properties.

Polymer blends are generally "structurally asymmetric" corresponding to speciesdependent local intramolecular features such as monomer shape, branch content, and persistence length [9, 10] or aspect ratio. Such asymmetries are expected to have a major impact on blend thermodynamics and phase diagrams, and can give rise to non-Flory-Huggins miscibility behavior. The nonideal free energy of such mixtures involves an excess entropic part due to athermal (packing) correlations induced by the structural asymetries, and also an enthalpic part [11]. The Flory-Huggins like theories [12] describe the dependence of the phase transition on the molecular weights of the two polymers, the composition of the blend, and the interaction parameter χ [12, 13]. Differences in the chemical structure may lead also to different spatial extension of the chemical repeat units corresponding to different persistence length [9, 10], i.e. the stiffness disparities. Such stiffness disparities may occur even in chemically very similar materials e.g., different polyolefins [14]. The phase behavior and the surface properties [15] of Polyolefins [16, 17] with varying microstructure has recently attracted considerable interest. The mixtures are often modeled [11, 16, 18, 19] as blends of flexible and semiflexible polymers. Helfand and Sapse [20] extended the self-consistent field theory to Gaussian chains with different statistical segment lengths. For infinitely long chains, in the strong segregation limit, they have obtained analytical expressions for interfacial width 'w' and the interfacial tension ' σ '. Both increase upon increasing the statistical segment length of one component, keeping χ and other components unaltered, see the chapter 2. Similarly, Fredrickson and Liu [21] have obtained an expression of free energy for a mixture of a flexible and semiflexible polymers based on two order parameters, the detailed is described in chapter 2. Morse and Fredrickson [22] have studied polymer interfaces using the self-consistent field theory. They have obtained analytic expressions for interfacial width and interfacial tension both of which decrease with the increase in rigidity of the semiflexible polymers. They considered a symmetric system of semiflexible polymers.

Fredrickson, Liu and Bates [18], and Liu and Fredrickson [23] have shown that a small positive contribution to the Flory-Huggins parameter χ arises due to the stiffness disparity of the chains. Similar results have been reported, by Singh and Schweizer [11] using the polymer reference interaction site model (PRISM), by Freed and Dudowicz [24] using the lattice cluster theories and by Mueller [25] in the Monte Carlo simulations. As the back folding of the chains becomes less probable with increasing stiffness and the number of intermolecular contacts increases the Flory-Huggins parameter χ increases and reflects so the increase of the repulsive interaction between different types of monomers. Worm like chain model [26] has been also used to study the stiffness disparity of the polymer blends.

Freed and Pesci [27] have obtained an entropic contribution to χ_{eff} that arises from differences in monomer shape using lattice cluster expansion [28]. Weinhold and coworkers [19] have estimated excess entropic contribution to the free energy of mixing of polymer blends of different stiffnesses. Mueller has studied [29, 30] the phase behavior of polymer mixture of flexible and semiflexible polymers by computer simulation for very low stiffness disparity. This author has shown that the critical temperature, at which two component phase separate, increases with the increase in stiffness of semiflexible components in flexible-semiflexible polymer blend.

Gauger and Pakula [31] have investigated a mixture of flexible and very stiff chains in the canonical ensemble and used the subblock method to analyze their simulation data. Due to the stiffness and the excluded volume constraints, they found evidences for a separation into a pure phase of stiff chains and a phase of mixed composition. Further Yethiraj and coworkers [32] have investigated an athermal mixture of flexible and stiff chains in the vicinity of hard walls. Their finding is an entropy-driven surface segregation of the stiffer chains at melt like densities, because the stiffer species packs more efficiently at the hard walls. For the general review of liquid-crystalline order in polymer systems the reader is referred to an article by Holyst and Oswald [33].

It is well-known that when there is a large difference in flexibility, such as in a blend of rods and coils, the system will phase separate for entropic reasons alone [34]. Liquidcrystal polymers and their mixtures are studied both because of their practical utility and due to fundamental interest [35, 36]. In the case of mixtures one wants to know how the location of varoius phases, isotropic and nematic, and their transitions depend on the properties of the two components, their rigidities, polymerization indices, interaction etc. An approach to this problem requires a model for the liquid crystal polymers. New high-performance materials which contain blends of small molecule liquid crystals or liquid-crystalline polymers with flexible polymers are typically multidomain composites. Since liquid crystals and liquid-crystalline polymers are quite stiff they mix poorly with flexible polymers [21, 37]. In spite of the fact that interfacial tension plays an important role to determine mechanical strength, adhesion and toughness of a polymer blend (as described above), relatively little is understood about the role of backbone stiffness in determining interfacial tension.

Most notably, Mueller and Werner [38] have studied the effect of the stiffness disparity in the interfacial properties of the well segregated phases by using the Monte Carlo simulations and compared their data with self-consistent field theory. They have used the bond fluctuation model (BFM) [39]. Due to limitations of this lattice based approach their work is restricted to rather small bending rigidities of the semiflexible components. In their study the stiffest chain exceeds the stiffness of the flexible one only by a factor of 1.5. Such a low stiffness disparity does not cover the whole range of the semiflexible chains whose flexibility lies between completely flexible chain and stiff rod. As mentioned above polymer blends are structurally asymmetric. Bates and Fredrickson [16] have calculated excess free energy of mixing in polymer blend in which two different types of monomers differ in volume. Sakurai *et al.* [40] have studied the effect of segment size asymmetry on the scattering function. They used small-angled neutron scattering techniques to study the effect of segment size asymmetry in the structure factor. They have studied the phase diagram and obtained upper critical solution temperature behavior. 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.

Computer simulation has become a major tool in polymer science, complementing both analytical theory and experiment. The physics of polymer blends possess universality [1, 4, 42, 43]. Further in polymer blends the global material properties and local interfacial properties are closely related. These properties of polymer blends make them particularly suited for computer simulation [42]. The computer simulation can simultaneously provide a detailed microscopic picture of the interfacial structure, and information on the thermodynamics of the intefaces. Comparing to experiment, simulation provides a test of the microscopic model which has been used and comparing to theories, they serve as a test of the theory within a well-defined microscopic model. Moreover, they may provide structural information which may not yet be accessible experimentally or theoretically. They can thus contribute substantially towards a deeper understanding of the connections between the microscopic parameters, the microscopic structure and the macroscopic properties of a material [4]. For example, the Flory-Huggins theory [12] is not free of uncontrolable approximations (see chapter 2). To test the reliability of the theory, one needs to compare theory and experiments. However, comparing theory with experiments is not sufficient because in most cases, the agreemnet is not good, but one cannot tell whether the discriptncies are due to inadequacies of the model used in the theory or due to inaccuracies of the approximations. Since the simulation can be performed on exactly the same model which the analytical theory considers (but avoiding the uncontrolled mathematical approximations of the later), the simulations provide "benchmarks" against which these theories can be reliably tested. Such a test of Flory-Huggins theory is carried out by Deutsch and Binder [44, 45]. True symmetrical monodisperse polymer mixtures hardly exist, and the temperature range over which $T_c(N)$ can be studied is limited by the glass transition temperature from below and by chemical instability of the chains from the above. Simulations are free of such limitations, of course, and can test such theories much more stringently than the experiment.

In the present work also the phase behavior and interface properties of polymer blends of different stiffnesses will be studied by using computer simulations. Further, the interface properties of polymers with different monomer sizes which is referred as 'monomer size disparity' will be discussed. The main goal of the present work is to test existing mean filed theories (dealing with the asymmetric polymer interfaces) using the computer simulations. Further, the development of off-lattice model [46, 47] to study the unsymmetric polymer-polymer interfaces is also one of the main aims of the present work. All the interface properties which characterize the interface for the stiffness disparity system and monomer size disaprity systems are studied. The critical value of Flory-Huggins parameter, χ , is estimated by the simulation data for the systems of low stiffness disparity.

1.2 Scope of the Present Work

This section is devoted to the scope of the present work. First part of the chapter 2 deals with a general review of analytical theories which are used to study phase behaviors of polymer blends and polymer-polymer interfaces. The second part of the chapter 2 is devoted to discuss computer simulation methodology to study phase behavior and interface properties of polymers.

The chapter 3 deals with different systems of study, model and technical details. Three different systems of polymers namely, flexible-semiflexible system, flexible-stiff rod system and polymers with different monomer sizes i.e., monomer size disparity have been studied. The models which are used to study the interfaces of flexible-semiflexible, flexible-stiff rod and system with monomer size disparity have been discussed. The techniques to determine the interfacial tension by using virial theorem and capillary wave spectrum are also presented.

In chapter 4 results will be presented and discussed. All the interface properties which characterize interfaces namely, interfacial tension, monomer density profiles, interfacial width, chain orientation near the interface, distribution of chain ends and center of mass of chains have been studied for flexible-semiflexible polymers and system with monomer size disparity. Studying interfacial properties at weak segregation limit (by reducing Flory-Huggins parameter), the critical value of χ below which the two types of polymers mix, have been estimated for flexible-semiflexible polymer systems. The simulation data have been compared with the mean filed data.

The chapter 5 deals with our findings and consclusions. Further we briefly discuss about an outlook on the future work.

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 catagorized 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 it's 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 lengh $\xi \sim (\frac{T}{T_c} - 1)$ 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];

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

where $z_A = \frac{v_A}{v_o}$, $z_B = \frac{v_B}{v_o}$ and v_o is any reference volume, v_i (i=A, B) is the volume of ith 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);

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

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 reserch 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 $\frac{\epsilon_{ij}}{k_BT}$ 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 Walls 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 handeled 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;

$$F = F_{FH} + F_{LdG} \tag{2.4}$$

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

$$F_{LdG} = \frac{1}{2} \left(B - w \right) \bar{S}^2 - \frac{C}{3} \bar{S}^3 + \frac{D}{4} \bar{S}^4$$
(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 poymers. 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 semiflexible 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];

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

where

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

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

and

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

for $\chi \to \chi_c$ 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 interfaces 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;

$$w = \frac{b}{\sqrt{6\chi}} \tag{2.10}$$

and,

$$\frac{\sigma}{k_B T} = \rho_o b \sqrt{\frac{\chi}{6}} \tag{2.11}$$

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,

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

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

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

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

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

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

and,

$$w = \left(\frac{\beta_A^2 + \beta_B^2}{2\chi\sqrt{\rho_{0A}\rho_{0B}}}\right)^{\frac{1}{2}}$$
(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 filed for flexible (Gaussian) and semiflexible chains. Within the framework of SCF theory, they have defined the end-segment distribution functions,

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

(for Gaussian chains) and,

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

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

(for Gaussian chains) and,

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

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

(for Gaussian chains) and,

$$\phi_i(\vec{r}, \vec{u}) = \int_0^1 ds Q_i(\vec{r}, \vec{u}, s) Q_i(\vec{r}, \vec{u}, 1 - s)$$
(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, distribution 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 incomressible 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;

$$F = F_{FH} + F_{LdG} + F_{grad} \tag{2.24}$$

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;

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

and

$$\frac{\sigma}{k_B T} = \frac{4}{9a_0^2} \sqrt{\chi} \frac{\kappa_A^{\frac{3}{2}} - \kappa_B^{\frac{3}{2}}}{\kappa_A - \kappa_B}$$
(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 Å 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 (≈ 1 Å) to the persistence length (≈ 10 Å) to the coil radius (≈ 100 Å) to the correlation length, ξ , which has lower bound (≈ 100 Å) of concentration fluctuations [42].

In this chapter we breifly 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 eachother 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 controling the angle between subsequent bonds along a chain (in semiflexible polymers), etc. These potentials then enter the transition probability $W(\phi) = \operatorname{Min}\left(1, \exp\left(-\frac{\delta E}{k_B T}\right)\right)$ 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 hoping. 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 occuring 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 semigrand-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 $\phi_A + \phi_B = 1 - \phi_v =$ *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;

$$W(c \to c') = \operatorname{Min}\left(1, \exp\left[\frac{\Delta\mu(M' - M)Nn}{2k_BT}\right] \exp\left[\frac{-(E - E')}{k_BT}\right]\right)$$
(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 $(N_A \neq N_B \text{ or } b_A \neq b_B \text{ or } V_A \neq V_B$ 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 $n_A, n_B \to \infty$, 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 garnd-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 $S^{-1}(q \to 0)$ versus $\frac{\epsilon}{k_B T}$ and then estimating the temperature T where $S^{-1}(q \to 0) = 0$ 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.

3 Systems, Model and Technical Details

3.1 General Consideration

We study **interface properties** of two different types of systems; (1) the first type of systems consist of interfaces between polymers of different stiffnesses which is called 'stiffness disparity', and (2) the second one consist of interfaces between polymers having different sizes of monomers which is called 'monomer size disparity'. In the first case, apart from interface properties, the **phase-behavior** of polymer blends with low stiffness disparity also has been studied. The models for these two types of systems are different and described in section 3.2 and 3.3 respectively. To study interface properties and phase separation for the systems outlined above, a numerical code based on coarse grained continuous-space (off-lattice) model, has been developed. Our approach differs significantly from the previous numerical studies which use lattice models almost exclusively [42]. For the systems with interfaces continuous space (CS) model serves better than the lattice model. Besides their inherent spatial isotropy and the absence of pinning the CS models offer a simple way to determine surface tension by measuring the pressure tensor which is one of the main goals of this work. Off-lattice polymer constructions [7, 42, 46], in which varying angles and free rotation about the covalent bonds are permitted, which is not possible due to restricted geometry in lattice models, is a more general way than the lattice models to create the semiflexible chains of any stiffness. Further provided the forces are short ranged, theoretical work [72] suggests that interfaces in the continuum exhibit no roughening transition. Moreover, lattice model is not a suitable choice to study monomer size disparity system.

The coarse-grained model can be obtained by combining n successive covalent bonds along the backbone of a polymer chain into one effective segment. The coarse-graining is done in such a way that the large-scale geometrical structure of the polymer coil is left invariant, e.g; properties such as radius of gyration of the coil and the probability distribution of its end-to-end distance are the same for the coarse-grained model and for the chemically detailed model. This invariance of long wavelength properties can be realized by introducing suitable potentials in the coarse grained model which control bond lengths of the effective bonds, angles between effective bonds along the sequence of the coarse-grained chain etc.. In coarse grained models, one loses the relevant information on a very small length scale only [42]. Coarse grained models which retain a minimal set of relevant polymeric properties like, the connectivity of the macromolecules along the bakbone, the excluded volume of the beads, and short ranged thermal interactions have proven extremely efficient in investigating the universal thermodynamic properties of polymeric multicomponent systems. Simulations performed on this coarse-grained level require only a small number of parameters to compare with experiments and analytical theory quantitatively [4].

Coarse grainning can be done in both lattice model and in off-lattice model. There is no unique model description of a polymer chain system; infact, for different physical questions somewhat different models are optimal. For example, constant pressure simulations of lattice models are difficult, whereas their implementation is relatively straight forward for off-lattice models. Even at constant volume, off-lattice models have the advantage that the pressure and the interfacial tension can be measured via the virial theorem [7, 73, 74]. Moreover, off-lattice models are useful to capture hydrodynamic flow in molecular dynamics simulations because by construction coarse grained CS model keeps the long wavelength properties invarient. At the same time, off-lattice models are more demanding with respect to computational resources while model like bond fluctuation and other lattice models are well suited to the study of polymer melt dynamics, the glass transition etc. [42].

3.2 Model for Stiffness Disparity

3.2.1 Model

We performed computer simulations of the interface properties of a three dimensional phase separated sandwich-type system of flexible and semiflexible polymers. Figure 3.1 shows a typical snapshot of such a system.

As chain models a coarse grained continuous space model has been used. This offlattice model provides a more direct way, by setting restriction on bond angles, to generate the semiflexible chains and allows the investigation of chains of any stiffness. The polymer chains are modeled using the rod-bead model [42, 7] by a succession of jointed spherical monomers. Each chain consists of N (with N =32) spheres of equal diameter $d_{min} = \sqrt{3}$ which are connected by (N-1) bonds of variable length $d_{min} \leq d$ $\leq d_{max} \approx \frac{4}{3} d_{min}$. In our model the excluded volume is taken into account by the following potential, $V_{ex}(r)$, between any two beads separated by a distance r;

$$V_{ex}(r) = \begin{cases} 0 & , \text{ if } r > d_{min} \text{ (diameter of the monomers)} \\ \infty & , \text{ else.} \end{cases}$$
(3.1)

This excluded volume potential between any two beads is shown in the figure 3.2.

Similarly, the connectivity of chains is taken into account by following potential, $V_{con}(r)$, between any two consecutive beads of a chain at a distance r;



Figure 3.1: A typical system of study in which green monomers are from flexible chains and red from semiflexible chains whose flexibility varies from flexible to almost stiff rod.



Figure 3.2: Excluded volume potential between any two beads separated by a distance r in stiffness disparity system.

$$V_{con}(r) = \begin{cases} 0 & , \text{ if } d_{min} \leq r \leq d_{max} \\ \infty & , \text{ else} \end{cases}$$
(3.2)

where d_{min} and d_{max} are already defined. The potential of connectivity $V_{con}(r)$, between

two successive beads of a chain is shown in the figure 3.3. In the same way as in ex-



Figure 3.3: connectivity potential between two consecutive beads of a polyme chain.

cluded volume and connectivity, the potential for the bending restrictions (in semiflexible chains) also is a stepwise potential see figure 3.4. Therefore, the bending restrictions is defined by the following potential;

$$V_{bending}(\theta) = \begin{cases} 0 & , & \text{if } \theta < \theta_{max} \\ \infty & , & \text{else} \end{cases}$$

where θ is the angle between any two consecutive bond vectors of a semiflexible chain (see figure 3.5) and θ_{max} is maximum angle between two consecutive bond vectors of a semiflexible chain permitted in the system. Choosing different values of θ_{max} we can generate semiflexible chains of any stiffness, ranging from flexible to stiff rod.



Figure 3.4: Bending potential for a semiflexible chain. θ is the angle between any two consecutive bond vectors of the chain.

Semiflexible chains in which the angle between two consecutive bond vectors (θ in Figure 3.5) is not larger than 90°, 75°, 60°, 45°, 30°, 15° and 5° (the stiffest case studied which is referred through out the present work as almost stiff rod) are generated. The whole system consists of 512 flexible and semiflexible chains respective.

The interaction between segments which are not jointed directly is also modeled by a stepwise potential. For simplicity, we assume that the interaction between equal



Figure 3.5: Semiflexible chain model. $\theta \leq \theta_{max}$, the maximum angle chosen between two consecutive bond vectors.

types of monomers A and B (type A for flexible chains and type B for semiflexible chains), $V_{AA} = V_{BB} = 0$ and a repulsive potential acts between different monomers $V_{AB} = k_B T \varepsilon$ where k_B is Boltzmann constant and T is temperature and ϵ is the repulsive interaction parameter between different types of beads and $\epsilon = 0.1$ to study the interface properties in strong segregation limit. However, to study phase behavior using the interface properties of weak segregation limit the value of ϵ is decreased. Therefore, ϵ is related to the Flory-Huggins parameter, χ , [12] in this model (see below). The interaction potential is depicted in figure 3.6. The assumed range of the interaction between two different types of monomers is denoted by d_{2type} , in the present work, and it has value $\sim \sqrt{\frac{5}{3}} d_{min}$. This interaction potential between any two different types of monomers can be expressed by following equation;

$$V_{AB}(r) = \begin{cases} k_B T \epsilon &, \text{ if } d_{min} < r < d_{2type} \\ \infty &, \text{ if } r < d_{min} \\ 0 &, \text{ if } r > d_{2type} \end{cases}$$

where $V_{AB}(r)$ is the interaction potential between monomers of type A and type B separated by a distance r. This potential is shown in the figure 3.6.

For estimations of the Flory-Huggins parameter the average number of interchain contacts z_{eff} of a monomer within a sphere of radius of the interaction range is determined for the pure components. The Flory-Huggins parameter

$$\chi = \frac{z_{eff,flex} + z_{eff,stiff}}{2} \cdot \varepsilon \tag{3.3}$$

increases slightly with increasing stiffness of the semiflexible component because in the semiflexible chains the contacts of monomers from other chains increase. For the flexible



Figure 3.6: Interaction potential between two different types of beads at a distance r.

chains χ is 0.32 and it is 0.366 for the stiffest case studied for $\epsilon = 0.1$ (see above). The value of $N\chi$ is much higher than two and therefore our results correspond to strongly immiscible blends and a stable interface can be expected for $\epsilon = 0.1$.

3.2.2 Generation of Chains and Equilibration

To generate a system of stiffness disparity, 32 random walk chains (flexible chains) with random bond length distribution $d_{min} \leq d \leq d_{max}$ with no overlap with next nearest neighbors within the chain [7] are generated. Other 32 random walk chains (semiflexible chains) are generated by setting additional constraint on the bond angles between two consecutive bond vectors of a chain viz; $0 \le \theta \le \theta_{max}$ where θ is angle between two consecutive bond vectors of a chain and θ_{max} is the maximum angle between two consecutive bond vectors of a chain chosen in the system of study. To generate the interface initially we have considered the initial box having three compartments in which the middle one has volume double than that of both sides (this simulation box has dimensions $64 \times 16 \times 16$). One fourth of both sides of the box (along x-dimension) occupy flexible chains and the remaining half of the box in the middle with semiflexible chains randomly. Therefore, there are two interfaces located at $\frac{1}{4}$ th and $\frac{3}{4}$ th of the x-dimension of the box. The overlaps between the segments are removed by stepwise increase ("blowing up") of the diameter of the spherical monomers followed by Monte Carlo steps. This process is started with the minimum distance of any non directly connected monomers and repeated until the minimum distance between any two monomers is equal or greater than d_{min} . After removing the overlaps the size of the system is doubled by shifting y and z coordinates to get a system of 256 chains in a $64 \times 32 \times 32$ - parallelepiped. We further multiply the system by shifting y and z coordinates to get finally the system of study with 1024 chains in a $64 \times 64 \times 64$ - cube. Figure 3.7 shows one of such a system which contains flexible chains and semiflexible chains with $\frac{l_p}{a} = 2$ where l_p is the persistence length (see page 27) and a is the average bond length (see below).



Figure 3.7: Initial configuration for a system with flexible chains and semiflexible chains of persistence length $\left(\frac{l_p}{a}\right) = 2$.

Since the systems of study considers also very high stiff chains which form a nematic phase, such a very stiff chains are generated in a different way than described above. We tried to get equilibrium configuration for systems in which persistence length $\left(\frac{l_p}{a}\right)$ of the semiflexible chain is greater than 13.6 following the method described above. However, the system containing highly stiff chains form several domains (within a domain the chains allign parallel to each other) and we could not get monodomain phase separated equilibrium system. Therefore, to generate a system with highly stiff chains, persistence length greater than 13.6, and flexible chains, we follow the method described below. First, 512 stiff chains each chain containing 32 monomers are generated. All the chains allign parallel to Z - axis of the simulation box and occupy middle half portion of the box having dimensions $64 \times 64 \times 64$. We performed random movement of the stiff chains (along Z-axis) such that the mean squared displacement (MSD) of the center of mass of chains is a few times of R^2 , mean squared end to end distance. The flexible chains which were already equilibrated occupy either side of the box whose center of mass is fixed to the $\frac{1}{4}$ th of both sides of the box. The number of flexible chains is 512. After having the system of flexible-stiff chains the overlapping between any two monomers is checked. The diameter of both types of monomers is d_{min} . Then Monte-Carlo moves were performed as described below for both types of the monomers with suitable angular restriction between two consecutive bond vectors of a stiff chain.

The interfacial properties of flexible polymers and liquid-crystalline polymers [9] depend upon the direction of nematic director (for example, see [75] for macromolecular systems and [76] for small molecular systems for the dependence of interfacial properties on direction of nematic director in isotropic-nematic interface). In the present study the most stable case in which nematic director is parallel to the interface plane will be considered.

For equilibration and thermodynamical averaging, we perform Monte-Carlo steps according the standard Metropolis algorithm with random choice of a monomer and cyclic choice of one of the six directions along the coordinate axes (see the flow diagram). A move is accepted according to transition probability $P(E) = Min(1, exp(-\frac{\delta E}{k_B T})) > \zeta$ where δE is difference of energy of new and old configurations, k_B is Boltzmann constant, T is temperature and $1 > \zeta > 0$ is a random number. The length of an attempted step between zero and a maximum step length $\sim 0.23 \times d_{min}$ is chosen randomly. To accelerate the tests for hard-core overlapping and the calculations of the interaction energy after each attempted move, we follow the standard way by dividing the simulation box into cubic cells of size l_c with single occupancy and checking the particles in the neighborhood of the moved particle only. Single occupancy is realized by the choice $d_{min} = \sqrt{3} \times l_c$. The details of the linked cell method are described in [77, 78]. Further Auhl [7] has applied the linked cell method for the flexible-flexible polymer systems. However, for semiflexible chains we have to check angle between two consecutive bond vectors of the chain (see the flow diagram). Two well defined interfaces are enforced in the canonical ensemble in a thick film geometry $(L \times L \times L)$, with periodic boundary conditions in all the three directions. The interfaces are on average located in $\frac{1}{4}$ th and $\frac{3}{4}$ th of the x-dimensions of the simulation box. A Monte Carlo step for a monomer from flexible chain and a monomer from semiflexible chain are described in the flow diagram, figures 3.8 and 3.9.

To know whether a system has attained equilibrium configuration, the following criterion is used. The parallel and the perpendicular (parallel and perpendicular according to the interface) components of the radius of gyration R_g and the displacement of center of mass of chains against the simulation time are monitored. According to this criterion, system with interfaces will be expected in equilibrium when the mean squared displacement (ΔMSD) of center of mass of chains, after removal of overlaps between monomers, is comparable to the mean squared radius of gyration of chains, R_g^2 . The figure 3.10 presents mean squared displacement of center of mass of chains and mean squared parallel and perpendicular components of radius of gyration for the system with chains having persistence length $(\frac{l_p}{a}) = 2.0$ and flexible chains. For each system of study, the ΔMSD of center of mass of chains and parallel and perpendicular components of R_g^2 are monitored. If both of theses quantities are comparable, calculations of interfacial tensions and other quantities (see below) are started. Further, the ΔMSD of individ-



Figure 3.8: Flow diagram for a monomer from flexible chains.

ual components (flexible and semiflexible) also are not significantly different than that of the sum of both components. To get equilibrium state 6.1×10^5 attempted moves



Figure 3.9: Flow diagram for monomers from semiflexible chains.

per monomer (AMM) were performed for the system with flexible chains. The AMM increase with the stiffness of the semiflexible components of the system and 6.1×10^7

AMM were performed for the system which contains flexible chains and chains with persistence length $\left(\frac{l_p}{a}\right) = 13.6$. For an isotropic-nematic interface also 6.1×10^7 AMM were performed by keeping the proper restriction on the angle between two consecutive bond vectors of a chain. To be ensured that the system is close enough to equilibrium, the values of interfacial tensions are monitored during the calculations. The values of interfacial tensions of the system, in which semiflexible component has persistence length $\left(\frac{l_p}{a}\right) = 2.5$, against number of calculations are depicted in figure 3.12. They also show that (as the values do not decrease monotonically with the time of calculations) the systems are close enough to equilibrium at the time of calculation. Figure 3.11 shows one typical configuration after achieving equilibrium condition.



Figure 3.10: Mean squared displacement of center of mass and parallel and perpendicualr components of radius of gyration during the Monte Carlo steps for a system containing flexible chains and semiflexible chains with persistence length $(\frac{l_p}{a})=2.$

3.2.3 Single Chain Properties and Nematic Order Parameter

After describing the methods to generate the chains and attain the equilibrium configuration in subsection 3.2.2, the single chain properties and ordering of the highly stiff chains will be described in this subsection.



Figure 3.11: Equilibrated configuration for a system with flexible chains and semiflexible chains with persistence length $\left(\frac{l_p}{a}\right) = 2$.

Single chain properties

Before going over to present the results, we first define the quantities which characterize the single chain properties by the help of figure 3.13. The end to end vector is denoted by \vec{R} and the mean squared end to end distance is, R^2 . Similarly, R_g^2 is the mean squared radius of gyration and $R_g^2(0)$ is the mean squared radius of gyration of the flexible chains. The lower bound of statistical segment length, b, is introduced in the following way;

$$b = \frac{R^2}{L} = aC_{1N}$$
(3.4)

where L = Na is contour length, a is the average bond length and C_{1N} is ratio of R^2 and Na^2 which is denoted by C_{∞} in literatures when $N \to \infty$. The aspect ratio Γ is defined as the ratio of statistical segment length b and diameter of the bead d_{min} i.e. $\Gamma = \frac{b}{d_{min}}$. The persistence length, l_p , is calculated by the average of projection of end to end vector along the unit vector in the direction of first bond. Therefore, l_p is calculated using the following formula [79];


Figure 3.12: Interfacial tension as a function of number of calculations for a system with flexible chains and semiflexible chains with persistence length $\left(\frac{l_p}{a}\right) = 2.5$. There are 3.4×10^4 AMM between two succesive calculations.

$$l_p = \left\langle \vec{R} \cdot \vec{u}_1 \right\rangle = \frac{1}{a} \sum_{i=0}^{N} \left\langle \vec{a}_1 \cdot \vec{a}_i \right\rangle \tag{3.5}$$

where a is the average bond length, \vec{a}_i are ith bond vectors, \vec{R} are the end to end vectors, $\vec{u}_1 = \frac{\vec{a}_1}{a}$ are the unit vectors along first bond vector and N is the number of monomers in a chain. l_p and/or C_{1N} defines the chain stiffness.

Figure 3.13 shows the projection of end to end vector along the first bond vector. In table 3.1, single chain conformational properties as a function of stiffness of semiflexible component for all the systems are discussed.

Nematic Order Parameter

To know whether the system is in nematic phase for highly stiff chains, the nematic order parameter has been calculated. To calculate nematic order parameter we need to know the nematic director. For stiff rod, it is very easy to find the nematic director



Figure 3.13: Projection of end to end vector (\vec{R}) along first bond vector in a semiflexible chain.

Flexibility	\mathbb{R}^2	R_g^2	$\frac{R^2}{R_g^2}$	$\frac{b}{a}$	$\Gamma = \frac{b}{d_{min}}$	$\frac{l_p}{a}$	χ	S
Flexible	193	32	6.03	1.51	1.74	1.25	0.32	0.0082
90°	356	55	6.47	2.8	3.23	2	0.327	0.01
75°	511	76	6.72	4.03	4.65	2.5	0.335	0.0215
60°	766	106	7.22	6.07	7.00	4.2	0.340	0.053
45°	1309	159	8.23	10.4	12.00	7.2	0.346	0.097
30°	2217	220	10.07	17.6	20.32	13.6	0.351	0.16
15°	3657	327	11.18	28.91	33.38	28.0	0.362	0.97
5°	3801	339	11.21	30.05	34.69	30.02	0.366	0.99

Table 3.1: single chain conformations as a function of the stiffness parameter, here the persistence length $\left(\frac{l_p}{a}\right)$ and statistical segment length $\left(\frac{b}{a}\right)$ are in unit of bond length and S is the nematic order parameter described in the text. All these quantities discussed in this table increase as a function of stiffness.

however for semiflexible chains first we have to calculate the ordering tensor (**Q**), for the chain ordering, by the following way [80]. The shape of the molecule is obtained by representing each chain in terms of semi-axis lengths of an equivalent spheroid with the same moment of inertia as the molecule and one can obtain this by diagonalizing the moment of inertia tensor of the molecule. For molecule 'k', the elements of the moment of inertia tensor, \mathbf{I}_k , are given by,

$$I_{\alpha\beta,k} = \sum_{i=1}^{N} (r_i^2 \delta_{\alpha\beta} - r_{i\alpha} r_{i\beta})$$
(3.6)

where $\alpha, \beta = x, y, z$ are the cartesian coordinates, $\delta_{\alpha,\beta}$ is the Kronecker delta, $r_{i\alpha}$ is the distance in the α direction of site i from the center of mass of the molecule, and $r_i^2 = r_x^2 + r_y^2 + r_z^2$ and N is the number of monomer in the molecule 'k'. The eigenvector which is denoted by \vec{e}_k corresponding to the smallest eigenvalue of $I_{\alpha\beta,k}$ is reffered to as the molecular axis vector of the chain. The nematic director for the semiflexible chains is obtained by diagonalizing the ordering tensor, **Q** defined by,

$$\mathbf{Q}_{\alpha\beta} = \frac{1}{N_p} \sum_{k=1}^{N_p} \frac{3}{2} e_{k\alpha} e_{k\beta} - \frac{1}{2} \delta_{\alpha\beta}$$
(3.7)

 $e_{k\alpha}$ is the α th ($\alpha = x, y \text{ or } z$) component of the molecular axis vector, \vec{e}_k . Then the order parameter is given by,

$$S = -2 < \lambda > \tag{3.8}$$

where λ is the middle eigenvalue of **Q**.

The nematic order parameters for the semiflexible component of the systems of study are presented in table 3.1. From table it is clear that upto persistence length $\left(\frac{l_p}{a}\right) = 13.6$ there is not nematic ordering but for higher values of persistence length the semiflexible polymers form the nematic phase.

Orientational parameters

Of special interest in a system containing stiff chains is the orientational order. In polymer systems, one can define orientational parameters in different length scales e.g. orientational parameter of bond vectors and chain orientational parameters. Systems with the planar interface in the y - z-plane has a distinguished direction along the x-axis, hence the order-parameter-field of bond ordering,

$$S(x) = \frac{3\langle a_x^2(x) \rangle - a^2}{2a^2}$$
(3.9)

is the most direct measure of the order near the interface and also in the bulk. $\langle a_x^2(x) \rangle$ and $\langle a^2 \rangle$ are the mean squared of x-component of bond vector and of the bond vector respectively (see chapter 4).

In similar way, the chain orientational parameters, perpendicular (ΔRg_{\perp}) and parallel (ΔRg_{\parallel}) , with respect to interface plane of chain orientation

$$\Delta Rg_{\perp} = \frac{3 \langle Rg_x^2 \rangle - \langle Rg^2 \rangle}{\langle 2Rg^2 \rangle} \tag{3.10}$$

and

$$\Delta Rg_{\parallel} = \frac{3(\langle Rg_z^2 \rangle + \langle Rg_y^2 \rangle)/2 - \langle Rg \rangle^2}{2 \langle Rg^2 \rangle}$$
(3.11)

can be introduced where $\langle Rg^2 \rangle$ is the averaged radius of gyration of the chains and $\langle Rg_i^2 \rangle$ (i = x, y, z) is the corresponding component of square of radius of gyration of the polymer chains. Therefore, when the chains orient parallel to the interface, parallel orientational parameter ΔRg_{\parallel} will be positive and has maximum value 0.25 while the perpendicular orientational parameter ΔRg_{\perp} will be negative and has minimum value -0.5. Similarly, when the chains orient perpendicular to the interface, parallel orientational parameter ΔRg_{\parallel} will be negative while the perpendicular orientational parameter Rg_{\perp} will be negative while the perpendicular orientational parameter Rg_{\perp} will be positive (see chapter 4).



Figure 3.14: Orientational correlation between two bonds of different chains. Long range orientational order is obtained for $\frac{l_p}{a} > 13.6$. Above shown persistence lengths $(l_p s)$ are in unit of average bond length (a).

Additionally, single chain orientational parameters introduced above, the orientational correlation between bond vectors of different chains is of interest. The orientational correlation, $(P_{\alpha}(r))$, between bonds from different chains is defined by the following way.

$$P_{\alpha}(r) = \frac{3 < \cos^2(\alpha) > -1}{2}$$
(3.12)

where α is the angle between bonds of different chains separated by a distance r. In the case of **nematic ordering** (when all the bonds in different chains are parallel), $P_{\alpha}(r) = 1$. In a complete uncorrelated case there is no orientational correlation between two different bonds and hence $P_{\alpha}(r) = 0$. When the bonds in different chains are perpendicular, $P_{\alpha}(r) = -0.5$. In the intermediate case (i.e. the case between nematic ordering and orientational disorder) $P_{\alpha}(r)$ lies between 0 and 1. Figure 3.14 shows the profile of $P_{\alpha}(r)$ for all the stiffness disparity systems studied in the present work. From figure 3.14, it is observed that there is no nematic ordering in our systems of study up to the persistence length $(\frac{l_p}{a})$ of the semiflexible component 13.6 which is consistent with the nematic order parameter calculated in the previous sub-subsection. As we expect the value of the orientation correlation increases when the stiffness of the semiflexible component increases.

3.3 Model for Monomer Size Disparity

In the previous section, the model for stiffness disparity was discussed. In this section the model for monomer size disparity will be discussed.

3.3.1 Model

We performed again computer simulations of a sandwich type two-component system of homopolymers with different monomer sizes. Figure 3.15 shows a typical snapshot of such a system. The coarse grained continuous space model is used, similar to the cas of stiffness disparity. In these systems, there are two types of monomers; type A having diameter $d_A = d_{min} = \sqrt{3}$, as in the case of stiffness disparity systems, and type B having diameter $d_B = 2 \times d_A$. These systems in general are known as "systems with monomer size disparity". The following types of dispair systems are studied;

(a) $d_B = 2 \times d_A$ and $N_A = N_B$ i.e. diameter of monomers of type B is double than that of type A and number of monomers per chain in type A chains is equal to number of monomers per chain in type B chains. Such a system is referred as "monomer size disparity with equal number of monomers per chain".

(b) $d_B = 2 \times d_A$ and $R_g^A \sim R_g^B$ ($N_B = \frac{3}{4}N_A$) i.e. diameter of monomers of type B is double than that of type A monomers and radius of gyration of type A chains is almost equal to that of type B chains which is referred as "monomer size disparity with almost equal radius of gyration".

The interfacial properties of above two kinds of systems are compared to that of the symmetrical system in which two types of monomers differ only by their interaction. The symmetrical system is same as flexible-flexible polymer system in the case of stiffness disparity case.

The polymer chains are modeled by a succession of jointed spherical monomers according to rod-bead model [42, 7], same model as in stiffness disparity case. A chain consists of N spheres of equal diameter which are connected by (N-1) bonds. For A types of chains we consider N =32. However, for B types of chains there are two cases to study two different kinds of systems (a) and (b) as described above. In the system of monomer size disparity with equal number of monomers per chain, each type B chain has N = 32 monomers whereas in the system of monomer size disparity with almost equal radius of gyration, each type B chain consists of N =24 monomers.

Since there are two types of monomers with different sizes, the excluded volume also depends upon the types of monomers and it is given by the following potential;

$$V_{BB,ex}(r) = \begin{cases} 0 & , \text{ if } r > d_B \text{ (diameter of type B monomers)} \\ \infty & , \text{ else} \end{cases}$$



Figure 3.15: A typical snapshot of a monomer size disparity system. Monomers from Red chains have diameter double than that of monomers from green chains.



Figure 3.16: Excluded volume potential between two type B monomers in monomer size disparity systems.

where $V_{BB,ex}(r)$ is the excluded volume potential between two type B monomers at a distance r. This excluded volume potential is shown in the figure 3.16.

Similarly, the excluded volume potential between type A and type B monomers is given by;



Figure 3.17: Excluded volume potential between type A and type B monomers in monomer size disparity systems.

$$V_{AB,ex}(r) = \begin{cases} 0 & , & \text{if } r > \frac{d_B + d_A}{2} \\ \infty & , & \text{else} \end{cases}$$

where $\frac{d_B+d_A}{2}$ is the minimum distance between type A and type B monomers and $V_{AB,ex}(r)$ is the excluded volume potential between type A and type B monomers at a distance r. $V_{AB,ex}(r)$ is shown in the figure 3.17. The excluded volume potential between any type A beads is same as the excluded volume potential between two beads in stiffness disparity case as discussed in subsection 3.2.1 (see Eq. 3.1 and figure 3.2). Similarly, the connectivity between two consecutive monomers in a type B chains is assured by the following potential;

$$V_{con,B}(r) = \begin{cases} 0 & , \text{ if } d_B \le r \le d_{Bmax} \\ \infty & , \text{ else} \end{cases}$$

where $d_{Bmax} \sim \frac{7}{3} d_{min}$, $V_{con,B}(r)$ is the connectivity potential between two consecutive beads of a type B chain separated by a distance r. This value of d_{Bmax} ensures that there is not intersection between type A and type B chains. $V_{con,B}(r)$ is shown in the figure 3.18. The potential for the connectivity of two consecutive monomers from type A chains is same as that in the case of stiffness diaparity, discussed in subsection 3.2.1. Therefore, the distance between any two consecutive beads of a chain depend upon whether the spheres are type A or type B.



Figure 3.18: Conectivity potential between two consecutive monomers from type B chains in monomer size disparity systems.

The interaction between segments which are not directly jointed is also modeled by a stepwise potential. For simplicity we assume that the interaction between equal types of monomers A and B, $V_{AA} = V_{BB} = 0$ and a repulsive potential acts between different types of monomers $V_{AB,int} = k_B T \varepsilon$ where k_B is the Boltzmann constant, Tis the temperature and ϵ is a parameter to be chosen in the model which defines the Flory-Huggins parameter χ and $\epsilon = 0.1$, in the present work. The assumed range of the interaction between two different types of monomers is $d1_{2type} \sim (\frac{1}{2} + \sqrt{\frac{5}{3}}) d_{min}$. Therefore, the interaction potential between two different types of monomers is given by the following potential;

$$V_{AB,int}(r) = \begin{cases} k_B T \varepsilon &, \text{ if } \frac{d_B + d_A}{2} \le r \le d \mathbf{1}_{2type} \\ 0 &, \text{ if } r > d \mathbf{1}_{2type} \\ \infty &, \text{ if } r < \frac{d_B + d_A}{2} \end{cases}$$

where $V_{AB,int}(r)$ is the interaction potential between type A and type B monomers separeted by a distance r. As mentioned above, the interaction parameter ϵ is related to the Flory-Huggins parameter χ which is estimated in our model in the following way;

$$\chi = z_{eff}\varepsilon \tag{3.13}$$

where z_{eff} is the average number of interchain contacts of a monomer within a sphere of radius of the interaction range between type A and type B monomers in an athermal mixture of two types of chains (see Fig 3.20). From table 3.2 it can be seen that χ decreases for the unsymmetric systems (that is system with different sizes of monomers) as z_{eff} decreases for such systems.



Figure 3.19: Interaction potential between type A and type B monomers separated by a distance r in the monomer size disparity systems.



Figure 3.20: Povray diagram of an athermal mixture of monomer size disparity system with equal number of monomers per chain.

3.3.2 Generation of Chains, Equilibration and Single Chain Properties

Generation of chains

To generate the system of monomer size disparity with equal number of monomers per chain, 32 random walk chains (type A chains) with random bond length distribution $d_{min} \leq d \leq d_{max}$ with no overlap with next nearest neighbors within the chain [47] are generated. Other four random walk chains (type B) are generated with random bond length distribution $d_B \leq d \leq d_{Bmax}$ with no overlap with next nearest neighbors within the chain. Each chain consists of 32 monomers per chain. To generate the size disparity system with almost equal radius of gyration, 6 random walk chains (type B chains, each chain having 24 monomers per chain) with random bond length distribution $d_B \leq d \leq d_{Bmax}$ with no overlap with next nearest neighbors within the chain are generated. The type A chains are generated following the same way as described above and there are 32 type A chains in both the systems. The symmetric system is same as the system of only flexible chains in the stiffness disparity case.

To generate the interface initially, a box having three compartments in which the middle one has volume double than that of both sides (this simulation box has dimensions- $64 \times 16 \times 16$) is considered. One fourth of both sides of the box (across x-dimension) occupy type A chains and the remaining half of the lattice in the middle with type B chains. The overlaps between the segments is removed by stepwise increase ("blowing up") of the diameter of the spherical monomers followed by Monte-Carlo steps. This process is started with the minimum distance of any monomers which are not directly connected. For symmetric system, the process lasts when the minimum distance between any two monomers is equal or greater than d_{min} . However, for unsymmetric systems, the process goes on until the distance between any two type B monomers is equal or greater than d_B , the distance between any two type A monomers is equal or greater than d_{min} and distance between type A and type B monomers is equal or greater than $\frac{d_B+d_A}{2}$. The system is enlarged by shifting y and z coordinates to get a system having dimensions $64 \times 32 \times 32$ - parallelepiped. In doing so number of chains is increased by four times. We further multiply the system by shifting y and z coordinates to get final system of study $64 \times 64 \times 64$ -cube. The final system consists of 512 type A chains and 64 type B chains in the system of monomer size dispartiy with equal number of monomers per chain. Similarly, it has 512 type A chains and 96 type B chains in the system of monomer size dispartiy with almost equal radius of gyration. Figure 3.21 shows an initial configuration for the system of monomer size disparity with equal number of monomers per chain.

Equilibration of chains

For equilibration and thermodynamical averaging the Monte-Carlo steps have been performed according to the standard Metropolis algorithm with random choice of a monomer and cyclic choice of one of the six directions along the coordinate axes, as



Figure 3.21: Povray diagram of initial configuration of monomer size disparity with equal number of monomers per chain.

described in the stiffness disparity system. The length of an attempted step is chosen randomly between zero and a maximum step length $\sim 0.23 \times d_{min}$. To accelerate the tests for hard-core overlapping and for the calculations of the interaction energy after each attempted move, we follow the standard way by dividing the simulation box into cubic cells of size l_c with single occupancy for type B monomers and checking the particles in the neighborhood of the moved particle only. There could be several particles of type A monomers in a cubic cell. Therefore, in this case we have to check overlapping of moved particle within cell also (see the flow diagrams 3.25, 3.26). For the symmetric system, we consider a cubic cell of size unity, so that there will be only single occupancy for type A and type B monomers. The techniques of equilibration of chains for the stiffness disparity systems and size disparity systems differ in the following way. In the former case, in linked cell method we chose the size of cell such that there is single occupancy for both types of monomers and in the later case, the size of a cell is such that larger size of beads occupy single cell and hence there could be many monomers of type A in the same cell. The details of the linked cell method are described by Allen and Tildesley and by Sadus [77, 78]. Auhl [7] has already applied the linked cell method for the flexible-flexible polymer systems. If there are many particles in one cell, during sorting of particles in appropriate cells two arrays are created namely, 'head-of-chain' (HEAD) and 'linked-list' (LIST). HEAD has one element for each cell and it contains the identification number of one of the particles sorted into that cell. This number is used to address the element of a LIST, which contains the number of the next particle in that cell. In turn, the LIST array element for that particle is the index of the next particle in the cell, and so on. By following the trial of link-list references, we will eventually reach an element of LIST which is zero. This indicates that there are no more particles in that cell, and we move on to the HEAD particle for the next cell and so on. Two well defined interfaces are enforced in the canonical ensemble in a thick film geometry $(L \times L \times L)$, with periodic boundary conditions in all the three directions. The interfaces are on average located in $\frac{1}{4}$ th and $\frac{3}{4}$ th of the x-dimensions of the simulation box.

To know whether systems have attained equilibrium configurations, the same idea like in the case of stiffness disparity, is followed. The parallel and the perpendicular (parallel and perpendicular according to the interface) components of the radius of gyration, R_a , and the mean squared displacement of center of mass of chains (ΔMSD) against the simulation time are monitored. The figure 3.22 presents (ΔMSD) of center of mass of chains and mean squared parallel and perpendicular components of radius of gyration for the system in which two types of monomers have different sizes but equal number of monomers per chain. For each system of study, the ΔMSD of center of mass of chains and parallel and perpendicular components of R_g^2 are monitored and until both of these are comparable we do not start calculation of interfacial tension and other quantities. The ΔMSD of individual components are also not significantly different than that of total system. Further the values of interfacial tensions after the calculations are also monitored. The values of interfacial tensions of the system, in which both types of chains have equal number of monomers per chain but different sizes of monomers, against number of measurements are depicted in figure 3.23. They also show that (as the values do not change monotonically with the time of measurements) the systems are close enough to equilibrium at the time of measurement. To get equilibrium state we performed 6.1×10^5 attempted moves per monomer (AMM) for the symmetric system, i.e. the system with the same sizes of monomers. However, for the system having different sizes of monomers we have to perform 10^7 AMM. Figure 3.24 depicts an equilibrium system in which both types of chains have equal number of monomers per chain but two types of monomers have different sizes.



Figure 3.22: Perpendicular and parallel components of square of radius of gyration and mean squared displacements of center of mass for the system with monomer size disparity with equal number of monomers per chain.

Single Chain Properties

The single chain conformations are presented in table 3.2 (page 37). When the diameter of type B monomers is larger than that of type A monomers the ratio $\frac{R^2}{R_g^2}$ will be higher than 6. The dependence of $\frac{R^2}{R_g^2}$ on segment number of the B type of chains shows that type B chains are slightly stiff. Here also the statistical segment length b is defined according to equation 3.4. The statistical segment length for the type B chains with 24 monomers per chain is determined according to equation 3.4 using C_{1N} for N = 32. In table 3.2, R^2 is the mean squared end to end distance, R_g^2 is the mean squared radius of gyration, b is the statistical segment length and χ is the Flory-Huggins parameter, N is number of monomers per chain and N_P is the number of chains in the system of study.



Figure 3.23: Interfacial tension versus number of calculations for the system with monomer size disparity with equal number of monomers per chain. There are 4.8×10^4 AMM between two successive calculations.

3.4 Calculation of the Interfacial Tension

In the present systems of study, due to different kinds of disparities, i.e. the stiffness disparity in the flexible-semiflexible blend and monomer size disparity in monomer size disparity systems, a straight forward application of the semi-grand-canonical identity changes between different polymer types are rather inefficient. Therefore, the interfacial tension cannot be calculated by the reweighting of the composition distribution as successfully applied in most Monte Carlo investigations interfacial tension [29]. Alternatively, we can calculate the interfacial tension by analyzing the spectrum of the capillary fluctuations and as advantage of off-lattice model by using virial theorem. The virial theorem method successfully applied to determine the free energy costs of a hard wall [74] in a concentrated polymer solution, and to determine the interfacial tension [7, 73] in a binary polymer blend. Auhl [7] has calculated anisotropy in the pressure tensor in flexible-flexible polymer systems for the same chain model as in present study. In the present work the method used by Auhl, is extended to apply for the flexible-semiflexible polymer systems and a system containing polymers with different monomer sizes.



Figure 3.24: Povray diagram of final configuration of monomer size disparity system with equal number of monomers in a chain.

Virial theorem method

Calculating the interfacial tension by using virial theorem [77] is one of the most direct and rigorous methods, it rests on the determination of the anisotropy of the pressure tensor of a system with an interface.

The interfacial tension, σ can be expressed as,

$$\frac{\sigma}{k_B T} = \frac{\Delta F}{\Delta A} \tag{3.14}$$

where ΔF is the change in the free energy for a corresponding change ΔA in the cross sectional area, k_B is Boltzmann constant and T is temperature.

The change of free energy can be calculated by considering the forces caused by a small deformation of the simulation box. This results in

$$\frac{\sigma}{k_B T} = \frac{f_\perp L_\perp}{L_\parallel^2} - \frac{f_\parallel}{L_\parallel} \tag{3.15}$$



Figure 3.25: Flow diagram for a monomer from type B chains that is, for a larger size monomer.



Figure 3.26: Flow diagram for a monomer from type A chains that is, for a smaller size monomer.

type of chains	N	N_P	R^2	R_g^2	$\frac{R^2}{R_g^2}$	$\frac{b}{a}$	χ
А	32	512	193	32	6.03	1.51	0.32
В	32	64	709	112.36	6.31	1.62	0.196
В	24	96	480	64	7.5	1.62	0.212

Table 3.2: Single chain conformations as a function of monomer diameter of chains. In this table statistical segment lengths are in units of average bond length for the respective type of chains. For the chains with smaller bead the average bond length is 1.998 whereas for the chains with larger beads it is 3.749.

where $f_{\perp,\parallel}$ are the forces acting on the boundary of the simulation box perpendicular and parallel with respect to the interface plane. L_{\perp} is the length of the system perpendicular to the interface plane and L_{\parallel} is the length of the system parallel to the interface plane. The force is calculated by a small homogeneous uniaxial deformation of the chains. The details of this method is described in [7]. The deformation (which we suppose a small uniaxial compression/expansion of the probe) matrix, we use in our method is given by;

$$\begin{pmatrix} 1+\alpha & 0 & 0\\ 0 & 1 & 0\\ 0 & 0 & 1 \end{pmatrix}$$
 (3.16)

ı.

where α is deformation parameter. Using virial theorem the force components $f_{\perp,\parallel}$ can be expressed as [7];

$$\frac{f_{\perp,\parallel}L}{k_BT} = \frac{d}{d\alpha} \bigg|_{\alpha=0} \ln \left\langle \exp\left(-\Delta E(\alpha)/k_BT\right) \right\rangle_0$$
(3.17)

where $\langle (\ldots) \rangle_0$ denotes average of (\ldots) in the undeformed system and $\Delta E(\alpha)$ is the difference in total potential energy of deformed and undeformed conformations. This formula is general and is valid for any models. The differential coefficient in equation 3.17 is not so easy to calculate. Therefore, we calculate the differential coefficient in right of Eq. 3.17 by a set of finite difference quotients. One can write,

$$\frac{d}{d\alpha}\bigg|_{\alpha=\alpha_i} \ln\left\langle \exp\left(\frac{-\Delta E(\alpha)}{k_B T}\right)\right\rangle_0 \approx \frac{\Delta \ln\left\langle \exp\left(\frac{-\Delta E(\alpha)}{k_B T}\right)\right\rangle_0}{\Delta \alpha}$$
(3.18)

for very very small $\Delta \alpha$. To evaluate right hand side of Eq. 3.17, we find a set of such finite differences for several α_i 's and extrapolate it to $\alpha = 0$.

In the case of the step potentials, U_i , Eq. 3.18 and hence Eq. 3.17 can be further simplified and finally we get,

$$\frac{f_{\perp,\parallel}L}{k_BT}\Big|_{\alpha} = \sum_{i} \frac{1}{\Delta\alpha} \left\langle \Delta W_i M_i(\alpha, \alpha + \Delta\alpha) \right\rangle_{configurations}$$
(3.19)

where i is the type of interaction (there are four types of interaction for semiflexible and three types of interactions for flexible polymer chains),

$$\Delta W_i = 1 - \left(\exp(-\Delta U_i/k_B T)\right)$$

is the change of weight and

$$M_i(\alpha, \alpha \pm \Delta \alpha)$$

is the number of monomers entering/leaving the interaction range for i of another monomer when changing the compression/expansion from α to

$$\alpha \pm \Delta \alpha$$

To use the full information contained in a given configuration of chains and to optimize the averaging we consider small $\Delta \alpha$, calculate the force for several α and extrapolate so obtained set $\frac{f_{\perp,\parallel}L}{k_BT}\Big|_{\alpha}$ to $\alpha = 0$. For the systems considered in the present work, the contributions to the pressure tensor from all the interactions present have to be calculated. These are the excluded volume, chain connectivity, the repulsing interaction between different types of the monomers and the bending energy (only for the semiflex-ible chains).

The distance between the monomer pairs in the case of small compression/expansion of the probe will be within interaction neighbourhood ('collisions'), divided by the deformation factor α and multiplied by a weight factor which is derived from the height of the step potential. The potential which models the connectivity in our model will play a role when the distance is larger than certain distance, the potential which models the repulsion between different types of monomers will play the role when the distance is larger/smaller than certain distance. The potential which takes into account excluded volume effect in our model plays a role when the distance between any two monomers is less than the certain distance and the potential which models the bending energy (in semiflexible polymers) in our model will play a role when the angle between two consecutive bond vectors of a chain is greater than a certain angle.

Next, the deformation factor α has to be considered, this depends up on the fact whether compression is considered or expansion. Further it depends up on whether our system is stiffness disparity or monomer size disparity. At the first we describe various weight factors for stiffness disparity systems and then for monomer size disparity systems.

For the four interactions which appear for monomer pairs in heterogeneous polymer models (flexible-semiflexible polymer system) used in present study, one obtains the following weight factor;

• Excluded Volume: E = 0, if the distance is $> d_{min}$, ∞ , else, between any two monomers and it is applicable just for compression, weight factor 1.

- Connectivity: E = 0, if the distance is $\langle d_{max}, \infty$, else, between any two consecutive monomers in a chain and it is applicable just for expansion, weight factor 1.
- Bending Energy: E = 0, if the angle is $> \theta_{max}$, ∞ , else, between any two consecutive bond vectors in a semiflexible chain and it is applicable for expansion/compression, weight factor 1.
- Repulsion: Repulsion between different types of monomers; $E = \epsilon$, if distance between two monomers is $\langle d_{2type}, E = 0$, else, and $\epsilon = 0.1$ acts between all the different types of monomers and applicable for compression/expansion with weight factor $(1 - \exp(-\epsilon))$ in the case of compression (in case a monomer falls to the interaction range of the other) and weight factor $\exp(\epsilon) - 1$ in the case of expansion (in case monomer just goes out of the interaction range of the others).

Similarly, for the three interactions which appear for monomer pairs in heterogeneous polymer models (polymer with different sizes of monomers) used in present study, one obtains the following weight factor;

- Excluded Volume: E = 0, if the distance between any type B monomers is $> d_B$, ∞ , else. E = 0, if the distance between any type A monomers is $> d_{min}$, ∞ , else. E = 0, if the distance between any different types of monomers is $> \frac{d_B + d_{min}}{2}$, ∞ , else, and it is applicable just for compression, weight factor 1.
- Connectivity: E = 0, if the distance is $\langle d_{Bmax}, \infty$, else, between any two consecutive monomers in a type B chain.

E = 0, if the distance is $\langle d_{max}, \infty$, else, between any two consecutive monomers in a type A chain, and it is applicable just for expansion, weight factor 1.

• Repulsion: Repulsion between different types of monomers; $E = \epsilon$, if distance between two monomers is $\langle d1_{2type}, E = 0$, else, and $\epsilon = 0.1$ acts between all the different types of monomers and applicable for compression/expansion with weight factor $(1 - \exp(-\epsilon))$ in the case of compression (in case a monomer falls to the interaction range of the other) and weight factor $\exp(\epsilon) - 1$ in the case of expansion (in case monomer just goes out of the interaction range of the others).

Capillary wave spectrum method

An alternative way of measuring the interfacial tension is the analysis of the capillary fluctuation spectrum [38, 73, 81, 82]. In general, polymer-polymer interfaces are not flat but exhibit long-wavelength capillary wave fluctuations. In the case of interface, there exits a type of fluctuation that survives even deep in the two-phase region. This is

because the interface breaks a continuous symmetry, the translational invariance, which results existence of long-wavelength transversal excitations known as Goldostone bosons [81]. The energy of these capillary waves of the local interface position vanishes as the wave length approaches infinity. These fluctuations strongly influence all quantities that depend on transversal degrees of freedom [81]. Capillary wave-like distortions of the interface can be thermally driven even at low temperatures because they cost very little energy. The effects of such fluctuations on interfacial properties were first considered by Buff et al. [83] and later systematically studied by Werner et al. [81, 84] and Lacasse et al. [73]. Capillary wave distortions can occur at large wave length with very little energy cost and are ultimately suppressed by finite size effects (system boundaries). The thermally excited capillary waves will be present at a polymer-polymer interface, even far away from the critical point, and such capillary waves may make a significant contribution to the measured interfacial width [85]. Moreover, the apparent width of a capillary-wave-roughend interface will depend on the length scale over which the interface will be averaged by the measurement (see figure 3.4) which will differ according to the technique used.

Let the deviation of the interfacial position from its mean position be h(y, z). According to the capillary wave theory [84] the free energy cost of these fluctuations is proportional to the increase in the interfacial area caused by these fluctuations. Hence, the free energy cost for the deviations from a flat planar interface is given by [84]

$$H_{cw} = \int \frac{\sigma}{2} (\nabla h)^2 \, dz \, dy + \dots$$
 (3.20)

In this expression, higher order gradient terms are assumed to be very small and neglected. σ is the interfacial tension. This capillary wave hamiltonian can be diagonalized by means of the Fourier transformation with respect to y and z which yields,

$$H_{cw} = \frac{\sigma}{2} \sum (\vec{q}^2) |h(\vec{q})|^2$$
(3.21)

where \vec{q} is the wave vector. From the equipartition theorem one can easily get the mean squared value of $h(\vec{q})$ which is,

$$<|h(\vec{q})|^2>=rac{1}{(\sigma \vec{q}^2)}$$
(3.22)

Therefore, the local mean squared displacement of the interface is given by,

$$s^{2} = \sum_{\vec{q}} \left\langle |h(\vec{q})|^{2} \right\rangle = \frac{1}{4\pi^{2}} \int \left\langle |h(\vec{q})|^{2} \right\rangle \ dq = \frac{1}{2\pi\sigma} \ln\left(\frac{q_{max}}{q_{min}}\right)$$
(3.23)

Here the lower cut-off q_{min} and the upper cut-off q_{max} have to be introduced as the integral $\int \frac{dq}{q}$ diverges logarithmically both for $q \to 0$ and $q \to \infty$. It could be necessary to cut off these divergences in a smooth way, using suitable correction terms in the capillary wave hamiltonian to get the more accurate description [86]. The maximum value of the

wave-vector clearly has to be set by a microscopic distance; it does not make sense to talk about a capillary wave whose wave length is much smaller than the intrinsic diffuseness of the interface, so this sets the value of q_{max} . The wave length cannot be bigger than the total size of the interface, so we are left with conclusion that the roughness of polymer-polymer interface depends on the size of the container. Therefore, the possible minimum value of q is $\frac{2\pi}{L}$ and the maximum value of q is $\frac{2\pi}{B_0}$ where L is the system size and B_0 is the coarse graining length on which the interface assumes its 'intrinsic' structure [81].

In principle, one can find the interfacial tension using capillary wave spectrum method by calculating the local mean squared displacement of the interface i.e. by using the formula 3.23 [81]. However, for this purpose the system should be very large and in the present system of study it cannot be applied. Therefore, in the present work the method used by Lacasse *et al.* [73] and by Auhl [7] is followed.

To find the total interfacial width which contains the effects of capillary wave fluctuations, it is assumed that the capillary waves can be decoupled from fluctuations in density and in order parameter. Hence, the averaged interfacial profile $\Psi(x)$ can be written as the convolution of the intrinsic interfacial profile $\psi(x - x_0)$ and the probability $p(x_0)dx_0$ of finding the interface at x_0 [73],

$$\Psi(x) = \int_{-\infty}^{\infty} \psi(x - x_0) p(x_0) \, dx_0 \tag{3.24}$$

Differentiating with respect to x one gets that $\Psi'(x)$ is the convolution of two wellbounded functions, $\psi'(x - x_0)$ and $p(x_0)$. Associating a functional measure to the well bounded function and using convolution theorem one gets,

$$\Delta^2 = \Delta_0^2 + \langle (\Delta X_0)^2 \rangle$$
 (3.25)

where Δ^2 and Δ_0^2 are related to the total and intrinsic interfacial width respectively (see below) and $\langle (\Delta X_0)^2 \rangle$ is the mean squared fluctuation on the interfacial position at x_0 .

Assuming equipartition of thermal energy on the modes of capillary waves and taking into account that a lower cutoff of wave vectors of capillary waves is given by the size L_s of the subsystem considered and a upper cutoff is determined by a scale l_0 of local bending rigidity or the intrinsic width of the interface, for $\langle (\Delta X_0)^2 \rangle$ results [85],

$$\left\langle (\Delta X_0)^2 \right\rangle = \frac{k_B T}{2\pi\sigma} \ln(\frac{L_s}{l_0})$$
 (3.26)

and we get finally

$$\Delta^2 = \Delta_0^2 + \frac{k_B T}{2\pi\sigma} \ln(\frac{L_s}{l_0}) \tag{3.27}$$

Determining the effective interface width for a set of subsystems of size L_s the interfacial tension can be determined without assumptions about the lower cutoff l_0 . For this purpose the density profile of the interface within a subbox of cylindrical shape was described by

$$\Psi(x - x_0) = 0.5 \left(1 + \tanh \frac{(x - x_0)}{w} \right)$$
(3.28)

and using the relationship $\Delta^2 = (\pi^2/12) \cdot w^2$ from the slope of the dependence of Δ^2 on $\ln(L_s)$ the interfacial tension is obtained by a least square fit. Fig. 3.4 shows the graph of square of interfacial width versus the system size and the least square fitted line for one of the configurations used for the analysis of the capillary wave spectrum.

In the Eq. 3.27, l_0 is the lower cutoff length which is the coarse graining length on which the interface assumes its 'intrinsic' structure [81]. To determine the intrinsic width, we choose persistence length, l_p , of the semiflexible chains as the lower cutoff length. The results obtained in this way will be discussed below.

Using both methods (analysis of capillary wave spectrum and virial theorem) described above, the interfacial tensions from 16 different configurations, such that output of former is input of successive, for each system of study have been calculated in stiffness disparity systems. We performed 2.4×10^4 attempted move per monomer (AMM) between two successive configurations for the systems of flexible chains and number of AMM increased with increasing stiffness of the semiflexible chains. For the system with the highest stiffness of our study the number of AMM between two successive configurations was 6.0×10^4 . Fig. 3.12 shows for a system with intermediate stiffness disparity $\left(\frac{l_p}{r}\right)$ =2.5) the values obtained by both methods for the 16 configurations used for the measurement of interfacial tension. For the size disparity system, the interfacial tension is calculated just by using virial theorem from 16 different configuration such that output of former is input of successive. 4.8×10^4 AMM between two successive configurations were performed. Figure 3.23 shows the interfacial tension from 16 different configurations for the system of monomer size disparity with equal number of monomers per chain. Capillary wave spectrum method could not be used to calculate the interfacial tension for monomer size disparity systems because of small system sizes considered in the present work.



Figure 3.27: Square of interfacial width versus the logarithm of subsystem size, (L_s) , as a function of stiffness of the semiflexible components. Arrows mark the square of intrinsic width for the respective systems.

4 Results and Discussions

4.1 General Consideration

In this chapter, results will be presented and discussed. Further, if possible, they will be compared with mean-field results. As mentioned in previous chapters, the interest is especially in the interfacial properties of asymmetric polymer blends and their phase behavior.

The interfacial properties of polymers with various degrees of flexibilities are discussed in section 4.2. The systems consist of flexible and semiflexible polymers whose flexibility varies fom flexible polymers to stiff rod. Various quantities which characterize the polymer-polymer interface have been studied. The interfacial tension as a function of statistical segment length of semiflexible component has been calculated using virial theorem and capillary wave spectrum method. Simulation results are compared with the mean field results of Helfand and Sapse [20], and Liu and Fredrickson [67]. Similarly, the interfacial width as a function of stiffness of semiflexible chains is studied by simulation and they are compared with the mean field results of Helfand-Sapse and Liu-Fredrickson. The monomer density profiles are also obtained as a function of chain stiffness of semiflexible components. Further, we study the orientaions of chains and bonds. The other interfacial properties which characterize the interface are distribution of chain ends and center of mass of polymer chains. All of these quantities are studied as a function of chain stiffness of semiflexible component.

In section 4.3, the interface properties of polymers with different monomer sizes will be presented. We study and compare our results for interfacial properties of two different types of systems; (1) a system having two different types (say type A and type B) of polymer chains such that the diameter of a type B monomer is double than that of type A monomer but the number of monomers per chain for both types of polymers is equal i.e, "monomer size disparity with equal number of monomers per chain", and (2) a system having two different types (say type A and type B) of polymer chains with almost equal radius of gyration, however, the diameter of type B monomers is double than that of type A monomers. The results of such asymmetric polymer-polymer interfaces are compared to the interfacial properties of symmetric system in which the size of monomers of both types of chains as well as number of monomers per chain are equal. The simulation results are compared with mean field results of Helfand and Sapse [20]. Other interfacial properties like density profile, chain orientation, distribution of chain ends near the interface and distribution of center of mass of polymer chains are also studied.

In section 4.4, we estimate the critical value of Flory-Huggins parameter as a function of degree of chain flexibility in a system of flexible-semiflexible polymers such that semiflexible chains are far from isotropc-nematic transition. In simulation, one can study phase diagram of polymer mixture by using semi-grandcanonical techniuqes in which types of chains are fluctuating but total number of particles remains constant. Because of high stiffness disparity for our systems of study such techniques will be inefficient for the present study. By calculating interfacial tension for weak segregation limit, we estimate the value of Flory-Huggins parameter χ at which the interfacial tension becomes zero, corresponding value of χ is critical value of χ at which two types of polymers get phase separated.

4.2 Interfaces of Flexible and Semiflexible Polymers

In this section we describe the results about the interface properties of flexible and semiflexible polymers at strong segregation limit. As mentioned before the present study covers the whole range of flexiblity of semiflexible polymers from flexible to stiff rods. We have studied interfacial tension, interfacial width, density profile, distribution of chain ends near the interface, distribution of center of mass of polymers near the interface, orientation of chains and bonds near the interface as a function of stiffness of the semiflexible chains. All these results will be presented and discussed in following subsections.

4.2.1 Interfacial Tension

Fig. 4.1 shows the obtained results for the interfacial tension of an interface between chains without additional bending restrictions and semiflexible chains described in previous chapter versus the statistical segment length of the stiffer chains estimated according to Eq. 3.4. The results obtained by the virial theorem and by the capillary wave method agree very well within the error bars estimated by the fluctuations of the single measurements (see above). The interfacial tension increases with increasing stiffness of the semiflexible component and levels of for values of stiffness beyond the semiflexible region $b \ll L$ which is visible also by the violation of the relationship $b = 2l_p - 1$ in Table 3.1. In Fig. 4.1 also simulation results obtained by Mueller and Werner [38] within the bond-fluctuation model for a rather limited range of stiffness disparity are displayed.

The interfacial tensions obtained by using virial theorem are higher than that by capillary wave spectrum method. This systematic difference can be attributed to the fact that virial theorem gives the difference of free energy per cross sectional area of the interface while capillary method is related to the interfacial area. Therefore, a little bit higher interfacial tension obtained by virial theorem is not unexpected.

In the simulation results it can be seen that there is a very strong tendency towards saturation of interfacial tension with increasing statistical segment length of semiflexible components. Moreover, from these results it can be seen that there is no change in the saturation property of interfacial tension even though the statistical segment length of semiflexible component crosses the isotropic-nematic transition region and hence we are dealing with isotropic-nematic (flexible-stiff rod) interface instead of isotropic-isotropic interface, provided in the isotropic-nematic interface the polymers forming nematic phase are parallel to the interface plane (when one considers the isotropic-nematic interface the interfacial tension (in fact, interfacial properties) depend on the direction of orientation of polymers which form the nematic phase [75]. In the present work, only one case of the isotropic-nematic interface of flexible-stiff polymers is considered in which the nematic director is parallel to the interface. The interfacial tension gets saturated before the stiffer chains form nematic phase and this trend of interfacial tension continues. The profile of interfacial tension against the statistical segment length of semiflexible component is very smooth after segment length in our model crosses the value 6.07.

These simulation results are compared with the mean-field results of Helfand and Sapse [20], and Liu and Fredrickson [67].

Helfand and Sapse [20] obtained for the interfacial tension, σ , of a planar interface between two phases of Gaussian chains with different statistical segment lengths interacting via a Flory-Huggins-type interaction

$$\frac{\sigma}{k_B T} = \frac{2}{3} \sqrt{\alpha} \left(\frac{(\beta_A^3 - \beta_B^3)}{(\beta_A^2 - \beta_B^2)} \right)$$
(4.1)

The β_i (i = A, B)

$$\beta_i = \sqrt{\frac{1}{6}\rho_{0i}}b_i \tag{4.2}$$

are the parameters which contain the chain statistics. The statical segment lengths b_i are defined in the same way as in Eq. 3.4 and the ρ_{0i} are the number densities of statistical segments in both bulk phases respectively. For comparison with simulation data we will use the mapping

$$\rho_{0i} = \frac{\rho_0}{C_{\infty i}} \tag{4.3}$$

which corresponds to the introduction of statistical segments by Eq. 3.4. ρ_0 is then the number density of beads which is the same for both chains. The interaction parameter α of the interaction between two statistical segments is then given by

$$\alpha = \rho_0 \chi \tag{4.4}$$



Figure 4.1: Interfacial tension as a function of statistical segment length of semiflexible polymers. The statistical segment lengths are in units of average bond length.

with the Flory-Huggins-parameter χ for the interaction of two beads of chains of different kind as defined by Eq. 3.3. For the interfacial tension of chains with the same segment length the Helfand Tagami result [65],

$$\frac{\sigma}{k_B T} = \rho_b b \sqrt{\frac{\chi_b}{6}} \tag{4.5}$$

is reproduced with now ρ_b and χ_b as the number density and interaction parameter of statistical segments. Fig. 4.1 shows clearly that the Helfand-Sapse results [20] agree well with the simulation data in the really semiflexible range of our system but differs increasingly with increasing stiffness. Expected reasons are as well effects of finite chain length as also the formation of local order with increasing stiffness. It will be discussed below.

Liu and Fredrickson [67] analyzed the interfacial tension of binary blends of polymers with different stiffness starting from a wormlike chain hamiltonian for both chains and with an interaction hamiltonian quadratic in both order parameters, concentration and orientation. Using a Landau-de Gennes expansion for the orientational part of the free energy, fixing the value of the Maier-Saupe parameter and assuming weak orientation only, they obtained;

$$\frac{\sigma}{k_B T} = \frac{4}{9a_0^2} \sqrt{\chi} \frac{\kappa_A^{3/2} - \kappa_B^{3/2}}{\kappa_A - \kappa_B}$$
(4.6)

where a_0 is the monomer length and κ_i (i = A, B) is the dimensionless persistence length (in units of a_0) of the ith component of the polymer blend. Eq. 4.6 has the drawback showing not the expected dependence on monomer density as eg Eqs. 4.1 and 4.5 and also not agreeing with Eq. 4.5 in the limiting case $\kappa_A = \kappa_B = 1$.

Using the correction factor $\sqrt{\frac{3}{8}}$ proposed in [67], with the replacement $\kappa = \frac{C_{1N}+1}{2}$ and using our values for the average bond length as monomer length i.e., $a_0 \sim a \sim 2l_c$ for two flexible chains, we get almost complete numerical agreement with the results from Eq. 4.5. With this choice of parameters the interfacial tension according to Eq. 4.6 in Fig. 4.1 shows a less increase with increasing stiffness disparity as the Helfand-Sapse result [20] and seems to agree better with the simulation result for large stiffness. But the above discussed problems and the behavior at small stiffness disparities rules Eq. 4.6 out to be a suitable expression for describing the interfacial tension for unsymmetrical polymer blends.

Up to now, the simulation results for finite segment numbers are compared with mean-field results for long chains. In literature (see e.g. [87]) several corrections for finite segment numbers are discussed. Ermoshkin and Semenov [87] reconsidered the problem most recently and proposed corrections for interfaces between blends with different molecular weight and also for the case $\chi N \sim 1$. Using the correction $(1 - 4\frac{\ln 2}{\chi N})$ obtained in [87] to Eq. 4.1 the reduction is too large but we get an almost complete agreement for the region of small stiffness disparity using the correction factor $(1 - 2\frac{\ln 2}{\chi N})$ obtained in [88] as is visible from Fig. 4.1. A detailed discussion of possible physical reasons for this disagreement is beyond the scope of this work but it may be related to the problem already discussed by Binder [1] that a minimization of a free energy functional in square gradient approximation is not sufficient for the strong segregation case $\chi N > 1$.

As main reason for the differences between mean-field results and simulation at higher stiffness disparities the strong orientation of bonds and chains near the interface must be considered (see below). This is not taken into account in the approaches discussed above. Moreover, when the persistence length $\left(\frac{l_p}{a}\right)$ of semiflexible chains is beyond ≈ 13.6 an isotropic-nematic transition will occur (see table 3.1). This strong increase in order in bulk is not accompanied by a visible change in the stiffness-dependence of the interfacial tension. This is an additional hint that the orientation near the interface is already large in the case of isotropic bulk phases and determines the stiffness dependence of interfacial tension. To derive the formula 4.6, Liu and Fredrickson assumed that the semiflexible polymers, in flexible-semiflexible polymer system, are far from nematic phase. By increasing the persistence length of semiflexible component, the system will be closer to isotropic-nematic transition. Therefore, the disagreement with their results for the system with flexible and highly stiff polymer chains is not unexpected. Further in their study, they fix Maier-Saupe parameter. When we increase the stiffness parameter of semiflexible chains the Maier-Saupe parameter of semiflexible chains also increases. These could be the reasons why the difference between mean-field and simulation goes on increasing with the stiffness of semiflexible component.

4.2.2 Density Profile and Interfacial Width

The entanglements in the interfacial zone are of major importance for the mechanical properties of the blend. Therefore, the monomer density profiles of different components of the polymer blends are also important. Figure 4.2 presents the density profiles of the individual components as well as total monomer density profile as a function of the stiffness parameter of the semiflexible component. The density profiles for the different stiffness parameters are not much different until the persistence length $\left(\frac{l_p}{a}\right)$ of semiflexible component is 13.6. The profiles become sharper in the semiflexible side as the stiffness increases. When the persistence length $\left(\frac{l_p}{a}\right)$ of the semiflexible components is larger than 13.6, it forms a nematic phase and the density profiles also become quite different and molecularly sharp which clearly shows decrease in interfacial width significantly. We can describe these profiles also by the tangent hyperbolic function 3.28. For example, figure 4.2 shows the tangent hyperbolic function fitted for the system with flexible-semiflexible polymers in which semiflexible component has persitence length $\left(\frac{l_p}{a}\right) = 2.5$. A reduction of the total monomer density is observed at the center of the interface and the effect increases with the increase in the stiffness of semiflexible component. When the persistence length $\left(\frac{l_p}{a}\right)$ of the semiflexible component of polymers is more than 13.6 the reduction of the total monomer density at the interface is very high as shown in the figure 4.2. The minimum value of total monomer density is 0.95 in the case of persistence length $\left(\frac{l_p}{a}\right)$ of semiflexible component 13.6 whereas it is about 0.85 and 0.63 for the systems with isotropic-nematic interfaces with persistence length $\left(\frac{l_p}{a}\right)$ of semiflexible component 28.0 and 30.02 see figure 4.3. It should be noted that in the present work, the nematic director in isotropic-nematic interface is parallel to the interface plane. Thus it is observed that as the stiffnes of the semiflexible component increases the density profile becomes sharper in semiflexible side and the depth of dip in the total density at the interface goes on increasing.

These results qualitatively agree with the previous results of Schmid and Mueller [66] for symmetric polymer-polymer interface and results of Liu and Fredrickson [67]. However, Mueller and Werner [38] have reported that the reduction of the total monomer density at the center of the interface is almost independent of the stiffness of the semiflexible component and the density profiles for stiffness disparity are almost independent of stiffness of semiflexible component. The reason may be that they considered very small stiffness disparity ($C_{1N} = 3.13$ is highest characteristic ratio, estimated from their data), therefore, in their results the reduction of total monomer density at the center of the interface is almost independent of stiffness. In the present results also if we just consider very small stiffness disparity as in their case (e.g. statistical segment length of semiflexible component = 1.51 and 2.8 only), we cannot see the small difference in the reduction of total monomer density at the center of the interface and density profiles are also almost independent of statistical segment length of semiflexible component which agrees very well with their results up to the stiffness disparity they studied. Comparing the flexible-flexible polymer interface with the interface of flexible polymers and semiflexible polymers with persistence length $\left(\frac{l_p}{a}\right)$ 13.6, the amount of reduction of total monomer density at the interface is little different and the density profiles are also not much different.



Figure 4.2: Normalized total monomer density and individual component density as a function of chain stiffness of the semiflexible polymers. Persistence lengths l_p s are in unit of average bond length. $\phi(x)$ is the normalized monomer density. Tangent hyperbolic function describing $\phi(x)$ of the system with $\frac{l_p}{a} = 2.5$ is also shown.

The total interface width w (compare to Eq. 3.27) is determined as already explained

in 3.4 by fitting the density profile to the model function 3.28. The intrinsic width w_0 follows then analyzing Eq. 3.27. As already discussed above as lower cutoff length the minimum of persistence length l_p is used. We get a slight decrease of total interface width with increasing stiffness disparity within the range of an isotropic phase for the semiflexible chains but a sharp decrease down to a molecularly sharp interface as visible in Figure 4.2 for the interface between flexible chains and stiff chains in nematic state. Figugre 4.4 shows also the data for the intrinsic width (considering persistence length as the lower cut off length).



Figure 4.3: Depth of the dip in monomer density profile as a function of chain stiffness of the semiflexible polymers.

Further, the intrinsic width keep on increasing until we consider the flexible-semiflexible interface such that semiflexible polymers are isotropic. But the intrinsic width has smallest value for isotropic-nematic interface (i.e. the interface between flexible-stiff rod polymers). Therefore, the intrinsic width also decreases when we pass from isotropic-isotropic interface to isotropic-nematic interface of polymers i.e. intrinsic width decreases with increasing statistical segment length of semiflexible component when the statistical segment length is greater than the value at which isotropic-nematic transition takes place. In figure 4.4, it can be seen that the difference in total interfacial width and intrinsic width decreases as a function of statistical segment length of semiflexible component. This means the contribution from the capillary wave to the interfacial width also de-

creases as a function of statistical segment length of semiflexible component. In all these



Figure 4.4: Interfacial width as a function of statistical segment length of semiflexible polymers. The width and statistical segment length both are in units of average bond length.

Within the work shortly characterized above Helfand and Sapse [20] obtained for the intrinsic interfacial width parameter w,

$$w = \sqrt{\frac{\beta_A^2 + \beta_B^2}{2\alpha}} \tag{4.7}$$

The results for our systems are again obtained with the replacements according to Eqs. 4.4 and 4.2 and shown also in Fig. 4.4. The end effect rises the value of interfacial width by a factor of $(1+\frac{2\ln 2}{\chi N})$ [89]. Figure 4.4 also presents the data obtained by using this correction factor in the mean-field expression obtained by Halfand-Sapse i.e Eq. 4.7. As for the interfacial tension a reasonable agreement between the intrinsic width and mean-field data with finite end corrections is observed in the semiflexible range and

increasing differences approaching the isotropic-nematic transition. The intrinsic width approaches the total width for large stiffness disparities because the increasing interface stiffness prevents the formation of capillary waves within the considered subsystems.

Liu and Fredrickson [67] obtained for their wormlike chain model

$$w = \frac{\sqrt{2}}{3}a_0\sqrt{\frac{\kappa_A + \kappa_B}{\chi}} \tag{4.8}$$

With the same treatment as for the interfacial tension the values for our systems are also shown in Fig. 4.4 and a similar relationship between the analytic results in [20] and [67] and our simulation data as in Fig. 4.1 can be observed for the predicted interfacial width.

Moreover, it should be noted that the results for the interfacial tension and the interface width derived in [38] from the Helfand and Sapse [20] results and also the results following from the free-energy-functional in [87] by minimization with the interface profile Eq. 3.28 and using the same mapping procedure as in Eqs. 3.4 and 4.3 agree completely with the results in Figs. 4.1 and 4.4 for the case $C_{\infty A} = C_{\infty B} = 1$ but show strong increasing deviations at larger stiffness disparities. Using instead Eqs. 3.4 the formal equivalent mapping procedure

$$b' = a\sqrt{C_{1N}}$$

$$\chi'_b = \chi$$

$$\rho'_b = \rho_0$$
(4.9)

leading also to Eq. 4.5 but now with parameters b', χ'_b and ρ'_b , an almost complete agreement with the analytic results in Figs. 4.1 and 4.4 up to large stiffness disparities is obtained.

Mueller and Werner [38] have also reported that the total interfacial width decreases with increase in the stiffness of semiflexible component in the blend of flexiblesemiflexible polymers which agrees with the present results.

4.2.3 Orientation of Chains and Bonds in the Interface Region

The thermodynamic quantities which were discussed in previous subsections are not sufficient to understand the microscopic structure of the polymer interfaces. The width of the interfacial region and the orientation of polymers on different length scales influence the material properties. They also play an important role for reactions at interfaces. The polymers stretch parallel to the interface. The shape of a polymer, near the interface is a prolate ellipsoid. The existence of a planar interface destroys the isotropy in the bulk polymer and consequently orientation of bonds as well as chains relatively to the interface will be observed. Quantitatively, the orientation of the bond vectors near the interface region have been studied. We study the following bond orientational parameter (defined in the chapter 3);

$$S(x) = \frac{3\langle a_x^2(x) \rangle / \langle a^2 \rangle - 1}{2}$$

$$\tag{4.10}$$

where \vec{a} are the bond vectors. The bond orientation parameter is positive for perpendicular and negative for the parallel orientation. The profile of the bond orientation is shown in the figure 4.5. In figure it is seen that bond vectors prefer to allign parallel to the interface. The orientation effects increases upon increasing the stiffness of the semiflexible component. Further the bond orientation parameter are not much different for different systems of studies in the flexible side whereas in the semiflexible side they are different which is the effect of stiffness of the semiflexible component. In the orientation profile the oriented region is broader in the compartment occupied by the stiffer chains. Further, in contrast to the width of the density profile, the spatial range over which the orientation of bonds extends grows with increase in the stiffness of the semiflexible component. Therefore, the orientational width and the width of the compositional profile are two independent microscopic length scales. Similar results are obtained by Mueller and Werner [38].

Further, we have studied the orientation of the parallel and the perpendicular components of the radius of gyration of the polymer chains. We have studied the following orientational parameter (as defined in the chapter 3) for the polymer chains near the interface;

$$\Delta Rg_{\perp} = \frac{3 < Rg_x^2 > - < Rg^2 >}{2 < Rq^2 >} \tag{4.11}$$

and

$$\Delta Rg_{\parallel} = \frac{3(\langle Rg_z^2 \rangle + \langle Rg_y^2 \rangle)/2 - \langle Rg \rangle^2}{2 \langle Rq^2 \rangle}$$
(4.12)

where ΔRg_{\perp} and ΔRg_{\parallel} are the perpendicular and parallel orientational parameters of the radius of gyration of polymer chains (perpendicular and parallel with respect to the interface plane), $\langle Rg^2 \rangle$ is the mean squared radius of gyration of the chains and $\langle Rg_i^2 \rangle$ (i = x, y, z) is the ith component of mean squared radius of gyration of the polymer chains. Therefore, if the chains orient parallel to the interface, parallel orientational parameter (ΔRg_{\parallel}) will be positive (maximum value 0.25) while the perpendicular orientational parameter (ΔRg_{\perp}) will be negative (minimum value -0.5). If the chains orient perpendicular to the interface, ΔRg_{\parallel} will be negative and ΔRg_{\perp} will be positive. If there is no preferred orientation of the chains, ΔRg_{\parallel} and ΔRg_{\perp} both the quantities will be equal to zero. The profiles of these quantities are shown in the figure 4.6.

As shown in the figure, ΔRg_{\parallel} and ΔRg_{\perp} in the flexible side remains almost constant (until the persistence length $\left(\frac{l_p}{a}\right)$ of the semiflexible chains increases up to 13.6) while in the semiflexible side they are different which is not unexpected as semiflexible chains


Figure 4.5: Orientation parameters of bonds as a function of stiffness of semiflexible component. l_p s are in unit of average bond length.

possess different degrees of flexibilities. In the isotropic-nematic interface, the chains in the flexible side remains unaffected till they are very close to interface. However, at the vicinity of the interface, they strongly stretch parallel to the interface. At the mean time, in the semiflexible region the semiflexible chains get stretched more and more parallel to the interface as the degree of flexibility decreases. In the isotropic-nematic interface the nematic chains prefer to allign parallel to the interface and they do it perfectly which is depicted in the figure 4.6. The polymer chains prefer to allign parallel to the interface as ΔRg_{\parallel} is positive in all the cases and ΔRg_{\perp} is negative (at the interface region) while in both bulk phases no preferential orientation takes place for the isotropic-isotropic interface. In the case of isotropic-nematic interface, nematic chains prefer to allign perfectly parallel to the interface plane even in the bulk phase. The orientation effects become stronger with the increase of the stiffness of semiflexible chains. For isotropic -isotropic interfaces, the orientational effect tends to be small unless the system is close to the isotropic-nematic transition. Passing through the interface region the elliptic chains first attempt to maximize the homocontacts with their own bulk phase (A-A and B-B segment contacts, respectively) in order to minimize the energy by rotating their longest axes into the interface plane as far as possible.



Figure 4.6: Orientation parameters of chains as a function of stiffness of semiflexible polymers. The persistence length are in units of average bond length.

4.2.4 Distribution of the Chain Ends and Density of Center of Mass of the Chains

The distribution of the chain ends are important for the interdiffusion and healing properties at interfaces between long polymers [15]. Further on the theoretical side, the behavior of chain ends is related to corrections to the ground state approximations [90]. Chain end effects give a large corrections to the interfacial tension and width (e.g., see the subsections 4.2.1 and 4.2.2) and they also play an important role for long range interactions between interfaces. Due to entropic reason polymers orient themselves by putting their ends preferentially at the center of the interfaces. Since A type of chains (in polymer blend of type A and type B) close to the interface prefer to put the chain ends into the B phase and vice versa, the chain ends are more at the interface than they are at the bulk side. A chain close to interface prefers to put its ends to its minority phase because of entropic reason. Therefore the density of ends of type A chains is increased at the side of type B chains and decrease close to the interface at the A side and vice versa. When this effect increases the interface becomes sharper and we cannot see such a effect in the weak segregation limit. If we calculate the total chain end distributions, we find effectively an enrichment of chain ends at the center of the interface and a depletion in the wings of the profile. The result of polymer chain ends being located preferentially close to the interface is that whole chains tend to orient themselves parallel to the interface and hence the shape of the polymer chains near the interface is prolate ellipsoid (see previous sul



Figure 4.7: Distribution of chain ends as a function of stiffness of semiflexible components in flexible-semiflexible polymer systems. The persistence lengths l_p s are in units of average bond length.

Figure 4.7 shows the profiles of the distribution of the chain ends as a function of stiffness of semiflexible components. In Fig. 4.7, $\frac{N\rho_e(x)}{2\rho(x)}$ versus x coordinate haven been plotted where $\rho_e(x)$ is the number density of chain ends at 'x', $\rho(x)$ is the total monomer density at 'x' and N is the number of monomer per chain. We have presented the above described quantity as a function of chain stiffnes of semiflexible component. It shows the chain end distributions for flexible chains, semiflexible chains and sum of them. Chain ends are enriched at the center of the interface, and this effect goes along with a depletion away from the interface. A - polymers like to put their ends into B rich phase and vice versa. Similar results are obtained theoretically for Gaussian chains by Schmid and Mueller [66]. The effect becomes stronger when the chain stiffness increases. In the figure 4.7, it can be seen that the maximum value of the profile increases with the increase of the stiffness of semiflexible component of the blend. As a result the minimum value away from the interface is smallest for the system having highest value of stiffness for semiflexible component. Further the total chain end distribution becomes more asymmetric as a function of stiffness of semiflexible component. In the flexible side the profiles are not much different but in the semiflexible side they are different which is reflected at the total value of end distributions.

Analogous observations apply to figure 4.8 which presents the normalized density of centers of mass of the chains, $\frac{\rho_{cm}(x)}{\rho_{cm}}$ (where $\rho_{cm}(x)$ is the number density of center of mass of polymer chains at x and ρ_{cm} is the average density of center od mass of polymer



Figure 4.8: Distribution of center of mass of flexible chains, semiflexible chains and sum of them. The persistence lengths l_p s are in units of average bond length.

chains) except for the maxima at the interface being now exchanged to minima due to the enrichment of centers of mass of chains in the interface region next to the bulk phase of the component. The density of center of mass has a minima at the center of the interface. This figure presents the normalized density of center of mass of flexible chains, semiflexible chains and the sum of them. The profile has minimum at the interface and this effect goes on increasing as the stiffness of the semiflexible component increases while the maxima at the interface in the profile of the chain ends distribution goes on increasing with the increase in the stiffness of the semiflexible component. As in the case of chain end distributions, the profiles in the flexible side are not much different but in the semiflexible side they are. Therefore, the total profiles are not symmetric. The maximum value in the profile which contains sum of center of mass of flexible and semiflexible chains away from interface increases as a function of stiffness of semiflexible component.

4.3 Interfaces of Polymers Having Different Monomer Sizes

In the previous section the results of interface properties of flexible-semiflexible polymer systems are discussed. This section is devoted to results and discussions about the interface properties of polymers with different monomer sizes. These systems consist of two types of polymer chains, viz; type A and type B. A type of polymer chains have monomers with diameter $d_A = d_{min}$ (which is defined already in chapter 3) whereas B type of polymer chains have monomers with diameter, $d_B = 2 \times d_A$. We study and compare interfacial properties of polymers having monomers of different sizes 'monomer size disparity with equal number of monomers per chain' and 'monomer size disparity with almost equal radius of gyration' (see chapter 3). The interface properties of monomer size disparity systems are compared to that of symmetrical system.

The interfacial properties which have been studied, are as those of stiffness disparity presented in section 4.2. The interfacial properties namely, interfacial tension, interfacial width, density profile, orientation of chains, distribution of chain ends and center of mass of chains for the systems described above have been studied.

4.3.1 Interfacial Tension

The interfacial tension for unsymmetric systems of two types of polymers which differ in the sizes of monomers are calculated as described above by virial theorem and these results are compared with the analytic expression given by Helfand and Sapse [20];

$$\frac{\sigma}{k_B T} = \frac{2}{3} \sqrt{\alpha} \left(\frac{(\beta_A^3 - \beta_B^3)}{(\beta_A^2 - \beta_B^2)} \right)$$
(4.13)

which is same as in Eq. 4.1. The β_i (i = A, B) are same as in equation 4.2 and ρ_{0i} are also same as in equation 4.3 in the section 4.2. However, the interaction parameter, α , between two statistical segments is now given by,

$$\alpha = \chi \sqrt{\rho_A \rho_B} \tag{4.14}$$

with the Flory-Huggins parameter χ for the interaction of two beads of chains of different types as defined in equation 3.13. The mapping procedures to compare simulation results with mean field are same as in the subsection 4.2.1. From equation 4.1 it is seen that the interfacial tension depends mainly on number density of different components, the interaction parameter χ and statistical segment length of the two components.

Table 4.1 shows simulation results and the data obtained from mean-field expression of Helfand and Sapse equation (4.13). From table 4.1, it can be seen that the interfacial tension decreases with the increase in 'monomer size disparity'. It is seen that the interfacial tension decreases in both cases, namely in monomer size disparity with equal number of monomers per chain and monomer size disparity with almost equal radius of gyration, in comparison to symmetrical system containing smaller size of beads. Moreover, for the asymmetric systems the interfacial tension is higher for the monomer size disparity with almost equal radius of gyration than that for the monomer size disparity with equal number of monomers per chain. We have compared also the ratio of interfacial tension to the Flory-Huggins parameter, χ , for different systems of studies. Table 4.1 presents the ratio of $\frac{\sigma}{k_B T}$ and χ for the systems of study. The ratio of interfacial tension ($\frac{\sigma}{k_B T}$) to Flory-Huggins parameter, χ also has larger value for the monomer size disparity with almost equal size of polymer chains than that of monomer size disparity with equal number of monomers per chain.

It is clear that simulation data agrees very well with the mean-field data by taking into account the finite chain length effects. Following the description in subsection 4.2.1

type of system	$\frac{\sigma}{k_B T}$	$\frac{\sigma/k_BT}{\chi}$	$\frac{\sigma}{k_BT}$ H-S	$\frac{w}{a}$	$\frac{w}{a}$ (H-S)
symmetrical	0.0615 ± 0.0058	0.192	0.0707	1.655	0.73
$N_A = N_B$	0.0261 ± 0.007	0.133	0.0284	1.05	0.723
$R_g^A \sim R_g^B$	0.0303 ± 0.0075	0.143	0.0331	0.979	0.659

Table 4.1: Interfacial tension and width for size disparity systems and symmetrical system. The total interfacial width are divided by respective bond lengths that is, 1.998 in symmetrical system and 3.749 in the unsymmetrical systems.

we take into account of finite length effects to describe the small difference between simulation and mean field results. Helfand et al. [88] have obtained the corrections in the interfacial tension due to the finite length of the chains. They have obtained that the interfacial tension is reduced by a factor of $\left(1 - \left(\frac{\ln 2}{\chi N_A} + \frac{\ln 2}{\chi N_B}\right)\right)$ because of finite chain length of the polymer chains. This factor becomes ~ 0.8 for unsymmetric systems and describes very well the very small difference between simulation results and mean-field data obtained from the analytic expression of Helfand and Sapse. When the statistical segment length of one of the components increases i.e., when the asymmetry in two types of chains increases, the interfacial tension increases but in our system of study it decreases because the Flory-Huggins parameter and number density of the type B chains also decrease. From table 4.1, it is seen that the interfacial tension for the asymmetric system is lower than that for the symmetric system. As seen in the table 4.1 for the size disparity case simulation data agree very well with the mean field results which implies that the mean field results describe the systems of lower values of χ and number density. The main resons for the lower value of interfacial tension for asymmetric systems are the lower value of χ and monomer density. As seen from the Eq. 4.5 the interfacial tension depends up on both of these quantities and increase with the increase with any of these quantities. It is seen that the small increase in interfacial tension due to increase in statistical segment length of the asymmetric system cannot compensate the huge reduction due to number density and χ .

4.3.2 Density Profile and Interfacial Width

Figure 4.9 shows the normalized monomer density profile for the type A monomers type B monomers and their sum. The number density of type B monomers is multiplied by eight as one type B bead has volume 8 times larger than that of the type A in monomer size disparity systems. As in the case of stiffness disparity, one can describe these profiles by the tangent hyperbolic function, Eq. 3.28. A reduction of the total monomer density profile for asymmetric polymer-polymer interfaces are not significantly different than that of the symmetric interfaces. In the case of asymmetric system the smaller beads penetrate more deep inside the bulk phase of larger beads than in the symmetrical system increasing the size of the interfacial region. The dip in the center of the interface increases slightly with monomer size disparity. But this increase is not



Figure 4.9: Monomer density profile of individual components and sum of them in the symmetric system and monomer size disparity systems.

significant as in the case of isotropic-nematic interface (see subsection 4.2.2). The dip at the center of the interface is highest for the system of monomer size disparity with equal number of monomers per chain for both types of chains whereas it has lowest value for the symmetric system.

Table 4.1 shows total interfacial width as a function of diameters of different types of beads. It depicted both the data one by simulation, and another by mean field expression using Eq. 4.7. The same mapping as in the stiffness disparity case has been used. These data show that total interfacial width increases with the asymmetry in the monomer volume, i.e., the radius of monomers. The interfacial width is larger for the system in which two types of monomers have different size but there are equal number of monomers per chain than that the system in which two different types of monomers have almost equal radius of gyration.

4.3.3 Orientations of Chains

In polymer blends the orientation of the polymers on different length scales influence the materials properties. The thermodynamic properties like interfacial tensions are not enough to understand the microscopic structure of the polymer interfaces. The shape of a polymer chain is a prolate ellipsoid near the interface. Due to entropic reasons polymers orient themselves by putting their ends preferentially at the center of the interface. In the present work, the orientation of chains have been studied by defining orientation parameter in terms of radius of gyration of polymer chains. The orientational profiles of monomer size disparity systems are compared with that of symmetric system. Orientations of the perpendicular and parallel (perpendicular and parallel with respect to interface) components of radius of gyration are studied. The orientational parameters which are studied are same as in the case of stiffness disparity Eq. 4.11 and 4.12. The orientational profiles are shown in the figure 4.10. The figure shows that the polymers in asymmetric systems with larger radius of beads orient more parallel to the interface plane compared to symmetrical systems. Further the effect is less for the system of the monomer size disparity with almost equal radius of gyration of chains than the system of the monomer size disparity with equal number of monomers per chain. Mostnotably, the orientation parameter in the side of small beads are not much different. If we see only A types of chains (chains with small beads, i.e. left side in the figure 4.10), they stretch more in the asymmetric system than that in the symmetric system. It is seen that A types of chains are not much influenced by the interface and B types of chains get more affected by the interface. Generally, there is weak nematic ordering near the interface but it is seen from our results that the effect is stronger in asymmetric system with smaller and larger beads than the symmetric system with the smaller beads. Passing through the interface region the elliptic chains first attempt to maximize the homocontacts with their own bulk phase (A-A and B-B segment contacts, respectively) in order to minimize the energy by rotating their longest axes into the interface plane as far as possible.

4.3.4 Distribution of the Chain Ends and Density of Center of Mass of the Chains

Since A types of chains (in polymer blend of type A and type B chains) close to the interface prefer to put the chain ends into the B phase and vice versa, the chain ends are more at the interface than they are at the bulk side. A chain close to interface prefers to put its ends to its minority phase because of entropic reason. Therefore the density of ends of type A chains is increased at the side of type B chains and decrease close to the interface at the A side and vice versa. When this effect increases the interface becomes sharper and we cannot see such a effect in the weak segregation limit. If we calculate the total chain end distributions, we find effectively an enrichment of chain ends at the center of the interface and a depletion in the wings of the profile. As a result whole chains tend to orient themselves parallel to the interface and hence the shape of the polymer chains near the interface is prolate ellipsoid (see above).

Figure 4.11 shows the distribution of the chain ends. Here we have plotted $\frac{N\rho_e(x)}{2\rho(x)}$ versus x coordinate where $\rho_e(x)$ is the number density of chain ends, $\rho(x)$ is the total monomer density and N is the number of monomers per chain. Here we have presented described quantity as a function of monomer size disparity in our systems of study. Figure shows the chain end distributions for type A chains (i. e. chains having small size of beads), for type B chains (i.e. beads with large size of beads) and sum of them. Fur-



Figure 4.10: Orientation of chains in the symmetric system and monomer size disparity systems.



Figure 4.11: Distribution of chain ends in symmetric systems and in systems with different monomer sizes.



Figure 4.12: Distribution of center of mass of chains in symmetric system and systems with different monomer sizes.

ther, it depicted chain end distribution for symmetrical system. It is seen that the chain ends are enriched at the center of the interface. The effect increases with the monomer size disparity. The peak has highest value for asymmetric system such that larger bead size component has equal number of monomers per chain as that of chains with smaller beads whereas the peak has lowest value for the symmetrical system. Total chain end distribution becomes asymmetric for the asymmetric systems which we studied.

The distribution of the center of mass of chains are also important to understand the interfacial properties as they give us insight of the location of chains. The profile for the distribution of chain center of mass, viz; $\frac{\rho_{cm}(x)}{\rho_{cm}}$, is shown in figure 4.12. $\rho_{cm}(x)$ is the density of center of mass of polymer chains at x and ρ_{cm} is the average density of center of mass of chains. Therefore, this figure presents the normalized density of centers of mass of the chains. In the chain end distributions, there is a maxima at the center of interface (in total chain end distribution) whereas the total density of center of mass has minima at the center of interface. In figure 4.12 we have presented the normalized density of center of mass for type A chains (i.e. chains having smaller beads), for type B chains (i.e. chains having larger beads) and sum of them. Further, to compare the results of asymmetric systems to that of symmetrical system, we have presented distribution of center of mass for the symmetrical system also. The minimum value at the center of interface is lowest for asymmetrical system in which both types of chains have equal number of monomers per chain and it is highest for the symmetrical system.

4.4 Phase Behavior in Flexible-Semiflexible Polymer Blend

We study the dependence of critical value of Flory-Hugins parameter, χ , and hence the critical temperature T_c on stiffness of semiflexible component.

In this section, the critical value of $\chi(\chi_c)$ has been estimated as a function of stiffness of semiflexible components in flexible-semiflexible polymer blend. As described in chapter 2, one can study phase diagram in polymeric systems by using semi-grandcanonical ensemble. In this method one types of chains are converted into other type and vice versa, to take into account density fluctuation. The total number of particles in the system remains constant. However, we consider very high stiffness disparity, so this method becomes inefficient as it violates excluded volume effect. The behavior of interfacial tension and interfacial width in weak segregation limit has been studied and from these data critical value of χ has been estimeted. In the present work, we estimate value of χ at which interfacial tension vanishes by studying behavior of interfacial tension at weak segregation limit. The behavior of interfacial tension at strong segregation limit will be also discussed.

To know whether the system has attained equilibrium in the weak segregation limit,



Figure 4.13: MSD of center of mass of polymers and square of interfacial width versus the AMM for weak segregation limit for flexible-semiflexible system in which semiflexible polymers have persistence length $\left(\frac{l_p}{a}\right) = 4.2$ when $\chi = 0.136$.

the interfacial width and the mean squared displacement (ΔMSD) of center of mass are monitored. For the weak segregation limit the interfacial width increases (see below) and hence the idea which was used for the strong segragation limit (see section 3.2.2) may not be enough for the equilibration. If the square of interfacial width and ΔMSD are comparable, the calculations of interfacial tensions and interfacial widths are started. Figure 4.13 shows the graph of ΔMSD and square of width for persistence length $(\frac{l_p}{a}) =$ 4.2. In all the systems of weak segregation limit, such graphs are produced before starting any calculations to ensure the system has attained equilibrium condition.

4.4.1 Interfacial Tension in Strong and Weak Segregation Limit

In the strong segregation limit, mean-field theory predicts that the interfacial tension varies as the square root of Flory-Huggins parameter, χ (Eq. 4.1). However, in the weak segregation limit the behavior is different. In weak segregation limit Flory-Huggins-de Geenes formula for interfacial tension and interfacial width are given by (from chapter 2);

$$\frac{\sigma}{k_B T} = \frac{9}{b^2 \sqrt{N}} \left(1 - \frac{\chi_c}{\chi} \right)^{3/2} \tag{4.15}$$



Figure 4.14: $\left(\frac{\sigma}{k_BT}\right)^{\frac{2}{3}}$ versus $\frac{1}{\chi}$ in flexible-flexible polymer system. The solid line is the straight line fitted to the weak segregation data and dashed line is the curve from the formula of strong segregation limit (Eq. 4.1).



Figure 4.15: $\left(\frac{\sigma}{k_BT}\right)^{\frac{2}{3}}$ versus $\frac{1}{\chi}$ in flexible-semiflexible polymer system in which semiflexible component has persistence length $\left(\frac{l_p}{a} = 2.0\right)$. The solid line is the straight line fitted to the weak segregation data and dashed line is the curve from the formula of strong segregation limit (Eq. 4.1).



Figure 4.16: $\left(\frac{\sigma}{k_BT}\right)^{\frac{2}{3}}$ versus $\frac{1}{\chi}$ in flexible-semiflexible polymer system in which semiflexible component has persistence length $\left(\frac{l_p}{a} = 2.5\right)$. The solid line is the straight line fitted to the weak segregation data and dashed line is the curve from the formula of strong segregation limit (Eq. 4.1).



Figure 4.17: $\left(\frac{\sigma}{k_BT}\right)^{\frac{2}{3}}$ versus $\frac{1}{\chi}$ in flexible-semiflexible polymer system in which semiflexible component has persistence length $\left(\frac{l_p}{a} = 4.2\right)$. The solid line is the straight line fitted to the weak segregation data and dashed line is the curve from the formula of strong segregation limit (Eq. 4.1).



Figure 4.18: Interfacial tension versus $\sqrt{\chi}$ for flexible-flexible polymer system. The solid line is the straight line from the Eq. 4.1 and the dashed line is the curve from Eq. 4.15.



Figure 4.19: Interfacial tension versus $\sqrt{\chi}$ for flexible-semiflexible polymer system in which semiflexible component has persistence length $(\frac{l_p}{a} = 2.0)$. The solid line is the straight line from the Eq. 4.1 and the dashed line is the curve from Eq. 4.15.



Figure 4.20: Interfacial tension versus $\sqrt{\chi}$ for flexible-semiflexible polymer system in which semiflexible component has persistence length $(\frac{l_p}{a} = 2.5)$. The solid line is the straight line from the Eq. 4.1 and the dashed line is the curve from Eq. 4.15.



Figure 4.21: Interfacial tension versus $\sqrt{\chi}$ for flexible-semiflexible polymer system in which semiflexible component has persistence length $(\frac{l_p}{a} = 4.2)$. The solid line is the straight line from the Eq. 4.1 and the dashed line is the curve from Eq. 4.15.

systems	Eq. 4.15	Eq. 4.1	Eq. 4.15 M-F	Eq. 4.1 M-F
$l_p = 1.25$	0.18402	0.109	0.1744	0.125
$l_p = 2.0$	0.1886	0.121	-	0.145
$l_p = 2.0$	0.1939	0.14	-	0.165
$l_p = 4.2$	0.2283	0.165	-	0.192

Table 4.2: Table of the prefactors in equations 4.15 and 4.1 obtained after comparing our data with mean filed. Here l_p s are in units of average bond length. In the column of system means, the system contains flexible polymers and semiflexible polymers of given persistence length.

and

$$w = \frac{b\sqrt{N}}{3} \left(\frac{\chi}{\chi_c} - 1\right)^{(-1/2)} \tag{4.16}$$

respectively. In these equations, b is statistical segment length, N is the number of monomers per chain and χ_c is the critical value of χ . To derive these formulas, it is assumed that the system is symmetrical, i.e. the number of monomers per chain in type A and type B polymers is equal and further the statistical segment length for both types of chains are equal. Therefore, when one considers asymmetrical systems the prefactors in equations 4.15 and 4.16 will be different. However, exponents in right hand side will be the same. From the equation 4.15, it is seen that interfacial tension decreases with decrasing χ and finally vanishes when $\chi = \chi_c$. Similarly, from 4.16 the interfacial width increases with decrasing χ and finally becomes infinite when $\chi = \chi_c$.

As described above (see Eq. 4.15), $\left(\frac{\sigma}{k_BT}\right)^{\frac{2}{3}}$ linearly varies with $\frac{1}{\chi}$ and the interfacial tension vanishes when $\chi = \chi_c$. Figure 4.14 shows the dependence of $\left(\frac{\sigma}{k_BT}\right)^{\frac{2}{3}}$ on $\frac{1}{\chi}$ for the flexible-flexible polymer system. We can describe the behavior by a straight line as shown. Further, the figure shows interfacial tension at strong segregation limit and described curve (see Eq. 4.1 and 4.5). It can be seen in the figure that the data of strong segregation limit (SSL) does not follow the straight line fitted for the data of weak segregation limit (WSL). From the fitted straight line for the data of interfacial tension in weak segregation limit, we have estimated the critical value of χ . Further, the prefactors in equation 4.15 also has been calculated. Table 4.2 shows the prefactors in the equation 4.15, from mean field and present work. The prefactors from mean-field and present work are not much different. The difference is less than 5%.

Figure 4.18 presents interfacial tension as a function of square root of χ for all the range of study in the present work for the flexible-flexible polymer system. From figure 4.18 it can be seen that the data of strong segregation limit follow a linear behavior whereas that of weak segregation limit shows different behavior. We have calculated the slope of the straight line described to the data at SSL which is not far from the mean-filed value. Table 4.2 shows the slope of the fitted line from present work and mean filed.



Figure 4.22: Total interfacial width as a function of the interaction parameter, χ for flexible and semiflexible with persistence length $(\frac{l_p}{a} = 1.25)$. Arrow marks the critical value of χ , estimated using the data of interfacial tension.

Figures 4.15, 4.16 and 4.17 presents the interfacial tension in WSL for the system of flexible-semiflexible polymers in which semiflexible chains have persistence length $\left(\frac{l_p}{a}\right)$ =2.0, 2.5 and 4.2 respectively. Also shown are the data for SSL. As described above, for the flexible-flexible polymer system, we have estimated the critical value of χ for all these systems of study and presented in figure 4.26. The prefactors in the equaion 4.15 are determined for all the systems of study and presented in the table 4.2. Figures 4.19, 4.20 and 4.21 presents the interfacial tension as a function of square root of χ for all the range of study in the present work for the system of flexible-semiflexible polymers in which semiflexible chains have persistence length $\left(\frac{l_p}{a}\right) =2.0, 2.5$ and 4.2 respectively. Further, table 4.2 presents the slope of the straight line fitted for SSL case.

4.4.2 Interfacial Width in Weak and Strong Segregation Limit

Figure 4.22 shows the dependence of total interfacial width on Flory-Huggins parameter, χ , for flexible-flexible polymer blend. In figure 4.22, the arrow marks the critical value of χ estimated from the interfacial tension. From figure, it can be seen that the interfacial width diverges at very very low value of χ . Werner and coworkers [81] also have studied the behavior of interfacial tension, width and other interfacial properties at weak segregation limit using Monte Carlo techniques. Similarly, other figures 4.22, 4.24 and 4.23 show the interfacial width as a function of χ for the system of flexiblesemiflexible polymers in which semiflexible chains have persistence length $(\frac{l_p}{a}) = 2.0, 2.5$ and 4.2 respectively. It can be seen from the figures that the interfacial width increases



Figure 4.23: Total interfacial width as a function of the interaction parameter, χ for flexible and semiflexible with persistence length $(\frac{l_p}{a} = 2.0)$. Arrow marks the critical value of χ , estimated using the data of interfacial tension.



Figure 4.24: Total interfacial width as a function of the interaction parameter, χ for flexible and semiflexible with persistence length $(\frac{l_p}{a} = 2.5)$. Arrow marks the critical value of χ , estimated using the data of interfacial tension.



Figure 4.25: Total interfacial width as a function of the interaction parameter, χ for flexible and semiflexible with persistence length $(\frac{l_p}{a} = 4.2)$. Arrow marks the critical value of χ , estimated using the data of interfacial tension.

with the decrease in the interfacial tension. The interfacial width will be infinite at the critical value of χ .

4.4.3 Estimation of Critical Value of χ

As described above we have estimated the critical value of χ as a function of stiffness of semiflexible component in our systems of study. We have carried out the study of flexible-flexible polymer blend and flexible-semiflexible (with varying persistence lenth up to 4.2) polymer blends. First, we studied the dependence of interfacial tension on Flory-Huggins parameter χ by reducing value of χ from strong segregation limit. The data are compared with mean-field expressions in equations 4.15 keeping the same meanfield exponents. Further comparison of our estimated value of critical χ with that of Werner *et al.* [81] for the flexible-flexible polymer blend shows that our result for this system ($\chi_C = 0.0795$) are not much different from their result ($\chi_C = 0.08$, estimated from their graph).

Figure 4.27 shows the ratio of critical temperature for a system with flexible-semiflexible chains to that of flexible-flexible system. It can be seen from the figure that the critical temperature increases with the increase in stiffness of semiflexible components.



Figure 4.26: critical value of F-H parameter as a function of stiffness of the semiflexible component. Here the persistence length are in units of bond length.



Figure 4.27: Ratio of critical temperature of semiflexible-flexible system to flexible-flexible system as a function of stiffness of the semiflexible component. Here the persistence length are in units of bond length.



Figure 4.28: $N\chi_c$ as a function of stiffnes of the semiflexible components.

The data have been compared to mean filed. From mean filed theory, one gets [1],

$$N\chi_c = \frac{1}{2} \left(\frac{1}{(C_{1NA})^{\frac{1}{4}}} + \frac{1}{(C_{1NB})^{\frac{1}{4}}} \right)^2$$
(4.17)

where C_{1Ni} (i = A, B) is the characteristic ratio as defined in chapter 3 of ith component and N is the number of monomers in a chain. The value of $N\chi_c$ as a function of stiffness of the semiflexible component, in the blend of flexible-semiflexible polymers, has been calculated using above formula and from simulation data. Figure 4.28 shows both the data. Both data show that the value of $N\chi_c$ decreases with increase in stiffnes of the semiflexible polymers. The mean filed theory gives lower values of $N\chi_c$ in comparison to simulation which is not unexpected as the mean field theory neglects the fluctuations. The nature of both data is the same.

5 Conclusions and Outlook

An extensive simulations of highly incompatible polymers with different stiffnesses and polymers with different monomer sizes have been presented. Of special interest is to study interfacial properties in both cases and phase behavior in stiffness disparity systems.

The flexibility of semiflexible polymers covers whole range, i.e. from flexible to stiff rod. The semiflexible chains are constructed by keeping restrictions on the consecutive bond vectors of a chain. The thermodynamic quantities like interfacial tension and interfacial width have been studied. The interfacial tension increases with increase in stiffness of the semiflexible component and there is a strong tendency towards saturation. It gets saturated well below the stiffness of semiflexible chains which form nematic phase. In this range of low stiffness of semiflexible chains the simulation data agree very well with the self-consistent field (SCF) theory data of Helfand and Sapse [20] by taking account of finite length of the polymers. The intrinsic interfacial width which is calculated by considering persistence length as the lower cutoff length also agrees very well with mean field SCF theory of Helfand and Sapse [20] by taking into account the finite length of the polymers. The intrinsic interfacial width increases with the stiffness of the semiflexible polymers whereas the total interfacial width decreases. The interfacial width decreases remarkably in the isotropic-nematic interface than in isotropic-isotropic interface. To characterize the local structure of the interface, the density profile of different monomer species, distribution of chain end, distribution of center of mass of chains, orientation profiles of chains and bonds are studied as function of stiffness of the semiflexible components. As the stiffness increases the density profile becomes sharper in semiflexible side and the depth in the total density profile goes on increasing. The flexible chains in a region rich in stiff chains cost more configurational entropy than stiff chains in a flexible-rich region. Therefore, flexible chains are expelled from the stiff-rich side, leading to steeper gradients in monomer density profile. A similar effect is seen in the phase behavior of blends of stiff and flexible chains [91]. The chain ends are more in the interface and the effect increases with the increase in the stiffness of the semiflexible component. Center of mass of chains have minima at the center of the interface. Near the interface, the polymers are stretched parallel to the interface. The polymers are strongly stretched on side of semiflexible polymers and the effect increases with the stiffness of the semiflexible component. The individual bonds also orient parallel to the interface and the effect is stronger on side of semiflexible polymers. The effect increases with the stiffness of the semiflexible components. Untill the semiflexible chains in a flexible-semiflexible system

are close to isotropic-nematic transition, the orientational effect tends to be small. This leads to interfacial tensions governed solely by the composition profile and so it agrees very well with that of Helfand-Sapse. In the case of flexible-highly-stiff polymer system the interfacial tensions governed not only by compositional profile and hence one has to take into account the orientational profiles also. For such a system a mean field theory beyond Helfand-Sapse is an essential.

The critical value of χ for a flexible-semiflexible polymer systems are estimated using the mean field exponents. From our results, it is seen that the mean field exponents are correct. The critical value of χ decreases with the stiffness of the semiflexible component hence the critical temperature increases.

The interfacial tension for a monomer size disparity system agrees very well in both cases namely, monomer size disparity with equal number of monomers per chain and monomer size disparity with almost equal radius of gyration of two types of chains. The interfacial width increases with the monomer size disparity. The monomer density profiles are calculated for the different species. Similarly, to the case of stiffness disparity the polymer chains prefer to orient parallel to the interface in the interface region. The chains having larger beads of unsymmetric systems orient more parallel to the interface in comparison to the symmetric system. The effect is not strong like the case of semiflexible chains close to isotropic-nematic transition. The chain ends are more at the interface and the effect is stronger for the monomer size disparity systems. The center of mass of polymers have minima at the interface.

The main conclusion of the present work is the following. The mean filed thoery of Helfand-Sapse is correct for the flexible-semiflexible polymer system provided semiflexible chain are far enough from isotropic-nematic transition. It can describe the monomer size disparity system also.

The effect of flexible-semiflexible diblock copolymers on the flexible-semiflexible homopolymer interfaces and polydispersity effect will be our future work in this field. Further the combination of stiffness disparity and monomer size disparity (which are studied in the present work) may help to model any polymer blends.

Summary

Motivation

The subject of phase behavior of polymer melts, polymer mixtures (or blends) and polymer interfaces [1, 4] has attracted a great deal of attention because of intriguing physical properties and an essential role in polymer technology. Polymers do not mix at a molecular level at equilibrium, under a wide variety of circumstances because any slight incompatibility of monomers in enthalpic interactions and/or entropic packing effect is amplified by the number of monomers in the macromolecule and cannot be balanced by the entropy of mixing. If such a pair of polymers are dispersed mechanically, there will be domains of one polymer in the other. In such a situation, one is interested to know the nature of the interface between the two coexisting phases and determination of the interfacial energy. The morphology of the mixture will be greatly influenced by the interfacial energy, which will control the domain size, while the microscopic structure of this interface will determine the degree of adhesion between the phases. Thus the mechanical properties of the whole mixture will be largly controlled by properties of these interfaces. Therefore, key to applications of polymeric materials is the ability to control surface or interfacial properties.

Polymer blends are generally "structurally asymmetric" corresponding to speciesdependent local intramolecular features such as monomer shape, branch content, and persistence length or aspect ratio. Therefore, a systematic study of unsymmetric polymerpolymer interface is highly demanding. Helfand and Sapse [20] extended the self consistent field theory to infinitely long Gaussian chains with different statistical segment lengths. In the strong segregation limit, they have obtained an analytical expressions for interfacial width w and the interfacial tension σ .

Computer simulation has become a major tool in polymer science, complementing both analytical theory and experiment. Comparing to experiment, simulation provide a test of the microscopic model which has been used and comparing to theories, they serve as a test of the theory within a well-defined microscopic model. Moreover, they may provide structural information which may not yet be accessible experimentally or theoretically. For example, the Flory-Huggins theory [12] is not free of crude approximations. To test the reliability of the theory, one needs to compare theory and experiments. However, comparing theory with experiments is not sufficient because in most cases, the agreemnet is not good, but one cannot tell whether the discripencies are due to inadequacies of the model used in the theory or due to inaccuracies of the approximations. Since the simulation can be performed on exactly the same model which the analytical theory considers (but avoiding the uncontrolled mathematical approximations of the later), the simulations provide "benchmarks" against which these theories can be reliably tested.

Keeping these views in mind we have carried out an extensive Monte Carlo simulations of unsymmetric polymer-polymer interfaces.

Systems and Model

As mentioned above, the main goal of this thesis is to test mean filed theories for two kinds of dispair systems, namely 'stiffness disparity' in which two types of chains have different stiffnesses and 'monomer size disparity' in which two types of chains have different sizes of monomers. The phase behavior in the case of low stiffness disparity systems has been also studied. The stiffness disparity in our systems covers the whole range of semiflexible polymers that is, from flexible to stiff rod. In the monomer size disparity systems the diameter of type B monomers is double than that of type A.

To do this we use a continuous space (CS) coarse-grained model. In the flexible polymers there are only three interactions, viz; excluded volume, chain connectivity and repulsion between two different typs of monomers. In the semiflexible polymers another interaction which restricts the flexibility of the polymers also acts. In our model all the interactions are modeled by step potentials. The semiflexible polymers are generated by the restriction on the angle between two consecutive bond vectors of a chain. After the generation of chains and removing the overlapping between any two monomers, the system is equilibrated using Monte Carlo techniques (standared Metropolis algorithm is used). For the strong segregation limit we believe that the systems attained the equilibrium when the mean squared dispalcement of center of mass of polymers is comparable to square of radius of gyration. For the weak segregation limit we believe that the systems attained the equilibrium when the mean squared dispalcement of center of mass of polymers is comparable to square of interfacial width. The interfacial tension is measured by virial theorem and capillary wave spectrum method. The virial theorem method which was used to measure interfacial tension for symmetric systems is developed further for the unsymmetric systems and it is tested by capillary wave spectrum method for the stiffness disparity systems.

Conclusions and Outlook

Our results reveal that the interfacial tension increases with the stiffnesses of the semiflexible components and there is strong tendency towards saturation. It levels of well below the stiffness of semiflexible polymers which changes phase from isotropic to nematic. For the really semiflexible region our results agree very well with that of Helfand-Sapse and of Liu-Fredrickson too by taking finite length effects. For the system with flexible-highly stiff polymers they do not agree as these theories does not take into account the ordering of polymers near the interface (chains orient parallel to the interface plane and the effect is stronger for the stiff chains). The intrinsic interfacial width increases with the stiffness of the semiflexible chains and it agrees with the mean field results. The monomer density profiles become steeper in the semiflexible side and the depth in the dip of profile increases with stiffness of the semiflexible components. The bonds orient parallel to the interface and the effect becomes stronger with the increase of stiffness of the semiflexible component. The profiles of chain ends and chain center of mass show that chain ends have peak at the interface whereas center of mass has minima. By studying interfacial properties at the weak segregation limit the critical value of χ has been estimated for low stiffness disparity systems. It is found that χ_c decreases (hence T_c increases) with the increase in the stiffness of the semiflexible polymers.

The interfacial tension decreases with the monomer size disparity and agrees within errorbars to the mean filed results. The interfacial width is higher for the monomer size disparity systems. The chains stretch parallel to the interface and the effect is stronger for the monomer size disparity system in comparison to the symmetric system. The profiles of chain ends and chain center of mass show that chain ends have maxima whereas chain center of mass has minima at the interface. This effect is stronger for the dispair system in comparison to the symmetrical system.

Thus our results show that the mean-field theories can describe a system of monomer size disparity (up to really semiflexible region). For highly stiff chains a more sophisticated theory which takes into account of orientation of chains needs. In principle Liu-Fredrickson theory should work but in the contribution which we cited, they assume that semiflexible chains are far from nematic phase. In addition, this theory does not produce correct limiting values for flexible chains. The polymer blends are always asymmetric and it is due to stiffness disparity or size disparity or combination of both. Therefore, our work can be extended to model any polymer blends in the coarse-grained level with a suitable choice in stiffness and size of respective components.

The open questions from the present work could be the following. One can further develop the CS model to study flexible-semiflexible diblock copolymer on the flexiblesemiflexible homopolymer interfaces. Further one can study polydispersity effect on both types of systems.

Zusamenfassung

Motivation

Das Phasenverhalten von Polymergemischen und die Eigenschaften von Polymer-Polymer-Grenzflächen [1, 4] haben sowohl wegen der interessanten physikalischen Probleme als auch wegen ihrer technischen Bedeutung beträ chtliches Interesse erlangt. Polymergemische können in vielen Fällen keinen einphasigen Zustand einnehmen. Bereits geringe Unterschiede der Wechselwirkung oder auch Packungseffekte wachsen linear mit der Zahl der Monomere und können deshalb durch die Mischungsentropie nicht kompensiert werden. Werden solche Systeme mechanisch dispergiert, bilden sie Domänen der nahezu reinen Phasen. In diesen Fällen sind die Struktur der Grenzfläche zwischen den koexistierenden Phasen und die Grenzflä chenenergie von besonderem Interesse. Die Morphologie der Mischung wird dabei stark von der Grenzflächenenergie beeinflußt, weil diese die Dom änengröße bestimmt. Die mikroskopische Struktur der Grenzflä che bestimmt dagegen den Grad der Adhäsion zwischen den Phasen. Die mechanischen Eigenschaften eines Polymergemischs werden damit wesentlich von den Eigenschaften der Grenzflächen bestimmt. Für viele Anwendungen ist die Steuerung der Grenzflächeneigenschaften deshalb von Bedeutung.

Polymergemische sind generell "strukturell unsymmetrisch", d.h. die Komponenten unterscheiden sich z.B. durch Größe und Form der Monomere, den Verzweigungsgrad oder die Persistenzlänge und das Aspektverhältnis. Systematische Untersuchungen unsymmetrischer Polymer-Polymer-Grenzflächen sind deshalb notwendig. Helfand und Sapse [20] erweiterten die SCF-Theorie auf den Fall langer Gaußketten mit unterschiedlichen statistischen Segmenten und konnten für den Grenzfall starker Inkompatibilität geschlossene Ausdrücke für die Grenzflächendicke w und die Grenzflächenspannung σ erhalten.

Computersimulationen sind zu wichtigen Werkzeugen der Polymerwissenschaft geworden, die analytische Theorien und Experimente ergänzen. Ein Vergleich mit Experimenten liefert einen Test der verwendeten mikroskopischen Modelle und Vergleiche mit analytischen Ergebnisse erlauben einen Test der Theorie im Rahmen eines wohldefinierten mikroskopischen Modells. Außerdem werden strukturelle Informationen erhalten, die weder experimentell noch analytisch zugänglich sind. Die Flory-Huggins-Theorie [12] enthält z.B. starke Näherungen, um diese zu testen, wäre ein Vergleich von Theorie und Experiment notwendig. Eine mangelnde Ü bereinstimmung der Ergebnisse kann dabei aber sowohl durch ein ungeeignetes Modell wie durch Näherungen im Verlauf der Auswertung verursacht sein. Um eine Theorie zuverlässig zu testen, ist es deshalb notwendig, für das von der analytischen Theorie untersuchte Modell sichere Ergebnisse zu gewinnen.

Unter Berücksichtigung dieser Uberlegungen wurden umfangreiche Monte-Carlo-Simulationen unsymmetrischer Polymer-Polymer Grenzflächen durchgeführt.

Systeme und Modell

Das Hauptziel der Arbeit ist der Test von "mean-field"-Theorien für unsymmetrische Systeme. Diese sind einmal Polymere mit Ketten unterschiedlicher Steifigkeit und weiterhin Polymere unterschiedlicher Segmentgröße. Außerdem wird das Phasenverhalten im Fall nicht zu großer Unterschiede der Kettensteifigkeit untersucht. Die Grenzflä cheneigenschaften werden für Unterschiede der Steifigkeit von völliger Flexibilität bis zum steifen Stab betrachtet. Als Unterschied der Segmentgröße wird der Faktor 2 verwendet.

Als Modell wird ein gitterfreies Kugel-Stab-Modell verwendet. Im Falle flexibler Ketten werden dabei nur drei Arten von Wechselwirkungen betrachtet: "Excluded volume", Zusammenhalt der Kette und eine abstoßende Wechselwirkung ungleichartiger Monomere. Bei semiflexiblen Ketten wird weiterhin eine eingeschränkte Biegsamkeit durch Einschränkungen für aufeinanderfolgende Bindungsvektoren berücksichtigt. Alle diese Wechselwirkungen werden durch Stufenpotentiale beschrieben. Nach der Erzeugung der Ketten und der Beseitigung vom Uberlappungen der Hartkugel-Bereiche der Wechselwirkungen werden die Systeme durch Monte-Carlo-Techniken äquilibrisiert (Standard Metropolis Algorithmus). Als Kriterium für die Einstellung des Gleichgewichts wurde dabei im Falle starker Wechselwirkung eine mittlere quadratische Verschiebung der Schwerpunkte der Ketten von der Größerordnung des Gyrationsradius angenommen. Für Systeme in der Nähe des kritischen Punktes wurde als Kriterium eine mittlere quadratische Verschiebung von der Größe der Grenzflächendicke verwendet. Die Grenzflächenspannung wurde durch Anwendung des Virialsatzes und aus einer Analyse des Kapillarwellenspektrums bestimmt. Die Anwendung des Virialsatzes wurde dabei auf den Fall semiflexibler Ketten erweitert und mittels der Kapillarwellenanalyse getestet.

Schlußfolgerungen und Ausblick

Die Ergebnisse zeigen, daß die Grenzflächenspannung mit der Steifigkeit der semiflexiblen Komponente anwächst und mit wachsender Steifigkeit schnell in einen konstanten Wert einmündet. Dieser konstante Wert wird bereits deutlich unterhalb der Steifigkeit erreicht, bei der die semiflexiblen Polymere einen Übergang vom isotropen zum nematischen Zustand erfahren. Im tatsächlich semiflexiblen Bereich ergibt sich bei Berücksichtigung der Effekte endlicher Kettenlänge eine gute Ü bereinstimmung mit den Ergebnissen von Helfand-Sapse und Liu-Fredrickson. Bei größerer Steifigkeit ergeben sich zunehmende Abweichungen, die auf die stark anwachsende Ordnung der Ketten parallel zur Grenzfläche zur ückgeführt werden. Die intrinsische Grenzflächendicke im semiflexiblen Bereich wächst mit der Steifigkeit und ist in Ü bereinstimmung mit "meanfield" Resultaten. Das Dichteprofil ist auf der Seite der semiflexiblen Ketten steiler und die Dichtereduktion in der Grenzflächenmitte nimmt mit der Steifigkeit der semiflexiblen Ketten ebenfalls zu. Die Bindungen der Ketten orientieren sich parallel zur Grenzfläche mit zunehmender Tendenz mit wachsender Steifigkeit. Die Profile der Kettenenden und der Kettenschwerpunkte zeigen Maxima bzw. Minima an der Grenzflächenmitte. Aus Untersuchungen der Grenzflächenspannung in der Nähe des kritischen Bereichs wurde χ_c für den semiflexiblen Bereich bestimmt. χ_c wächst mit zunehmender Steifigkeit der semiflexiblen Komponente an.

Die Grenzflächenspannung verringert sich bei ungleichen Segmentgrößen und stimmt innerhalb der Fehler mit "mean-field" Resultaten überein. Die Grenzflächendicke wächst dabei an. Die Ketten orientieren sich parallel zur Grenzfläche bei stärkerer Orientierung als im symmetrischen System. Die Profile der Kettenenden und der Kettenschwerpunkte zeigen Maxima bzw. Minima an der Grenzflächenmitte mit ebenfalls verstärkten Effekten im Vergleich zu symmetrischen Systemen.

Die Resultate zeigen, daß "mean-field" Theorien das Verhalten im semiflexiblen Bereich richtig wiedergeben. Für größere Steifigkeiten erscheinen Theorien notwendig, die die Orientierung in der N ähe der Grenzfläche berücksichtigen. Die Theorie von Liu-Fredrickson ist dafür vorgesehen, kann die Orientierung aber nur in ausreichendem Abstand von der nematischen Phase beschreiben und außerdem den flexiblen Grenzfall nicht korrekt reproduzieren.

Gemische realer Polymere können im Rahmen einer vergröberten Beschreibung durch eine Kombination von unterschiedlicher Steifigkeit und unterschiedlicher Segmentgröße beschrieben werden, die verwendete Methode ist dafür geeignet. Weitere mögliche Fragestellungen sind die Untersuchung von Grenzflächen mit Blockcopolymeren unterschiedlicher Steifigkeit und Effekte der Polydispersität.

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