

# Behavior of Diblock–Copolymers and Semi–flexible Polymers at Interfaces



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## Glossary of Symbols

$R_g$	radius of gyration
$v$	the monomer volume
$l$	the statistical segment length
$N$	the total number of monomers in the polymer chain
$N_i$	the number of monomers of the copolymer chain in the block $i$
$f$	the number fraction or the composition of the copolymer chain
$T$	the temperature
$\chi$	the Flory - Huggins interaction parameter
$\rho$	density of the polymer chain
$\nu$	the interfacial excess
$\mu$	the chemical potential
$\gamma$	the interfacial tension
$\Delta\gamma$	the reduction in the interfacial tension
$T_c$	the critical Adsorption temperature
$w$	the ineterfacial width
$l_p$	the persistence length
$L$	the total length of the semiflexible chain
$R$	mean-square end-to-end distance
$f_l$	the Boltzmann weight of a semiflexible chain with $l$ monomer
$w(r, v, t)$	the probability density of the semiflexible chain
$D_v$	the diffusion constant
$t$	the time
$\varepsilon$	monomer-monomer interaction energy
$z$	the interfacial excess
$\phi$	volume fraction of the copolymer chain
$\theta$	the angle between two successive segments of the semiflexible chain
$t(s)$	the tangent vector of the semiflexible chain
$\kappa$	the bending modulus of the polymer chain
$H$	the hamiltonian of the polymer system
$G(r, t, r_0)$	the Green's function of the polymer chain

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## Abstract

The adsorption of polymer chains at surfaces or interfaces is an important subject in wide range of applications. The adsorption of the copolymers at interfaces (*i.e.*, liquid–liquid interface) plays an important role in determining the interfacial properties. It is capable to improve the mechanical properties of the interfaces. Also they are very efficient as compatibilizers. The adsorption phenomenon of the copolymer at interface in immiscible polymer blends systems results in producing optimal mechanical properties of such blends. The simplest copolymer candidate is the diblock copolymer. This is because it has a very simple structure compared with the other kinds of copolymer chains. As an example the diblock compatibilizer of  $P(S - b - MMA)$  is a good agent for experimental realizations. Also studying the adsorption of semiflexible polymeric materials onto surfaces or interfaces is of significant technological importance in variety of applications ranging from industry to biology. These wide range of applications are determined preliminary by an intrinsic character of the polymer chain. This stiffness character of the semiflexible polymer chain is controlled by an intrinsic parameter called the persistence length  $l_p$ . Such a length exists in the nature of the polymer chain, beyond which the semiflexible chain loses its stiffness completely and begins exhibiting the flexible nature.

The first part of the thesis was concerning with the interfacial properties of a diblock copolymer at penetrable interfaces. In particular we studied the density profiles, the stretching, and the interfacial tension. These interfacial properties of diblock ( $AB$ ) copolymers near an interface between two solvents are studied by using the exact Green's function of a Gaussian copolymer chain at an attractive penetrable interface. We have studied the mean-square end-to-end distance of the copolymer,  $\langle R^2(z) \rangle$ , as a function of the distance of the joint point of the copolymer to the interface,  $z$ , the segment density distribution  $\rho(z)$ , and the reduction of the interfacial tension  $\Delta\gamma_c$  due to the presence of the diblock copolymer. The density profile and the stretching of the copolymer chain are in agreement with both experimental results and simulations. The reduction of the interfacial tension is found to decrease with the increase of the degree of polymerization of the copolymer chain. A simple scaling law for the reduction of the interfacial tension is derived.

The second part of the work focuses on studying the adsorption of a semiflexible polymer chain onto a penetrable interface. The adsorption of a flexible and a semiflexible polymer chain onto a penetrable sphere, and the adsorption of a semiflexible polymer onto a structured interface in the framework of the integral equation for the Green's function of polymer chain has been discussed. In this part we confirmed the old studies concerning the adsorption of a semiflexible polymer at interfaces, and found that it adsorbs easier than the flexible one. Also we have found that in contrast to the adsorption of a flexible polymer, the distribution of the free end of the semiflexible polymer decays non–exponentially as a function of the distance to the interface.

# 1. Introduction

## Motivation

Polymer surfaces and interfaces play an essential role in polymer technology. Polymers can have different kinds of interfaces *e.g.*, air or solid interface. However it can form an internal interface (see Fig.(1.1)), for example the interface between two incompatible homopolymers (see Fig.(1.2)). The subject of polymer surfaces and interfaces has been attracting many of the chemists, physicists, material scientists, and engineers. The problem of adsorption of polymers on surfaces or at interfaces is a topic of fundamental importance in a wide range of applications such as adhesion, blending, resisting, coating, and lubrication. The adsorption phenomenon of copolymer chains onto such interfaces plays an important role in fascinating outstanding properties of the interfaces. Among the different kinds of copolymer, diblock copolymers are the mostly used agents in producing optimal mechanical properties of interfaces in immiscible polymer blend systems. Thus the technological importance and the simple structure of the diblock copolymers have motivated many recent theoretical and experimental studies of their interfacial behavior [1], [2].

Many research work connected with the problem of adding a diblock copolymer into the interfaces has been done in the recent years. Theoretical as well as experimental investigations have demonstrated that diblock copolymers can be used as a successful compatibilizer between two highly incompatible homopolymers  $A$  and  $B$ . Thus reinforcing the interface between two immiscible homopolymers blend by a efficient compatibilizer reduces the interfacial tension and improves the mechanical properties of the blend. The reduction of the interfacial tension of such interfaces is meanwhile well studied for several systems and different molecular architectures (*e.g.*, diblock, and triblock). Although such block copolymers are very efficient as compatibilizer, they also have some deficiencies, such as high tendency to form micelles and their slow migration to the interface. A diblock copolymers of *poly(styrene)* ( $PS$ ) and *poly(methylmethacrylate)* ( $PMMA$ ) which are denoted by  $P(S-b-MMA)$  are useful example which is frequently used in the experimental investigations. Furthermore, random copolymer molecules are assumed to cross the interface multiple times and might therefore reinforce the interface more efficiently than the corresponding block copolymers. Therefore, motivating recent

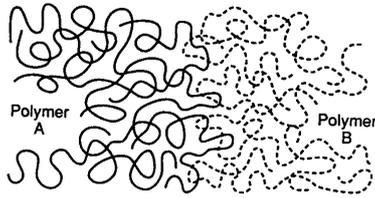


Figure 1.1.: A melt interface between immiscible homopolymers.

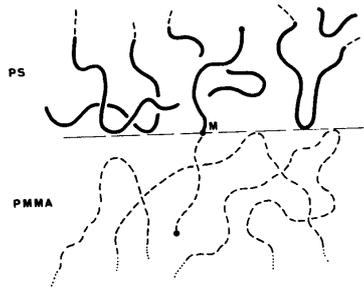


Figure 1.2.: Interface between two incompatible polymers, decorated by block copolymer molecules  $M$ .

studies of considering it as a possible compatibilizer like diblock copolymer [2]-[4].

Several attempts to develop a theory of copolymer adsorption have been made, and many experiments have been carried out. Yet, models which could make detailed predictions and extensive test of such predictions were still under consideration. The theoretical attempts have been addressed the problem of adsorption copolymers onto interface by different ways. Such as the self-consistent field theory, scaling concepts, and Monte Carlo methods. These theoretical studies are accompanied by numerous powerful experimental tools for probing the structural and dynamical properties of the polymer chains at interfaces: neutron reflection or scattering, forward recoil spectroscopy, and the sophisticated pulsed *NMR* spectrometers [5].

The most general theory to describe the multicomponent polymer interface has been developed using a diffusion equation approach [6]. This theory can be considered as the continuum version of the self-consistent model. The structure of polymer-polymer interface in the presence of a block copolymer can be modulated by this theory. Fig.(1.3a and b) show the interfacial structure for a diblock copolymer  $AB$  (*polystyrene – polybutadiene*) between concentrated homopolymer solution  $A$  and  $B$  (assumed to be of infinite chain length) in a common solvent (*styrene*). Diagram **a** gives the overall volume fraction profiles of the homopolymers and the individual blocks

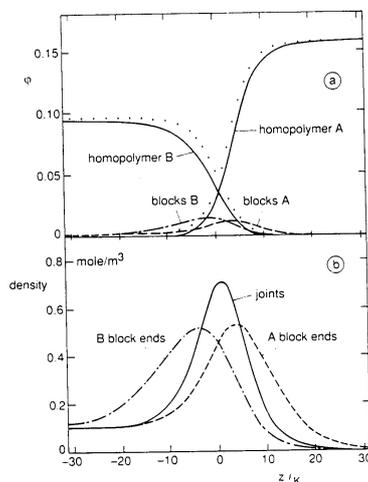


Figure 1.3.: Volume fraction profiles (a) and molar density distribution for the end segments and  $A - B$  connecting segments (b) for a block copolymer  $A_{200}B_{400}$  (representative for styrene-butadiene compatibilizer) at the interface between the respective homopolymer solutions in styrene.

of the copolymer; in **b** the normalized distributions of the  $AB$  joint and of the two end segments of the copolymer are plotted. A strong partitioning of the polymer into their respective homopolymer solution is associated, of course, with the reduction of the interfacial tension. Fig.(1.4) shows the result of an experimental neutron reflectometry study of a diblock copolymer of *poly(styrene)*,  $PS$ , and *poly(methylmethacrylate)*,  $PMMA$ , at  $P(S - b - MMA)$  interface. The results are in qualitative agreement with the theoretical figure (1.3a) which showing a strong partitioning of the two blocks into their respective homogeneous phases [7], [8].

The above mentioned polymer is the one in which completely free rotation is possible, and is often referred to as 'flexible' polymer. But completely free rotation is difficult in the case of some polymers, where the chain backbone is stiffer due to the obvious chemical structures. They are referred to as semiflexible or stiff chains depending upon the extent of their stiffness. Flexible polymer chains are often treated by the continuous chain model and semiflexible chains by wormlike chain (also known as Kratky-Porod) model. The behavior and the adsorption properties of such kind of polymers are totally different from that of the flexible polymers. The adsorption of such macromolecules at interfaces (*i.g.* liquid-liquid interface) is of major importance in a wide variety of relevant systems, ranging from food products to oil recovery. While the behavior of flexible polymer chains is described by an equation which depends only on the space coordinates, the behavior of the semiflexible polymer chain is different and obeys another differential equation which depends explicitly on the orientation and the space coordinates. This equation takes into account the stiffness of the polymer in describing its dynamics near surfaces

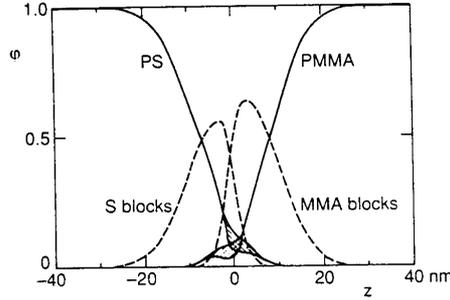


Figure 1.4.: Experimental volume fraction profiles for a diblock copolymer of polystyrene (*PS*) and polymethylmethacrylate (*PMMA*) at the *PS*–*PMMA* interface, obtained by neutron reflectometry.

or interfaces. For example, the adsorption of proteins on membranes. Another useful example is the nematic liquid–crystalline ordering of semiflexible polymer segments. Therefore, the problem of adsorption of the semiflexible polymers near surfaces and interfaces is affected directly by its stiffness. The key word of describing this stiffness is the persistence length  $l_p$ , which is the distance over which two successive tangent vectors of the semiflexible polymer chain are correlated. Many theories treated the problem of the adsorption of the semiflexible polymer chain. These theories were able to predict the adsorption properties of it in the limit of very large stiffness. In other word, the above mentioned models put  $l_p = 0$  and keep  $D_v$  constant in Fokker–Planck equation (see Eqs.2.3, and 2.11)), which may lead to incorrect adsorption properties of the semiflexible polymer onto the surfaces and/or interfaces [9], [10].

The thesis is organized as follows:

In the first part of chapter two a general review of the interfacial properties of the copolymer onto interfaces is presented. The theoretical and the experimental background of the problem is discussed in different types of polymeric systems such as the adsorption behavior of the copolymer in a blend of immiscible homopolymers. The second part of this chapter is devoted to discuss the adsorption properties of the semiflexible polymers at surfaces and interfaces. Different kinds of theories are presented and discussed for the scope of the thesis.

In chapter three, the problem of the adsorption properties of the diblock copolymer at penetrable interfaces will be presented. The interfacial properties of the diblock copolymer near an interface between two solvents are studied. In particular, the mean–square end–to–end distance of the copolymer, the density distribution, and the reduction of the interfacial tension due to the presence of the diblock copolymer are calculated. A simple scaling law for the reduction of the interfacial tension is derived.

The adsorption of a semi-flexible polymer chain onto a penetrable interface is studied in chapter four. The Fokker-Planck equation which describe correctly the conformational properties of the semiflexible polymers is used. It can be transformed to an integral equation of the Green's function of the polymer chain in an external potential. Several types of the interaction potentials are considered. The results show that the adsorption of semiflexible polymer is easier than the adsorption of flexible one.

Finally in chapter five, a discussion is given and in chapter six the conclusions.

## 2. Background and Review

### 2.1. Behavior of Copolymers at Interfaces

Adsorption of various types of polymers on regular [11], random surfaces [12], [13], and also on interfaces has been a subject of numerous experimental [14]-[17] and theoretical [18]-[27] investigations. This was primarily due to their importance in various practically useful cases such as gel permeation or size exclusion chromatography, and diffusion in porous media etc. There have been considerable interest in the problem of adsorption of copolymers onto interfaces owing to many practical applications, especially for increase compatibilizing properties of polymer blends. We will now discuss the effect of adding a copolymer chain to the interfaces. Of course, the properties of a polymer near an interface are different from the bulk properties.

Blending two or more polymers has proven to be a convenient method to improve and adjust the properties of the polymeric materials. Polymer blends usually have strong chemical incompatibility between the components, because of repulsive interactions. Most of the polymer mixtures are immiscible, so that the components separate into macroscopic domains, and the mechanical properties of such blends are poor. For such mixtures the bulk properties are strongly influenced by the interfacial properties between immiscible phases. Compatibilizer added to the interface of this immiscible phase affects the interfacial properties and enhances the mechanical properties of the blends. Due to strong incompatibility, the interfacial tension of the polymer mixtures is quite high. Moreover, the narrow interfacial width results in poor adhesion, because of the limited interpenetration across the interface. Therefore adding a compatibilizer to the such polymer systems can overcome these difficulties. Most experimental works use either block or grafted copolymer as compatibilizer. The practical importance of using them is that outstanding properties may be obtained by properly choosing the type and molecular weight of the polymer chain. When the diblock copolymer is added into the system, the entropy of mixing of the block copolymer with the homopolymer favors a random distribution of the copolymer in the bulk. The localization of copolymer at the interface, with the blocks extending into their respective homopolymer phases (*i.e.*,

block  $A$  in the homopolymer  $A$  phase and vice versa) not only minimizes the contacts between the unlike segments of the copolymer and the homopolymer but also displaces the two homopolymers away from the interface. This reduces the enthalpy of both the copolymer and the homopolymer in their own rich phase. The tendency to adsorb at the interface is balanced by the loss of the entropy of mixing and of the conformational entropy as the copolymer stretch into its appropriate volume, and therefore accommodate a greater areal density. Thus the adsorption at the interface competes with the creation of micelles in the bulk phases [18]. This maximally lower the interfacial tension of highly incompatible homopolymers thereby facilitating phase separations into ordered microstructure domains. This ordered microstructures are formed due to the topological constraint imposed by the  $A - B$  chemical block link, at low temperatures and/or high molecular weights. This chemical bonding between the pair of the blocks constraint them to remain within, roughly a radius of gyration  $R_g$  of each other. As the diblock copolymer works as a compatibilizer, the  $A$  block of the copolymers stick into  $A$ -rich phase, the  $B$  block of the copolymers stick into  $B$ -rich phase, while the junction point between  $A$  and  $B$  blocks are confined and the chains as a whole act as reinforcing rods. Such amphiphilic molecules are, of course, most likely to be found at the interface between  $A$  and  $B$  homopolymer phases. Recently, homopolymers and random copolymers were used as compatibilizer [5], [20].

There are several limitations associated with using the block copolymers as compatibilizer. Firstly, block copolymer are expensive in comparison with homopolymers or random copolymers. Secondly, if not applied directly to the interface, block copolymers have to diffuse to the interface and therefore their effectiveness can be limited by the kinetics. Also, at concentrations greater than the critical micelle concentration, block copolymers form micelles (when asymmetric diblock copolymers are added). Diblock copolymers with two incompatible block chains are known to form a variety of microphase-separated structure such as spheres, cylinders, lamellae, *etc.*, depending upon their intrinsic parameters. The characteristic parameters describing the diblock copolymer system are  $v$  the monomer volume,  $l$  the statistical segment length, the total numbers of monomer on the chain  $N = N_A + N_B$ , the number fraction of  $A$  monomers  $f = N_A/N$ , and the temperature ( $T$ ) dependent Flory–Huggins interaction parameter ( $\chi = a/T + b$ ). Theoretical as well as experimental works provide a description of the order disorder transition (*ODT*) as a function of  $\chi N$ . The micelles usually tend to segregate at the homopolymer-homopolymer interface which reduce the effective space for the compatibilizer rather than random distribution in the bulk of the homopolymer. In this case the micelles could compete with the interfacial region for the copolymer chains, and the amount in each state would depend on the relative reduction of the free energy, as well as the surface area [21]-[23].

The most important parameter characterizing the interface in immiscible polymer blends systems is the interfacial tension  $\gamma$ . This parameter is directly related to the free

energy of the polymer system. An especially favorable situation arises when the diblocks drive the interfacial tension to very small values or nearly to zero. However, the decrease of the interfacial tension is found to be limited by the micelle formation or the saturation of the interfacial region. It is well known that the localization of the surfactants at the water/oil interfaces can reduce the interfacial tension. Many previous studies have demonstrated that block copolymers play an analogous role when added to the interface. It is generally believed that this is a result of their ability to alter the interface between two immiscible liquids or homopolymer phases. Interfacial tension can be experimentally determined by using the automated pendant drop tensiometer. Measurement of this kind are performed to calculate the incompatibility between unlike monomers, and therefore determine the interaction strength of the polymer system. However, the various theories that relate the interfacial tension with the interaction parameter assuming infinite chain length, are not accurate. Real polymer samples are composed of finite chains and are polydisperse. Intuitively, we expect chains with different molecular weights will behave in different ways at the interface. In particular, there should be an excess of small chains at the interface because this is lower the interfacial tension [1], [24].

The incompatibility of the two species of the copolymer leads to remarkable microphase separation between the two blocks of the copolymer, and various microstructure, such as lamellae (when symmetric diblock copolymer added), and micelles. However this *ODT* is associated with the chain stretching. If we consider a copolymer chain at a solvent–solvent interface, assuming the first solvent to be hydrophilic, the other one to be hydrophobic, and the chain to be composed of both hydrophilic–hydrophobic segments. Such diblock copolymer exhibits stretching or elongation state, which is associated with the non-Gaussian behavior. The existence of the chain stretching is clear hint that the system exhibits a crossover from the weak segregation to the strong segregation regimes. In the weak segregation regime, where it is assumed that the chain is Gaussian coil, the structure is not affected by the parameter  $\chi N$ , in contrast, in the limit  $\chi N \rightarrow \infty$  (strong segregation regime) the coil is stretched. Such systems can be important in understanding the properties of the biological macromolecules like protein at penetrable interfaces [25],[26].

Studying the localization of the block segments near or away from the interface is important in determining the properties of the diblock copolymer. Theoretical attempts have been made to study the effect of adding diblock copolymer near interfaces. Leibler [27] investigated the nearly compatible mixture of two homopolymers *A* and *B* with the corresponding *AB* copolymer. For these systems, two mechanisms of the interfacial activity of the copolymer chains have to be distinguished: (*i*) there is mixing of the *A* and *B* segments since copolymer chains are present in both phases, and (*ii*) the copolymer chains have a tendency to locate at the interface. For miscible systems, the first mechanism dominates, whereas, for the highly incompatible case, the second is the dominant factor. Therefore, the mechanisms involved in the two different cases of highly

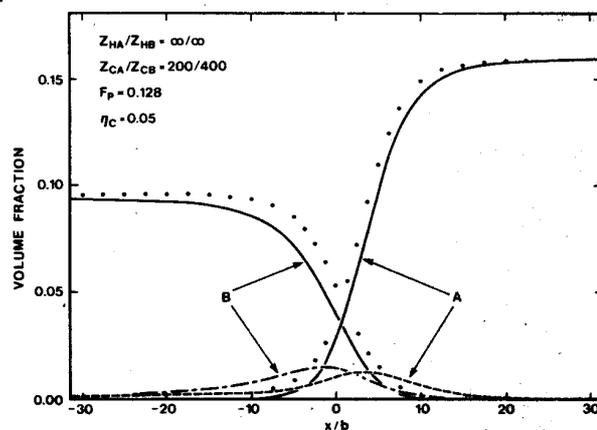


Figure 2.1.: Interfacial density profiles of styrene homopolymer (*A*, solid line), styrene blocks of copolymer (*B*, dashed line), butadiene homopolymer (*B*, solid line), and butadiene blocks of copolymers (*B*, dashed line). The dots correspond to the total volume fraction of the *A* and *B* components, respectively, and the length through the interphase is measured in the units of the average Kuhn length

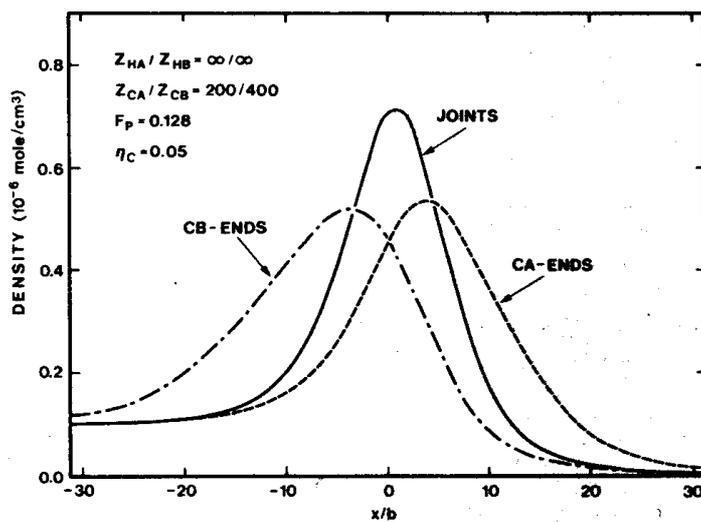


Figure 2.2.: Copolymer end and joint distribution functions for the interfacial profiles shown in Fig.(2.2)

immiscible systems compared to nearly compatible blends are quite different. In the first case, it is the surfactant activity of the block copolymer chains that causes the reduction in the interfacial tension. In the second case, the presence of copolymer molecules in the bulk homopolymer phases causes the compatibilizing behavior. Noolandi and Hong [28] used the general mean-field theory of inhomogeneous multicomponent polymer system, developed earlier by the same authors [6], to study the interfacial properties of the diblock copolymers in immiscible homopolymer blends. In this theory they model the experimental results of Riess *et al.* [29] on *polystyrene–polybutadiene–styrene* system. The interfacial density profiles are calculated (see Figs.(2.1), (2.2)). These calculations show that the greater exclusion of the homopolymers from the interfacial region appears as the molecular weight of the block copolymer is increased. The reduction of the interfacial tension as a function of the block copolymer concentration is calculated for a range of copolymer and homopolymer molecular weights, and is compared with the experimental results of Riess. Fig.(2.3) shows the main area of disagreement between the theory and experiment, where the interfacial tension falls to zero much faster than the measured values. This discrepancy can be explained in terms of the amount of the block copolymer used at the interface of the spinning drop, is much less than the calculated theoretically assuming complete thermodynamic equilibrium. Also an estimation of the critical concentration of the block copolymer required for micellar aggregation in the bulk of the homopolymer. In the above work Noolandi *et al.* set up and solve numerically the mean field equation for a system consisting of two highly incompatible homopolymers, with the associated diblock copolymer, diluted with a good solvent. On the other hand a more refined theory was developed by them in [30]. They have started by the functional integral representation of the partition function, then a statistical thermodynamic theory is derived. Mean–field equations for a system consisting of two immiscible homopolymers ( $A$  &  $B$ ), diluted with a solvent and with added diblock copolymer ( $AB$ ) were presented. Taking into account the detailed microscopic information about the interfacial region between the homopolymers. The importance of different terms in the free energy of the system are carefully analyzed. These equations are solved numerically. They found that the reduction in the interfacial tension,  $\Delta\gamma$ , with increasing copolymer molecular weight and the concentration arises mainly from the energetically preferred orientation of the blocks at the interface into their respective compatible homopolymers. The main term in  $\Delta\gamma$  is the entropy loss of the copolymer which localized at the interface. They found that the loss of the conformational entropy of both copolymers and homopolymers at the interface contributes very little to  $\Delta\gamma$ . Shull *et al.* [31] have treated a three component system of  $A$  homopolymer,  $B$  homopolymer, and an  $A–B$  diblock copolymer in the framework of the mean field theory. A complete set of self–consistent–field equations is solved numerically in order to determine the profiles of the different polymeric components and the interfacial tension. The results of the density profiles and interfacial tension give quantitative predictions, and avoid approximations typically associated with analytical calculations. These quantities are controlled by the homopolymer and copolymer degrees of polymerization, a Flory–Huggins  $\chi$  parameter describing the thermodynamic interactions between  $A$  and  $B$  segments, the statistical segment length, and the copolymer chemical potential. An

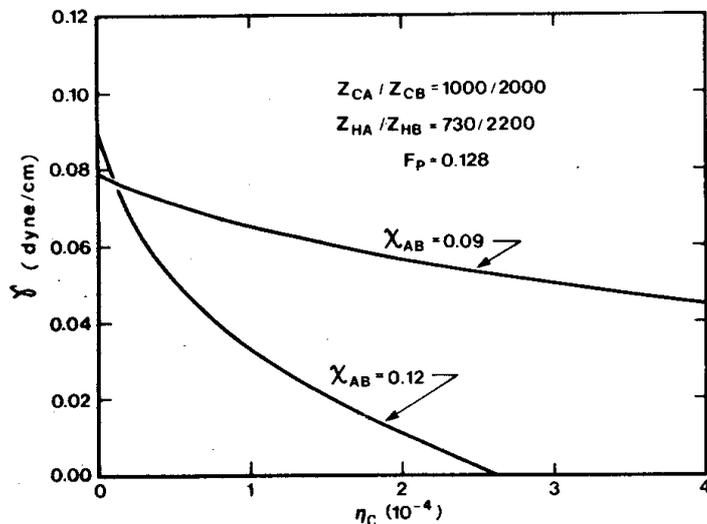


Figure 2.3.: Calculated interfacial tension for the phase-separated quaternary *PS – PBD – CopSBD – S* system with varying weight fraction  $\eta_c$  of block copolymer ( with respect to one of the two homopolymers, of equal weight in this case ) and two different values of  $\chi_{AB}$ .  $F_p$  gives the initial weight fraction of homopolymer, and  $Z_{CA}$  and  $Z_{CB}$  refer to the degrees of polymerization of the polystyrene and polybutadiene blocks of the copolymer, respectively. For  $\chi_{AB} = 0.12$  and  $\eta_c = 0$  the theoretical values of  $\gamma$  agrees with Riess measurement.

increase in the copolymer chemical potential is accompanied by an increase in the density of the copolymer chain and decrease in the interfacial tension (Fig.(2.4a, and b)). The interfacial tension tends to vanish (Fig.(2.5)) at reasonable values of the chemical potential and at the same time the volume fraction become close to one at the interface. The degree of polymerization of the longer copolymer block affects the interfacial properties and therefore the copolymer blocks extend away from the interface. Due to the constraint that the junction between the copolymer blocks must lie within narrow region near the interface, the width of the region over which *A* and *B* segments mix increases.

Sommer *et al.* [32] discussed copolymers of various structure at selective interfaces between two immiscible solvents using analytical calculations. They tried to answer questions connected with the architecture of the copolymer, the conditions necessary for adsorption, and the influence of the copolymer structure (random, strongly correlated, periodic) on the adsorption behavior of an ideal chain without excluded volume effects. The copolymer structure can be characterized by a structural correlation function  $\Phi(s)$ , which describes the monomer distribution along the chain. A copolymer chain made of

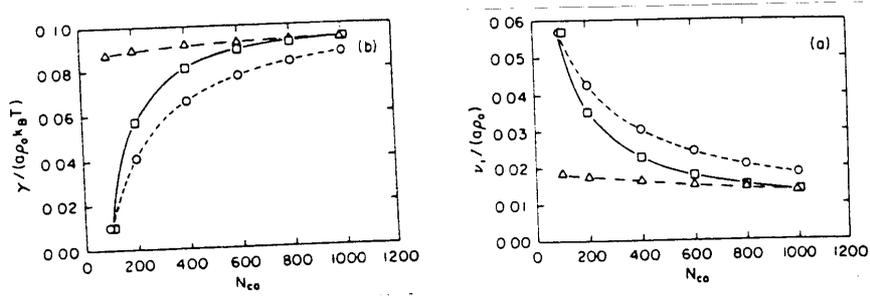


Figure 2.4.: A normalized interfacial excess (a) ( $\nu$ ) & interfacial tension (b) ( $\gamma$ ) of the copolymer as a function of  $N_{ca}$  for  $N_{ha} = N_{hb} = 1000$ ,  $\mu_c = 4k_B T$ , and  $\chi_{ab} = 0.1$ , with  $N_{cb} = N_{ca}$  ( $\square - - -$ ),  $N_{cb} = 100$  ( $\circ \cdot \cdot \cdot$ ), and  $N_{cb} = 1000$  ( $\Delta - \cdot -$ ).

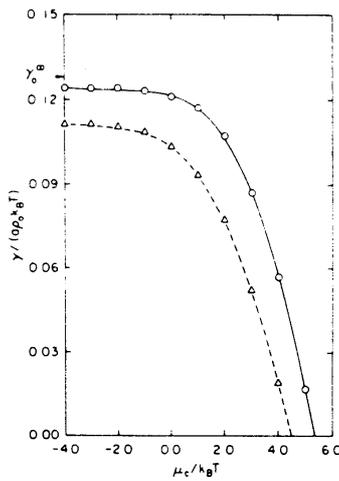


Figure 2.5.: Normalized interfacial tension as a function of  $\mu_c$  for  $N_{ca} = N_{cb} = 200$  and  $\chi = 0.1$ ;  $N_{ha} = N_{hb} = 1000$  ( $\circ - -$ ),  $N_{ha} = N_{hb} = 200$  ( $\Delta \cdot \cdot$ ).

a random or periodic succession of monomers  $A$  and  $B$ , which feeling a potential steps of height  $\chi_A$  with probability  $p_A$  and  $\chi_B$  with probability  $p_B = 1 - p_A$  respectively. In the case of random copolymer chain the adsorption is caused by the random excess of  $A$  and  $B$  monomers, while in the case of periodic chains the adsorption is mainly due to a weak orientation of  $AB$ - units crossing the interface. This means that the adsorption of the polymer chain at the interface is very sensitive to the architecture of the chain. The scaling theory as well as Imry–Ma–type argument used to predict a critical desorption temperature for asymmetric copolymer and/or interface. They found that desorption temperature  $T_c$  is different for both cases. Grosberg *et al.* [33] investigated the heterogeneity of polymer chains consisting of two types of links at selective oil–water interface. They did not take into account the excluded volume interactions in their calculations. They consider a chain of hydrophobic ( $A$ )–hydrophilic ( $B$ ) was character such that : the  $A$  links are repelled from the water into the oil whereas  $B$  links prefer to be located in the water. They studied the behavior of the free energy near the point of transition from a delocalized (Gaussian) to a localized (adsorbed) regime of periodic and annealed random sequence of links, and found that the transition is sensitive to the type of repulsive interaction of the links with the interface. The effect of the sequence distribution on the adsorption of the copolymer chains at liquid–liquid interface was analyzed in ref. [35]. Analytical arguments and molecular dynamics simulations are used. In particular  $AB$  polymers with sequence distribution characterized by  $0 < f < 1/2$  were examined. The chains were assumed to be Gaussian. They were able to determine the range of  $f$ 's for which the chain was highly localized. The localization occurs at a given set of solvent–polymer interaction energies and a fixed temperature. Both methods show the same trend, namely, the copolymer chains weave across the interface. For long block lengths, the different segments are segregated in their respective good solvents. The Monte Carlo simulations of self–avoiding polymers [36] have been employed to determine monomer distribution profiles, and surface excess for homopolymers and copolymers at solid-liquid and liquid-liquid interfaces in the dilute limit. Fig.(2.6) shows the monomer distribution profiles. The alternating copolymer requires a higher value of  $\chi$  (the energy increase associated with a monomer in an unfavorable environment) than the diblock to be bounded to the interface. The diblock monomer distributions have their maxima at 3-5 lattice units, while the alternating copolymer monomer distribution have their maxima adjacent to the interface, with approximately 70% of the monomer at this position. For the liquid–liquid interface the diblock polymer is predicted to be adsorbed at the interface more strongly than the alternating polymer, the opposite is found for the solid-liquid interface (see Fig.(2.7)).

Phenomena associated with polymer blends may also occur in polymer melts. Fried *et al.* [37] studied the stretching or elongating properties of symmetric diblock copolymer dense melts using Monte Carlo methods of the lattice model. The calculation were performed in three dimensional embedded space. A range of copolymer chain lengths, at different temperatures above the microphase separation transition have been studied. Their important result concerns with the existence of approximate scaling laws; with

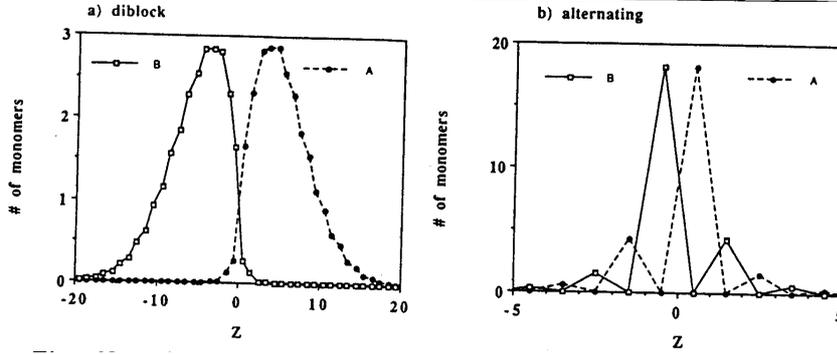


Figure 2.6.: Normalized distribution of  $A$  and  $B$  segments with respect to the liquid - liquid interface ( $Z = 0$ ) (a) for diblock copolymer ( $\chi = 1.0$ ) and (b) for alternating copolymer ( $\chi = 2.$ ).

$\varepsilon N$  as the scaling variable ( $\varepsilon$  being the monomer-monomer interaction energy). The most interesting result is that the radius of gyration scales with this quantity, which the Leibler theory [38] treat essentially as free parameter. The infinite temperature results were compared with the weak segregation theories. They found a quite good agreement with it, by establishing the expected Gaussian conformation of the copolymer chain. However, at finite temperatures, the copolymer exhibits non-Gaussian behavior, which differ from the predictions of the weak segregation theories. This non-Gaussian conformational behavior of the copolymers can be directly attributed to the stretching of the copolymers. This stretching represents a local segregation of the two monomer species composing the copolymer, which indicates that the polymer system exhibits a crossover from the weak to strong segregation regimes. The above study of Fried *et al.* extended to the asymmetric (composition  $f = 3/4$ ) case of a diblock copolymer melt in ref. [39]. The polymers are represented as a self-avoiding walks with different chain lengths. The results show that the gyration radius of the chains increases gradually by several percent (compared with the symmetric case), although the gyration radii of the individual blocks decrease slightly.

Sommer *et al.* [40] considered the random  $AB$ -copolymers at an asymmetric interface between two good solvents. Using the lattice version of the three dimensional bond fluctuation model. This model allows us to take into account the excluded volume effect, and to treat the dense polymeric systems. The simulation results predicted that the asymmetry of the interfacial potential gives rise an adsorption-desorption transition. Also the adsorption-desorption phase diagram shows that for infinitely long chains a critical point is exist. In the adsorption regime, the density profiles are sharply peaked around the interface. In contrast, in the nonadsorbed region, the polymer tends to be dissolved in the better solvent. When the interface is symmetric an infinitely long chain is always adsorbed, since the small entropy gain on the desorption is compensated at

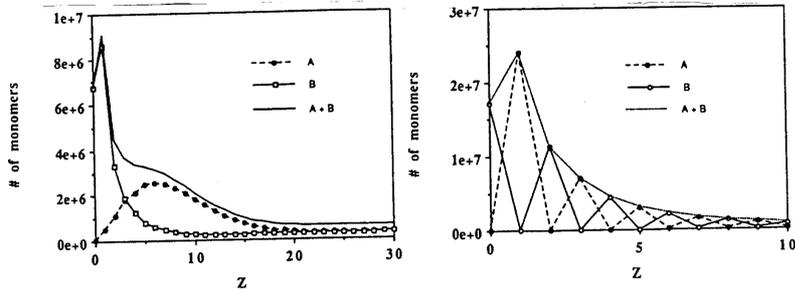


Figure 2.7.: Monomer distributions for a polymer with respect to the wall at  $Z = 0$  (a) for diblock copolymer  $\chi = 1.8$ , and (b) for alternating copolymer  $\chi = 1.6$ .

all temperatures by the very large gain in energy at the interface. On the other hand in the case of an interface asymmetry, the polymer desorbs if the temperature is larger than critical temperature  $T_c$ .

Motivated by constructing the compatibilizing activity of diblock and multiblock copolymers at interfaces Balazs *et al.* [41] examined the adsorption behavior of a single multiblock  $AB$  copolymer near penetrable interface between two immiscible fluids,  $A$  and  $B$ . They determined the values of  $\chi_{AB}$ , the interaction energy between the comonomer and the fluid, that were necessary to localize the chain at a fluid-fluid boundary and investigate the dependence of this value on the block length. The values of  $\chi_{AB}$  were sufficiently high that the chains are preferentially located at the interface. The findings on the multiblock and diblock copolymers can be summarized as follows. A low concentration of multiblock copolymers, where each block is relatively short, will provide a better interfacial coverage than the comparable volume fraction of diblock copolymers. Thus, these multiblock copolymers are more efficient in reducing the interfacial tension. However, a high concentration of diblock copolymer can provide high interfacial coverage, and the advantage of the interpenetration of the blocks into the favored phase. The latter property will enhance the adhesion between the two components of the polymeric system.

The model presented by Tang *et al.* [42] of diblock copolymer chain stretching in the disordered state obtained by separating  $A$  and  $B$  block of the corresponding  $A - B$  binary blend. The model assumes that correlations within each block remain Gaussian as the blocks segregate. The phase separation would occur for  $\chi N > (\chi N)_c = [f^{1/2} + (1 - f)^{1/2}]$ . However, the experiment of Hadziioannou *et al.* [43] provides a description of this microphase separation in which the  $ODT$  occurs at  $\chi N = (\chi N)_t$ . This experiment displays a chain stretching for  $\chi N < (\chi N)_t$ , where the individual

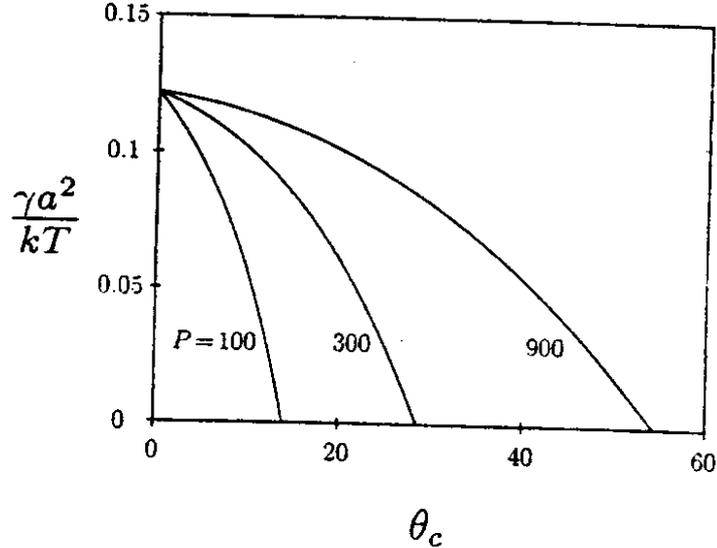


Figure 2.8.: The interfacial tension of an A/B interface as a function of the amount of copolymer adsorbed at this interface. Parameters:  $\chi = 0.1$ ,  $N = 300$

chains are assumed to be Gaussian. The connection between the two blocks stabilizes the homogenous diblock copolymer phase. Spatially neighboring  $A$  and  $B$  monomers cannot discern whether they belong to the same or different block, unless they both located near the junction bond on the same chain. When  $\chi N > (\chi N)_c$ , monomers of different species are forced to segregate, and the chain stretching occurs. The stretched diblock copolymer chain develop a preferred spatial direction for the vector connecting the centers of mass of the two blocks.

A two-dimensional self-consistent field theory, which determines the interfacial behavior of symmetric  $AB$  diblock copolymer at the boundary between immiscible homopolymers  $A$  and  $B$ , is presented in ref. [44]. Their results reveal that when the blocks in the diblock are longer than the corresponding homopolymer, the symmetric  $AB$  diblocks can drive the interfacial tension to zero (see Fig.(2.8)). Also, the self-consistent calculations reveal that shorter diblocks form lamellar structure in the blend, whereas a microemulsion is formed when relatively long copolymers are added to the system. The above observations were compared with experimental measurements on blends of *polystyrene* ( $PS$ ), *polymethyl methacrylate* ( $PMMA$ ), and  $PS - PMMA$  symmetric diblock copolymers. The decrease in interfacial tension caused by adding diblock copolymer is determined via measurement of the microcontact angle. The experimental predictions confirm that the interfacial tension can be reduced to a very small values through the addition of diblocks whose block lengths are greater than the length of the homopolymer. The experimental work of Genzer *et al.* [45] of a three-component, two-phase

$A/B : C$ , (where  $B$  and  $C$  were miscible with each other but not with  $A$ ) blend are investigated to understand the effect of the  $A$  and  $B$  length on the interfacial excess of  $B$ ,  $z_B^*$ , the interfacial tension,  $\gamma_{ABC}$ , and the interfacial width,  $w_{ABC}$ . The model is designed to be a direct test of the *SCF* methods. The  $A/B : C$  components are *polystyrene/poly( $d_8$ -styrene-co-4-bromostyrene)* : *poly(styrene-co-4-bromostyrene)*. The Low-energy forward recoil spectrometry (*LE-FRES*) is used to measure  $z_B^*$  as a function of the  $B$  volume fraction in the  $B : C$  blend,  $\phi_B$  (see Fig.(2.9)). Because the  $A-B$  segmental interactions were less unfavorable than  $A-C$  ones,  $B$  was preferentially attracted to the  $A/B : C$  interface. As  $\phi_B$  increases,  $z_B^*$  increases initially, reaches a maximum, and then decreases. At a given  $\phi_B$ , the  $z_B^*$  was found to be larger for larger values  $N_B$ . However,  $z_B^*$  was relatively insensitive to  $N_A$ (see Fig.(2.10)). The experimental values of  $z_B^*$  were found to be in excellent agreement with those calculated using *SCF* method. In addition, the *SCF* model was used to evaluate the interfacial tension  $\gamma_{ABC}$ . It was found that at low  $\phi_B$ ,  $\gamma_{ABC}$  rapidly decreases with the increases of  $z_B^*$ . The application of a modified pendant drop method used by Hu *et al.* [46] to measure the effect of adding diblock copolymer on the interfacial tension of immiscible homopolymer blends. They used a binary homopolymer blend *PS4K/PDMS4.5K* and nearly symmetric diblock copolymer *P(S-b-DMS)* ( $f = N_{ps}/N = 0.42$ ). They found that the interfacial tension of the blend is initially decreasing with increasing the copolymer concentration, and then attains a constant value above a certain critical concentration. They attributed their result due to a localization of copolymer at interface. When the copolymer was blended with *PDMS*, the amount of reduction increases with increasing molecular weight, which drives the copolymer chain to the interface. This is associated with the reduced entropy of mixing for higher molecular weight of the host. A maximum interfacial tension reduction was achieved at a critical concentration of 0.002% diblock copolymer. On the other hand, when the copolymer is mixed with the *PS* phase, the amount of the reduction of interfacial tension is much less than the reduction when it is blended with *PDMS* phase. This indicated that the degree of the reduction of interfacial tension depends on the sample preparation procedure. Also the experiment of Anastasiadis *et al.* [47] has shown that only small amounts (*e.g.*, percent or less) of block copolymer can considerably reduce the interfacial tension by 80 – 90%. Russell *et al.* [48] who studied the segment density distribution of symmetric diblock copolymer at interfaces between two homopolymers by Neutron Reflectivity. In the case of *poly(styrene)* *PS* and *poly(methylmethacrylate)* *PMMA* homopolymers with the corresponding diblock copolymers, it was found that the addition of the copolymer to the interface between the *PS* and *PMMA* homopolymers significantly broaden the interface between them. Also it has been shown that the diblock copolymers are located at the interface between the homopolymers, and the *PS* segments of the copolymer chain were located in the *PS* rich phase, and the *PMMA* segments of the copolymer chain were located in the *PMMA* rich phase. It was also found that the junction points of the copolymer were localized to a region around the interface. As a final comment on the adsorption of the random copolymer, recently Stepanow *et al.* [49] considered the problem of adsorption of a random copolymer coil at interfaces. They introduced a novel variational principle for

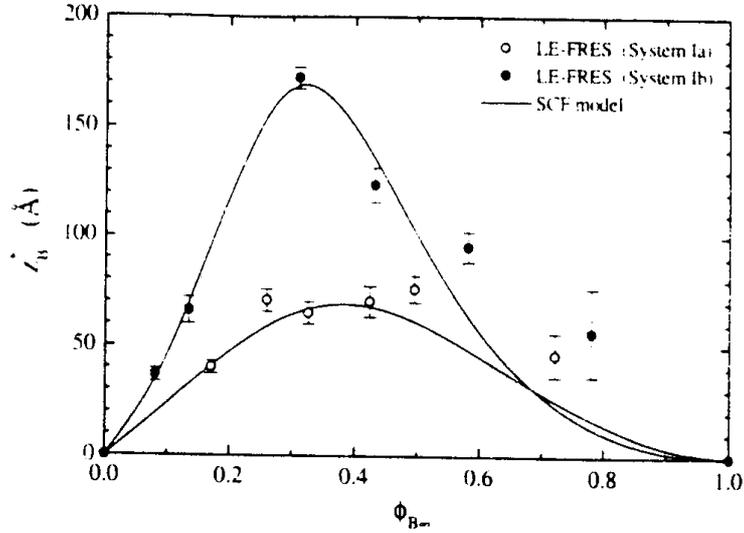


Figure 2.9.: Interfacial excess of  $B1$  ( open circles ) and  $B2$  ( closed circles ),  $z_B$ , for a system of  $Ia$  and  $Ib$  as a function of the bulk volume fraction,  $\phi_B$ ,  $z_B$  is measured by  $LE - FRES$  and samples are annealed for 30 days at  $181\text{ C}$ . The solid lines are the result obtained from the  $SCF$  model.

the Green's function. This technique is generalization of the well-known Rayleigh-Ritz method of Quantum Mechanics to nonstationary states. Using appropriate trial Green's function and minimization procedure, they were able to find the phase diagram for the localization-delocalization transition for the ideal random copolymer at interfaces.

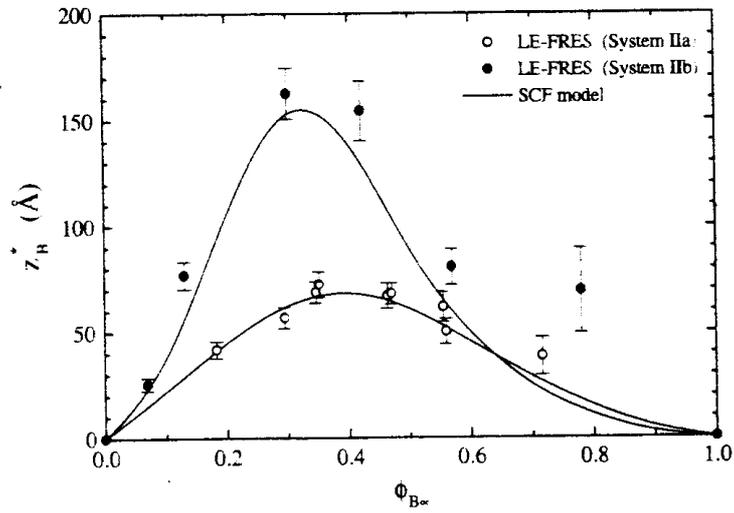


Figure 2.10.: Interfacial excess of  $B1$  ( open circles ) and  $B2$  ( closed circles ),  $z_B$ , for a system of  $Ia$  and  $Ib$  as a function of the bulk volume fraction,  $\phi_B$ ,  $z_B$  is measured by  $LE - FRES$  and samples are annealed for 30 days at  $181\text{ C}$ . The solid lines are the result obtained from the  $SCF$  model.

## 2.2. Behavior of Semiflexible polymers at Interfaces

Many polymeric materials are flexible, and are well modeled by the random walk model for neutral polymers. It is known that the long flexible chains take a random coil structure, which can be viewed as a Brownian curve. However, there is a large class of polymers which are not flexible and assume a considerable stiffness in their structure. These class of polymeric molecules are called semiflexible or stiff chains. For such polymers the angles between segments are not uncorrected, as in the case for flexible chains, but exhibit nonvanishing spatial correlations [50], [51].

A simple way to account for the stiffness of a semiflexible chain is to constrain the angles between two successive segments  $\theta$  to be fixed. The value of  $\theta$  depends on the local stiffness of the chain. This prescription leads to the freely rotating chain model. If we describe the configurations of a polymer chain by the set of position vectors  $\{\mathbf{r}_N\} = (\mathbf{r}_0, \dots, \mathbf{r}_N)$ , then the spatial correlation,  $\langle \Delta\mathbf{r}_n \cdot \Delta\mathbf{r}_{n-1} \rangle$ , in the freely rotating chain has the value  $a^2 \cos \theta$ . In the continuous limit ( $a \rightarrow 0, \theta \rightarrow \infty, Na = L$ ) the freely rotating chain becomes the so-called wormlike chain. In this case, the ratio  $2a/\theta^2$  defines the persistence length  $l_p$ , which is the typical length scale over which the chain changes its direction appreciably. In contrast to flexible polymers the persistence length of these polymers is of the same order of magnitude as their total contour length [52]. In the following, a discussion of the famous semiflexible models will be presented.

The simple and the most famous wormlike or Kratky-Porod model, introduced to account for the chain stiffness, assumes that the tangent vector  $\mathbf{t}(s) = \partial\mathbf{r}(s)/\partial s$  is fixed, where  $\mathbf{r}(s)$  is parameterized in terms of the arc length  $s$ . The adopted constraint of the semiflexible polymer chain is,  $|\mathbf{t}(s)| = 1$ . The statistical properties of the wormlike chain are determined by a free energy functional ( or the "Hamiltonian"),

$$H = \int_0^L ds \frac{\kappa}{2} \left( \frac{\partial\mathbf{t}(s)}{\partial s} \right)^2, \quad (2.1)$$

where  $L$  is the total length of the semiflexible chain, and  $\kappa$  is the dimensionless bending modulus which is proportional to the persistence length  $l_p$ .

This model predicts the tangent-tangent correlation function  $\langle \mathbf{t}(s)\mathbf{t}(s') \rangle$ , to decay exponentially as  $\exp(-|s - s'|/l_p)$ . This quantity characterizes the properties of a

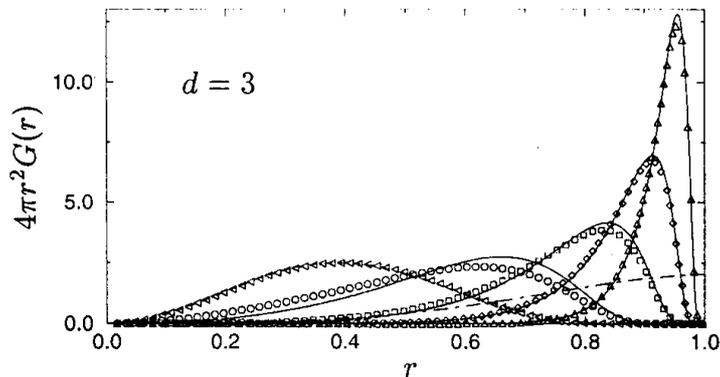


Figure 2.11.: Comparison of  $G(r)$  from Monte Carlo simulation ( symbols ) for  $t = 10, 5, 2, 1,$  and  $0.5$  ( left to right ) to analytical result ( solid lines ). For  $t = 10$  it almost coincide with the numerical data while it is quit far off for  $t = 2$ .

semiflexible chain. Thus the statistical properties of the semiflexible chain beyond the length scale  $l_p$  reduces to those of flexible chain, *i.e.*, one can view the stiff chain as being made up of several rigid segments of length  $l_p$  which are freely joined. One of the most important mathematical quantities, which can be calculated exactly using this model is the mean-square end-to-end distance  $\langle R^2 \rangle$  as

$$\langle R^2 \rangle = 2l_p^2(e^{-L/l_p} - 1 + L/l_p) = \begin{cases} L^2 & \text{for } L/l_p \rightarrow 0 \text{ (rigid rod)} \\ 2l_p L & \text{for } L/l_p \rightarrow \infty \text{ (radom coil)} \end{cases} \quad (2.2)$$

The former quantity shows clearly that the chain is locally rigid, while, the latter is a typical characteristic of the Brownian behavior. These properties of the semiflexible or stiff chains plays an important role in synthetic polymers as well as biopolymers (*i.e.*, *actin* filaments). Thus, when the concentration of the stiff polymers becomes sufficiently high, stiff polymers spontaneously orient towards some direction, and form a liquid crystalline phase [53].

When the total contour length  $L$  of a polymer chain is comparable with the persistence length (*i.e.*, semiflexible polymer), the probability distribution function  $G(R; L)$ , deviates strongly from the Gaussian shape found for the flexible polymers. For example, many of biologically important macromolecules show this property. The non-Gaussian

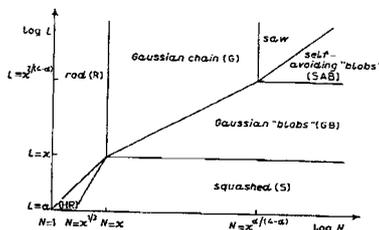


Figure 2.12.: Different regimes for a *SFC* constrained between two walls for  $2 < d < 4$ . Note that transition between regimes are not sharp; continuous crossovers occur in the vicinities of the lines indicated.

behavior of such biopolymers, stems from their intrinsic properties of having a wide range of stiffness, *e.g.*,  $l_p \approx 10 \text{ nm}$  for spectrin,  $l_p \approx 10 \text{ nm}$  for *DNA*,  $l_p \approx 17 \text{ }\mu\text{m}$  for *actin*, and  $l_p \approx 17 \text{ mm}$  for *microtubules* [54], [62].

Old as well as recent attempts tried to study the conformational properties of various models for the stiff chain molecules. Among them, the wormlike chain model of Kratky and Porod retained a valid place for many years. Although, it cannot mimic exactly the dimensional behavior of real chains, it does often offered a rather good approximation [55]. An explicit solution for the probability distribution function describing both the position and the unit tangent vector at the endpoint of a continuous wormlike chain is obtained in a form of corrections to the Gaussian distribution function up to  $t^{-2}$ , where  $t$  is the ratio of the total contour length to the statistical segment length [56]. However, the same probability distribution function was derived taking into account the excluded volume effect by Yamakawa *et al.* [57]. In order to derive the mean-square end-to-end distance for the stiff chains, a suitable extrapolations from the coil region to the high-stiffness are made. On the other hand Yamakawa *et al.* [58] used the path integral method and *WKB* approximation to derive asymptotic forms of the distribution functions for two and three dimensional continuous wormlike chains near the rod limit. They found the asymptotic solution for these distribution functions gives the correct first-order correction to the rod limit. A more satisfactory work which describes the behavior of the semiflexible polymer chain was proposed by S. Stepanow [59]. In this article he proposed a model for semiflexible polymers based on the extension of the analogy between the theory of the Brownian motion and the polymer statistics. The starting point was the Kramers equation (Fokker-Planck equation with inertia) which possesses a ballistic regime for small time [60] (or see the text book [61]). The probability density  $w(\mathbf{r}, \mathbf{v}, t)$  obeys the equation

$$\frac{\partial w(\mathbf{r}, \mathbf{v}, t)}{\partial t} = \frac{\partial}{\partial \mathbf{v}} (\gamma \mathbf{v} w + D_v \frac{\partial}{\partial \mathbf{v}} w) - \mathbf{v} \frac{\partial}{\partial \mathbf{r}} w, \quad (2.3)$$

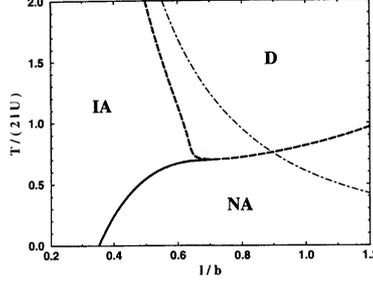


Figure 2.13.: The phase diagram obtained by the Green's function first-order perturbation theory. The region ( $D$ ) corresponds to the desorbed phase, the region ( $IA$ ) and ( $NA$ ) are the isotropic and nematic-type adsorbed phases. The solid and dashed lines correspond to the first- and second-order phase transitions, respectively. The dot-dashed line describes adsorption-desorption boundary in the zeroth-order perturbation theory, *i.e.*, the Edwards equation for flexible polymers

where  $\mathbf{v}$  is velocity,  $\mathbf{r}$  denotes the position of the particle,  $D_v = \gamma k T m^{-1}$  is the diffusion coefficient in the velocity space,  $\gamma$  is the friction coefficient, and  $m$  is the mass of the particle. The transition probability  $P(\mathbf{r}, \mathbf{v}, t; \mathbf{r}_0, \mathbf{v}_0, 0)$  from the point  $\mathbf{r}, \mathbf{v}$  at time  $t$  to the point  $\mathbf{r}_0, \mathbf{v}_0$  is obtained as a solution of Eq.(2.3) as

$$\begin{aligned}
P_0(\mathbf{r}, \mathbf{v}, t; \mathbf{r}_0, \mathbf{v}_0, 0) = & \left( \frac{1}{2\pi [1 - \exp(-2t/l_p)]} \right)^{d/2} \\
& \left( \frac{1}{4\pi/l_p^2 t/l_p - 2 + t/l_p \exp(-t/l_p) + 2 \exp(-t/l_p)} \frac{1 + \exp(-t/l_p)}{1 + \exp(-t/l_p)} \right)^{d/2} \\
& \times \exp \left[ -\frac{1}{2 [1 - \exp(-2t/l_p)]} [\mathbf{v} - \mathbf{v}_0 \exp(-t/l_p)]^2 \right. \\
& \left. - \frac{1}{4/l_p^2 t/l_p - 2 + t/l_p \exp(-t/l_p) + 2 \exp(-t/l_p)} \right. \\
& \left. \left( \mathbf{r} - \mathbf{r}_0 + l_p \frac{1 - \exp(-t/l_p)}{1 + \exp(-t/l_p)} (\mathbf{v} + \mathbf{v}_0) \right)^2 \right] \quad (2.4)
\end{aligned}$$

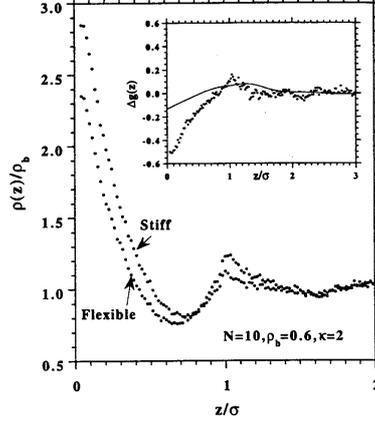


Figure 2.14.: Simulation results for the density profiles (normalized to the bulk density) of stiff and flexible chains in the blend for  $N = 10$ ,  $\kappa = 2$ . The inset shows the difference between the density profiles for the flexible and stiff components.

The correlation function of the velocity is obtained using Eq.(2.4) and performing the average over  $v_0$  by using the Maxwell distribution,  $P(v) \sim \exp(-d/2v_0)$ , as

$$\langle v(t_2)v(t_1) \rangle = \frac{dD_v}{\gamma} \exp(-\gamma|t_2 - t_1|), \quad (2.5)$$

where  $t_1, t_2 \in (0, t)$ . The latter can be used to compute the correlation function

$\langle [\mathbf{r}(t_2) - \mathbf{r}(t_1)]^2 \rangle$ . The result is

$$\langle [\mathbf{r}(t_2) - \mathbf{r}(t_1)]^2 \rangle = \frac{dD_v}{\gamma} \frac{2}{\gamma} \left( |t_2 - t_1| + \frac{1}{\gamma} \exp(-\gamma|t_2 - t_1|) - \frac{1}{\gamma} \right). \quad (2.6)$$

Kramers equation can describe the polymer chain, if we fix  $D_v$  according to  $dD_v/\gamma = dk/m = 1$ . The time  $t$  will be identified with the coordinate  $s$  along the contour of the polymer chain. Equations (2.5, 2.6) expressed in terms of the polymer quantities as

$$\langle v(s + s_0)v(s_0) \rangle = \exp(-s/l_p), \quad (2.7)$$

$$\langle [\mathbf{r}(s + s_0) - \mathbf{r}(s_0)]^2 \rangle = 2l_p (s + l_p \exp(-s/l_p) - l_p). \quad (2.8)$$

In this model the tangent of the polymer chain is fluctuates with the mean square value  $\langle \mathbf{v}^2 \rangle = 1$ , but Equations (2.7, 2.8) coincide exactly with the results of Kratky–Porod model [50].

In a recent work by Wilhelm and Frey [62] the radial distribution function  $G(r)$  of a semiflexible polymers in two– and three– dimensional embedding space valid for small  $t$  has been calculated. They have calculated these distribution functions by two technique, analytical and Monte Carlo simulations. The analytical expressions were calculated adopting the continuum version of the wormlike chain model. They found that the radial distribution function in three dimensional space has the form

$$G(r) \frac{2\kappa}{4\pi N} \sum_{l=1}^{\infty} \pi^2 l^2 (-1)^{l+1} e^{-\kappa\pi^2(1-r)} \quad (2.9)$$

where  $N$  is a normalization factor, and  $\kappa$  is the bending factor, which is related to the persistence length by  $l_p = \kappa/k_B T$ . Fig.(2.11) shows a comparison between the analytical one with the numerical results obtained from Monte Carlo simulations. The agreement is very good for  $t = L/l_p < 2$ . It shows a strong deviation from the Gaussian shape found for the flexible polymers.

Maggs *et al.* [63] considered a model for a semiflexible chain adsorbed on a wall by a constant external field  $h$  or a short-range surface potential  $V_s$ . A simple model describing a semiflexible chain consisting of  $N$  monomers of size  $a = 1$  in the potential  $V(r)$  can be introduced through the Hamiltonian

$$\beta H = \sum_i \beta v(\mathbf{r}_i) - \kappa \sum_i n_i \cdot n_{i-1}, \quad (2.10)$$

where the vector  $n_i = r_{i+1} - r_i$ ,  $\beta = 1/(k_b T)$ , and  $\kappa$  plays the role of the persistence length. They have studied such a semiflexible chain in two different situations, which both leading to unbinding (or delocalization) transitions. In the first case the chain held against a wall by an external potential  $V(z) = hz$ . Then the unbinding transition occurs as the field is reduced. Therefore when  $h \rightarrow 0 : \langle z \rangle \sim h^{-\lambda}$ , where  $z$  is the distance from the wall,  $\lambda$  is the unbinding exponent, and the brackets denote the thermal average. In the particular case of a semiflexible in a constrained geometry. They found three different values of  $\lambda$  depending on the type of the external potential. In the second situation which they considered a semiflexible chain is adsorbed on a wall by an attractive, short-ranged surface potential  $V_s$ . They found that a continuous unbinding transition undergoes by

the system. The results obtained above have been confirmed by the Flory–de Gennes type of arguments [18], and also by the numerical simulations (see Fig.(2.12)). Moreover they have used the Fokker–Planck equation [64], [65] in the limit of  $\kappa \rightarrow \infty$ , which can be written as

$$\frac{\partial f_l}{\partial l} = \frac{1}{2\kappa} \frac{\partial^2 f_l}{\partial v^2} - v \frac{\partial f_l}{\partial z} - \beta V(z) f_l, \quad (2.11)$$

where  $f_l$  is the Boltzmann weight of a semiflexible chain with  $l$  monomers,  $z$  is the position of the monomer, and  $v$  is the velocity. The mean difference between Eq.(2.3) and Eq.(2.11) is that the term linear in  $\partial/\partial \mathbf{v}$  is absent in Eq.(2.11). The models [63], [66] described by Eq.(2.11) can be obtained easily from Eq.(2.3) by putting  $\gamma = 0$  (or alternatively  $l_p^{-1} = 0$ ) and keeping  $D_v$  constant. The scaling arguments were used by imposing the constraints that the semiflexible chain does not cross the wall. From the scaling form of Boltzmann weight  $f_l(z, v)$  they demonstrated that, for a finite  $\kappa$ , a first order continuous unbinding transition can occur. To conclude, they have studied the unbinding transition of the semiflexible chain adsorbed on a wall by various analytical and numerical methods. When the amplitude of  $h$  or  $v$  decreases the system undergoes an unbinding transition. On the other hand, in the case of an attractive  $V_s$  a discontinuity in the unbinding transition occurs at a very rigid chains. The same problem of a semiflexible model is addressed and studied by Burkhardt [66]. In this model Burkhardt proposed a simple continuum model of a linear semiflexible polymer chain with non-zero bending energy. The polymer constraint to be in the half plane  $x > 0$ . The potential energy was taken to be short–ranged. This enables him to obtain complete and exact analytical solution of the problem. The adsorption or pinning transition of an infinitely long polymer is determined by the statistical weight  $Z(x, v; x_0, v_0; t)$ , which satisfies Eq.(2.11). Within the framework of necklace model [67]. The polymer is built up of segments (beads) that leave the boundary with zero slope and return to the boundary with zero slope. The mean result of his work is that, there exist binding–unbinding phase transition, and the polymer chain adsorption is first order. On the other hand Burkhardt [68] studied the free energy of a semiflexible polymer chain confined strongly along an axis. A continuum model of a fluctuating semiflexible polymer chain based on the differential equation (2.11) is adopted. In general, the equation is difficult to solve in a bound geometry due to the correlation between  $r$  and  $v$  coming from the second term. The free energy of the polymer chain can be optimize approximately by the extremum principle. In the case of a harmonic potential  $V(r) = \frac{1}{2}br^2$ , an exact as well as an approximate solution of the ground state energy of the polymer chain are found to be equal. Therefore, the lower bound for the confinement free energy of a polymer in a tube is obtained. Recently the same author [69] obtained the confinement free energy per unit length  $\Delta f$  of a continuous semiflexible polymer or wormlike chain in a tube with rectangular cross section. The mean result of this letter was,

$$\Delta f = A \frac{k_b T}{l_p^{1/3}} (L_1^{-2/3} + L_2^{-2/3}) , \quad (2.12)$$

where  $A$  is a universal constant,  $l_p$  is the persistence length, and  $L_1$  and  $L_2$  are the sides of the rectangle. The universal amplitude  $A = 1.1036$  is determined exactly by one dimensional integral equation.

In a letter by Morse *et al.* [70], the self-consistent-field theory has been used to analyze a symmetric interface between two immiscible, semiflexible polymers. Their starting point, was the wormlike chain model, since this model is capable in interpolating between Gaussian chains and rigid rods. In the limit of a very large rigidity, they obtained a very narrow region of polymer interpenetration, a universal form for the orientational distribution outside of this region, and a simple limiting form of the interfacial tension. Their finding of the density profile of the semiflexible polymer chain near a sharp wall is associated with a divergency. For finite interfacial tension, this singular behavior is cut off by a nonzero width of the density interface. This behavior can be understood by noting that a typical polymer approaching such an interface is forced to change its orientation over a distance of order of its persistence length  $l_p$ . An approximate scheme in the framework of the Green's function formalism of the semiflexible and wormlike polymers, which treats the polymer stiffness and persistence systematically, developed in ref.[71]. They have analyzed the phase diagram and the transition behavior near attractive surfaces. The results show novel features in adsorption-desorption transitions coupled with types of isotropic to nematic ordering transitions (see Fig.(2.13)). They also found that their scaling theory of semiflexible polymers near attracting surfaces, has given a qualitative picture of the various polymer phases, *i.e.*, the desorbed phase, the adsorbed phases with isotropic and nematic-type segmental distributions, and their transition that occur as competition between the thermal fluctuations, surface interaction, and chain stiffness [72]. More recently the same authors [73] considered a homogeneous semiflexible polymers with a persistence length  $l_p$  much smaller than the contour length  $L$ , near attractive surface. They also neglected intersegmental interactions (including the *excluded volume interactions*) other than that incorporated in chain connectivity. The interaction between the monomers along the polymer chain and the surface were characterized by the range  $b$  and the depth  $U$ . The scaling theory as well as the Green's function perturbation theory for semiflexible polymers shown that the polymer chain can exhibit a adsorption-desorption transition. They attributed this result as an outcome of the competition between surface attraction, thermal fluctuation, and the chain stiffness.

The self-consistence-field theory model for the adsorption of the semiflexible chains in a cubic lattice is presented by Fler *et al.* [74]. The theory presented here is appli-

cable for molecules that have rigid and flexible blocks. In a sense, these molecules can be considered to be block copolymers, although the blocks do not differ in mixing or adsorption energy. Thus, the entropic effects of the surface segregation of the block copolymer can be investigated. Using this model they were able to model copolymer chains where parts of the chains are stiffer than the other parts (stiff–flexible copolymer). They found that block copolymers with blocks that differ only in rigidity of the blocks adsorb with more stiffer block on the surface. This adsorption on the surface is purely entropic. This effect is the same order of magnitude as energetic interactions, so that neglecting rigidity differences between blocks seems unjustified. Also they found that for homopolymers, the model reproduces the results of Birshstein *et al.* [54] regarding the dependence of the critical adsorption energy on the rigidity. Although the radius of gyration for a stiff polymer in a dilute solution can be rescaled to a flexible polymer by increasing the step length, this procedure does not work for the adsorption profile of a polymer adsorbing from a dilute solution. The fundamental reason for this is that the characteristic ratio is not conserved in rescaling attempts. The characteristic ratio is apparently important in a lattice-based description of polymer adsorption. Confirming the previous studies, almost similar study by Yethiraj *et al.* [75] found that in polymer blends containing stiff and flexible molecules stiffer molecules segregate to the surface (see Fig.(2.14)). In this paper, they investigated the behavior of a binary athermal blend near a solid, non-interacting surface where one component is stiffer than the other. This athermal system was chosen in order to isolate the effects of entropic factors on surface segregation. The results from Monte Carlo simulations and integral equation calculations, both suggest that the stiff chains are always present in excess in the immediate vicinity of the surface. The net surface excess, however, displays an interesting density dependence. At low densities the net surface excess favors the flexible chains at the surface. They could reconcile these theoretical findings with recent experiments [76], [77] by suggesting that enthalpic interactions are the dominant physical effect. At liquidlike or meltlike densities, however, the net surface excess favors the stiff chains at the surface. This is purely entropic effect : the stiffer polymers lose less entropy when adsorbing than flexible ones. The adsorption of a single semiflexible polymer chain with excluded volume interaction near an impenetrable attractive flat solid surface has been investigated by Molecular Dynamics simulations in [78]. They apply Molecular Dynamic simulations to the adsorption problem of polymer chains of variable degree of rigidity. This method allows them to explore the static properties of the polymer chain. In particular, it allows an independent estimation of the scaling exponents and test the universality of the adsorption transition. It enables them to study the behavior of the chain, not only near the transition point but in the highly adsorbed state. Furthermore, they simulate chains with various stiffness to find how this internal property of a chain influences its adsorption. The adsorption of a single semiflexible polymer chain with excluded volume interaction near an impenetrable attractive flat solid surface has been investigated. They also investigated the influence of the chain stiffness on the morphology of the adsorbed chain, such as average length of loop, monomer density profiles, and segment orientation. In addition, scaling law of the adsorption degree and radius of gyration is obtained. They investigated the influence of the chain stiffness on the

adsorption. Chains with variable stiffness have been studied in details. They concluded that stiffer chains adsorb more easily onto attractive impenetrable wall. On the other hand Burkhardt *et al.* [79] studied the unbinding transition of semiflexible membranes ( or polymers) in (1+1) dimensions. This study is an extension of the work done by Maggs *et al.* [63] for a short-range wall potentials. They found that the unbinding transition is first-order. In this formulation they were able to determine the universality classes and critical exponents as a function of the range of the interaction potential and recover the results of Maggs *et al.* as a special case. The wall potential was taken to fall off with the distance  $z$  as  $z^p$ . They found that for  $p > \frac{2}{3}$  the unbinding transition is first order, and for attractive potentials with  $p < \frac{2}{3}$  the membrane ( or the semiflexible polymer) is always bound. Leermakers *et al.* [80] used the a numerical SCF theory to study the behavior of a polymer  $A_N$  near interface formed by the phase boundary of two monomeric liquids. By varying the Flory–Huggins interaction parameter between the two solvents, they were able to control the interfacial width. This interfacial width is the relevant parameter, even when this width is very small. Also they varied the stiffness ( or alternatively the persistence length  $l_p$ ) of the polymer to study its influence on the adsorption behavior at the interface. Obviously, the interplay between these two parameters plays an important role in the adsorption phase diagram in the polymeric system. In conclusions, they have shown that the adsorption of the semiflexible polymers onto liquid–liquid interface is strongly influenced by the competition between the different length scales in the system. Increasing the stiffness of a polymer chain gives rise to a minimum in the adsorbed amount at a certain persistence length. This phenomenon originates from the transition of the polymer from flexible to stiff, but it also depends on the width of the interfacial region. However, in this perspective one should also be aware of the fact that it is in practice difficult to change the stiffness of the molecules without changing the interactions. This observations is of importance for preferential adsorption problems, where one is interested in whether a stiff or a flexible polymer is more likely to adsorb. Related to this drawback, it should be noted that in several experimental systems enthalpic effects play a more important role than entropic ones. In other words, when one tries to change the stiffness of a polymer, one possibly also changes its energetic interactions with its surroundings. Most recently Lässig *et al.* [81] studied the semiflexible manifold transition. Semiflexible manifold such as fluid membranes or semiflexible polymers undergo delocalization ( or it called unbinding ) transition if they are subject to attractive interactions. An important class of low-dimensional manifolds are stretched objects with mainly transversal fluctuations. These are described by a  $d$ -dimensional displacement field  $\mathbf{r}(t)$  which depends on a  $D$ -dimensional internal variable  $t$ . In this letter, they developed a field theory of a semiflexible manifolds with local short ranged interactions. Physically, interesting interactions are polymers ( $D = 1, d = 1, 2$ ) and, in particular, fluid membranes ( $D = 2, d = 1$ ). The results are exact to all orders in perturbation theory. The randomness of the potential is always relevant for fluid membranes, while for semiflexible polymers there is a first order transition to the strong coupling regime at finite temperature.

# 3. Interfacial Properties of Diblock Copolymer at Penetrable Interfaces: Density Profile, Stretching, and Interfacial Tension

In this chapter the interfacial properties of diblock copolymer chain at penetrable interfaces will be discussed. The statistical behavior of the polymer chains at interfaces is different from that at surfaces, and leads to different adsorption behavior. The problem of interfacial properties of diblock copolymer at interface depend strongly on the type of the interactions present between the monomers of the chain and the interface. Also the monomer-monomer interactions play a role in determining these properties. The interaction adopted here is of the simple type and it is modeled by the step potential.

## 3.1. Introduction

Adsorption of polymer chains onto surfaces and interfaces have raised an increasing interest in recent years. One interesting problem in this field is the adsorption of block copolymers at interfaces. The practical relevance of the copolymer adsorption is connected with their use as compatibilizer. Most of the polymer mixtures are immiscible, so that the components segregate into macroscopic domains, which results in poor mechanical properties of such blends. Adding diblock copolymer affects the interfacial properties and improves the mechanical properties of the blends. The diblocks that constitute the most effective additives contain blocks that have a specific affinity for one or other of the homopolymer phases. One of the most interesting interfacial property is the interfacial tension. The addition of a certain type and molecular weight of the block copolymer is addressed by lowering the interfacial tension of the polymer system. The use of the diblock copolymer as a compatibilizer is restricted for several reasons. One among them is that their production for commercial applications is very expensive.

Another limitation of using the block copolymers as compatibilizer is that at larger concentrations block copolymers form micelles. Recent studies have shown that the random copolymers and homopolymers may also be used as compatibilizer. For example Brown and co-worker [82], [83] showed that a longer random copolymer, made by inexpensive free radical polymerization with  $A$  and  $B$  units randomly arranged along the chain, was an effective agent in reinforcing polymer interface.

The adsorption of copolymers at interfaces has been studied very intensively in recent years. A theoretical study of adsorption of an ideal random copolymer chain was made by Garel *et al.* [19]. They have considered a simple model of a random chain at interface between two fluids. They have supposed that monomers have random affinities with both fluids. A simple Imry-Ma type of argument, and replica theory led to the prediction of a localization transition of the chain. This transition separates a low-temperature phase (localized) in which the density of the random coil is strongly peaked around the interface, from the high-temperature phase (delocalized), where the density extended on one side of the interface. These results were confirmed qualitatively by numerical studies. The interfacial behavior of the  $AB$  diblock copolymers in a blend of immiscible homopolymer by applying the numerical self-consistent field theory were studied by R. Israels *et al.* [44], and more intensively by Monte Carlo methods. Werner *et al.* [25] studied the properties of diluted symmetric  $A-B$  diblock copolymers at the interface between  $A$  and  $B$  homopolymer phases. They investigated this system using Monte Carlo simulations of the bond fluctuation model. They calculated the density and the orientational properties of the  $A$  and  $B$  blocks, and of the whole copolymer chain. They found that the distribution of the copolymer monomers  $A$  and  $B$  supports the experimental foundation: Monomers of type  $A$  are more concentrated in the  $A$ -rich phase, whereas monomers of type  $B$  in the  $B$ -rich phase. Also the conformations of single blocks are not different from that of the homopolymers coils. Single blocks tends to orient themselves parallel to the interface. However copolymer chain shows different behavior, they stretch in the direction perpendicular to the interface. This behavior can be understood as if the copolymer chain is a dumbbell with  $A$  sticking into  $A$ -rich phase, and the  $B$  block sticking into the  $B$ -rich phase. On one hand Sommer *et al.* [40] used the scaling methods and Monte Carlo simulations of random  $AB$ -copolymers at the interface between good solvents. They showed that when the interface potential is symmetrical, then infinitely long chain is always adsorbed, but for a finite polymer chains the small gain of the entropy can't trap it at the interface, which leads to adsorption-desorption transition. Therefore a crossover exponent is introduced to relate the desorption temperature with the chain's length. On the other hand in the case of an asymmetric interface leads to a finite adsorption threshold even for infinite chains. If the temperature is larger than the critical temperature  $T_c$  associated with the adsorption threshold the polymer desorbs. For more details see [26], [84]. The theoretical studies are accompanied by numerous experimental investigations using different techniques such as neutron reflectivity or forward recoil spectroscopy [48], [45]. Torikai *et al.* [85] studied the segment distribution of styrene in an alternating lamellar structure of styrene-2-vinylpyridine diblock copoly-

mer by neutron reflection. As mentioned in chapter 2 the mean field theory of Noolandi applied to study the effect of adding block copolymer on the interfacial properties of the immiscible homopolymer blend as a theoretical model for the experiment of Riess and co-worker. They used the general formalism for the inhomogeneous multicomponent polymer system. The reduction of the interfacial tension with the increase of the block copolymer concentration is observed. Also they calculated the interfacial density profile of the multicomponent polymer system. The calculated value of the interfacial tension was found to decrease rapidly compared to experiment with increase the copolymer concentration. The experimental investigations proved that only small amounts (*e.g.*, a percent or less) of block copolymer can considerably reduce the interfacial tension by 80 – 90%. Hu *et al.* [46] applied the modified pendant drop method to measure the interfacial tension of immiscible homopolymer blends. They used a binary homopolymer blend *PS4K/PDMS4.5K* and nearly symmetric diblock copolymer *P(S – b – DMS)* ( $f = N_{ps}/N = 0.42$ ). They found that the interfacial tension of the blend is initially decreasing with increasing the copolymer concentration, and then attains a constant value above a certain critical concentration. The dependance of the interfacial tension on the molecular weight has been studied by Koberstein [86]. He found that the interfacial tension of polymer melt between immiscible homopolymers scales inversely with the number average molecular weight.

In the present chapter we consider the behavior of an ideal diblock copolymer chain in an external potential, which is thought to model the interface of a segregated polymer blend. A set of equations describing the interfacial properties of the diblock copolymer near a penetrable interface are derived. These equations give exact results of the various quantities under consideration. We have considered the mean-square end-to-end distance of the copolymer,  $\langle R^2(z) \rangle$ , as a function of the distance of the joint point of the copolymer to the interface,  $z$ , the segment density distribution  $\rho(z)$ , and the reduction of the interfacial tension in the presence of the diblock copolymer  $\Delta\gamma_c$ . In contrast to the self-consistent field theory [20], [28], and [87] in which the mean field potential is related to the local composition of the polymer system, the potential acting on the diblock copolymer chain is considered as an external one and it is not subjected to the self-consistent procedure. The advantage of such a simplified approach is that it makes possible to use the exact analytical solution for the Green's function in the present of an penetrable and attractive interface.

The chapter is organized as follows. Section 3.2 is concerned with deriving analytical results of density profile of the diblock copolymer chain, the mean-square end-to-end distance of the joint point of the copolymer chain, and finally the reduction of the interfacial tension when diblock copolymer added onto the interface. The results of the computation of these quantities, and the discussion is presented in chapter 5.

## 3.2. Theory

The Green's function of a Gaussian polymer chain on a penetrable attractive interface separating two solvent can be obtained by using the Green's function technique. We will consider a Gaussian polymer chain consisting of  $N$  independent statistical segments (monomers) with statistical segment length  $l$ , interacting with the interface. The statistical weight or the propagator  $G(r, N; r_0, 0)$ , which describes the behavior of the Gaussian chain in the continuum limit, is given by the path integral as follows

$$G(\mathbf{r}, N; \mathbf{r}_0, 0) = \int_{\mathbf{r}(0)=\mathbf{r}_0}^{\mathbf{r}(N)=\mathbf{r}} D\mathbf{r}(s) \exp \left\{ -\frac{d}{2l^2} \int_0^N ds (\partial\mathbf{r}/\partial s)^2 - \int_0^N ds V[\mathbf{r}_z(s)] \right\}, \quad (3.1)$$

where  $\mathbf{r}, \mathbf{r}_0$  are the ends of the Gaussian chain, and  $V[\mathbf{r}_z(s)]$  is the interaction energy of the monomers with the interface, which lies at the  $\mathbf{r}_z = 0$  plane,  $\mathbf{r}_z$  is the projection of the vector  $\mathbf{r}$  in the direction perpendicular to the interface ( $\mathbf{r} = \mathbf{r}_{tr} + \mathbf{r}_z$ ) and  $\mathbf{r}_{tr}$  denotes the projection of  $\mathbf{r}$  in the direction parallel to the interface. It is possible that the statistical weight  $G(z, N; z_0, 0)$  can be obtained from Eq.(3.1) by integrating out the transversal degree of freedom. This is can be only done in the case that the potential acting on each monomer is one dimensional. Thus

$$G(z, N; z_0, 0) = \int d\mathbf{r}_{tr} G(r_z, \mathbf{r}_{tr}, N; \mathbf{r}_0, 0).$$

Therefore the statistical weight  $G(z, N; z_0, 0)$  obeys the following differential equation

$$\frac{\partial}{\partial N} G(z, N; z_0, 0) - D \nabla_z^2 G(z, N; z_0, 0) + V[z(s)] G(z, N; z_0, 0) = 0, \quad (3.2)$$

where  $D = l^2/2d$ , ( $d = 1$  in this case), and we have used the notation  $z = r_z$ . It is convenient to consider the Laplace transform of  $G(z, N; z_0, 0)$  with respect to  $N$

$$pG(z, p; z_0, 0) - P_0(z, z_0) - D\nabla_z^2 G(z, p; z_0, 0) + V[z(s)]G(z, p; z_0, 0) = 0, \quad (3.3)$$

where  $p$  denotes the Laplace conjugate with respect to  $N$  and  $P(z, z_0) = G(z, N = 0; z_0, 0)$ . The proper value of  $P(z, z_0)$  is  $\delta(z - z_0)$ . According to Eq.(3.1),  $G(z, N; z_0, 0)$  fulfills the identity

$$G(z, z'; N) = \int dz'' G(z, z''; N - n)G(z'' z_0; n), \quad (0 < n < N). \quad (3.4)$$

The exact Green's function in the asymmetric potential well  $V[z(s)] = \chi\Theta(z(s))$ , where  $\chi$  represents the asymmetry, has been calculated in a previous paper by Stepanow *et al.* [88] as follows

$$\begin{aligned} G_\chi(z, p; z_0) = & \left\{ G_0(z - z_0, p)\Theta(-z_0) + \frac{\sqrt{p} - \sqrt{p+\chi}}{\sqrt{p} + \sqrt{p+\chi}} G_0(z + z_0, p)\Theta(-z_0) + \right. \\ & \left. \frac{2\sqrt{p+\chi}}{\sqrt{p} + \sqrt{p+\chi}} \exp(z\sqrt{p/D}) G_0(z_0, p + \chi)\Theta(z_0) \right\} \Theta(-z) + \\ & \left\{ G_0(z - z_0, p + \chi)\Theta(z_0) + \frac{\sqrt{p+\chi} - \sqrt{p}}{\sqrt{p} + \sqrt{p+\chi}} G_0(z + z_0, p + \chi)\Theta(z_0) + \right. \\ & \left. \frac{2\sqrt{p}}{\sqrt{p} + \sqrt{p+\chi}} \exp(z\sqrt{(p+\chi)/D}) G_0(z_0, p)\Theta(-z_0) \right\} \Theta(z), \end{aligned} \quad (3.5)$$

where  $G_0(z, p) = 1/(2\sqrt{Dp}) \exp(-|z|\sqrt{p/D})$  is the Laplace transformation of the Green's function of the ideal polymer chain, and  $p$  is the Laplace conjugate with respect to  $N$ . This  $G_\chi(z, p; z_0)$  has been obtained by an arbitrary initial condition  $P(z, z_0)$  in the half planes  $z < 0$  and  $z \geq 0$  and appropriate boundary conditions for  $z \rightarrow \pm\infty$ . Equation (3.5) correctly reproduces the limit case  $\chi = 0$  and  $\chi = \infty$ . For  $\chi \rightarrow \infty$   $G_\chi(z, p; z_0)$  gives the Green's function for a half space with boundary condition  $G(z, p; z_0)_{z=0} = 0$ .

The simplest representative of a block copolymer is the diblock copolymer, which is built of two homopolymers  $A$  and  $B$ , joined together by a covalent bond. We now consider an  $AB$ -block copolymer chain, which is composed of  $A$ -block of length  $N_A$ , and  $B$ -block of length  $N_B$ . The copolymer interacts with the interface, which is placed at  $z = 0$  in such a way that  $A$  monomers prefer to be in the right half plane, while the  $B$  monomers prefer to be in the left half plane. The interaction potential reads

$$V(z) = \begin{cases} \chi\Theta(z) & \text{for A monomers} \\ \chi\Theta(-z) & \text{for B monomers} \end{cases} \quad (3.6)$$

where  $\chi$  is the Flory-Huggins parameter of the  $A$ -sequence (or  $B$ -sequence) of monomers in the chain. The Green's function of the copolymer chain can be obtained from the Green's function of the  $A$  and  $B$  homopolymers in the potential  $V(z)$  as follows

$$G_{AB}(z, N; z_0, 0) = \int_{-\infty}^{+\infty} G_\chi(z, N_A; z') G_\chi(z', N_B; z_0, 0) dz'. \quad (3.7)$$

$G_{AB}(z, N; z_0, 0)$  is proportional to the number of conformations of the diblock copolymer with ends fixed at  $z$  and  $z_0$ . The number of conformations of the diblock copolymer chain as a function of the position of the joint point of  $A$  and  $B$  blocks is given by

$$\rho(z) = \frac{1}{\Omega} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} G_\chi(z', N_A; z, 0) G_\chi(z, N_B; z_0, 0) dz' dz_0, \quad (3.8)$$

where the normalization constant  $\Omega$  is given by

$$\Omega = \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} G_\chi(z', N_A; z, 0) G_\chi(z, N_B; z_0, 0) dz' dz_0 dz \quad (3.9)$$

$\rho(z)$  gives the density profile of the diblock copolymer. The use of the Green's function (3.5) in the potential (3.6) enables one to compute the density profile of the copolymer chain  $\rho(z)$ . Therefore the density of the diblock copolymer  $\rho(z)$  reads

$$\rho(z) = \frac{1}{\Omega}(\rho_-(z)\Theta(-z) + \rho_+(z)\Theta(z)), \quad (3.10)$$

where  $\rho_-(z)$  and  $\rho_+(z)$  are obtained as

$$\rho_-(z) = I_-(z, f)I_+(-z, 1 - f), \quad (3.11)$$

$$\rho_+(z) = I_-(-z, 1 - f)I_+(z, f), \quad (3.12)$$

with

$$I_-(z, f) = -\operatorname{erf}\left(\frac{z}{\sqrt{12fR_g^2}}\right) + \frac{1}{\pi} \int_0^1 \frac{\exp\left(-\frac{(z/R_g)^2}{12fu} + \chi f N(u-1)\right)}{\sqrt{u(1-u)}} du, \quad (3.13)$$

$$I_+(z, f) = \operatorname{erf}\left(\frac{z}{\sqrt{12fR_g^2}}\right) + \frac{1}{\pi} \int_0^1 \frac{\exp\left(-\frac{(z/R_g)^2}{12fu} - \chi f N u\right)}{\sqrt{u(1-u)}} du, \quad (3.14)$$

where the composition,  $f = N_A/(N_A + N_B)$ , and the radius of gyration,  $R_g^2 = Nl^2/6$ , of the copolymer are introduced. The expression for  $\Omega$  is presented in Appendix A.

The mean square end-to-end distance of the copolymer as a function of the distance to the interface is given by

$$\langle R^2(z) \rangle = \langle (z' - z_0)^2 \rangle = \frac{1}{\Omega'(z)} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} (z' - z_0)^2 G_\chi(z', N_A; z) G_\chi(z, N_B; z_0, 0) dz' dz_0, \quad (3.15)$$

where the normalization factor  $\Omega'(z)$  is given by

$$\Omega'(z) = \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} G_\chi(z', N_A; z, 0) G_\chi(z, N_B; z_0, 0) dz' dz_0. \quad (3.16)$$

Therefore, the normalization constant is

$$\Omega'(z) = \rho(z). \quad (3.17)$$

In order to calculate  $\langle R^2(z) \rangle$  we need to calculate the following two quantities

$$\langle z_0^2 \rangle = \frac{1}{\Omega'(z)} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} z_0^2 G_\chi(z', N_A; z) G_\chi(z, N_B; z_0, 0) dz_0 dz', \quad (3.18)$$

$$\langle z_0 \rangle = \frac{1}{\Omega'(z)} \int_{-\infty}^{+\infty} z_0 G_\chi(z', N_A; z) G_\chi(z, N_B; z_0, 0) dz_0 dz'. \quad (3.19)$$

After carrying out the integrations in (3.18, and 3.19) we arrive at

$$\langle z_0^2 \rangle = J_-(z, N_B)\Theta(-z) + J_+(z, N_B)\Theta(z), \quad (3.20)$$

$$\langle z_0 \rangle = L_-(z, N_B)\Theta(-z) + L_+(z, N_B)\Theta(z), \quad (3.21)$$

with expressions for  $J_-$ ,  $J_+$ ,  $L_-$ , and  $L_+$ , given in appendix A. Similar expressions hold for  $\langle z_0'^2 \rangle$ ,  $\langle z_0' \rangle$ . Using the expressions of  $\langle z_0^2 \rangle$ ,  $\langle z_0 \rangle$ ,  $\langle z_0'^2 \rangle$ , and  $\langle z_0' \rangle$ , the mean square end-to-end distance of the copolymer  $\langle R_z^2 \rangle$  is obtained as

$$\begin{aligned} \langle R_z^2 \rangle = & J_-(z, N_B)\Theta(-z) + J_+(z, N_B)\Theta(z) + J_-(-z, N_A)\Theta(z) + J_+(-z, N_A)\Theta(-z) \\ & - 2 \{L_-(z, N_B)\Theta(-z) + L_+(z, N_B)\Theta(z)\} \{L_-(-z, N_A)\Theta(z) + L_+(-z, N_A)\Theta(-z)\}. \end{aligned} \quad (3.22)$$

The results of studying the stretching of the copolymer at the interface using the above expression will be presented in chapter 5.

In order to study the reduction of the interfacial tension  $\Delta\gamma_c$  due to addition of diblock copolymer chains at the interface we use the Gibbs' adsorption equation [34]

$$d\gamma_c = -\nu_c d\mu_c, \quad (3.23)$$

where  $\gamma_c$ ,  $\nu_c$ , and  $\mu_c$  are the surface tension, interfacial excess, and the chemical potential of the copolymer, respectively. The interfacial excess, and the area under the density profile of the copolymer  $z_c^*$  (see figure (5.1) for example ) are related by the following relation  $\nu_c = z_c^* \rho_0 / N_c$ , where  $\rho_0$  is the molar density and  $N_c$  is the total number of the monomer in the copolymer chain. The area under  $\rho_c(z)$  is given by

$$z_c^* = \int_{-\infty}^{+\infty} (\rho_c(z) - \rho^{bulk}) dz, \quad (3.24)$$

where  $\rho^{bulk}$  is the value of the copolymer density in the bulk  $A$ -rich (for positive values of  $z$ ) phase or  $B$ -rich phase (for negative values of  $z$ ). The chemical potential of the chain is given by [89]

$$\frac{\mu_c(z)}{N_c} = \frac{\partial(f_c/\rho_0)}{\partial\rho_c(z)} + (f_c/\rho_0) - \rho_c(z) \frac{\partial(f_c/\rho_0)}{\partial r} \quad (3.25)$$

where  $f_c$  is the usual Flory-Huggins free energy of the copolymer chain

$$\frac{f_c(z)}{k_B T \rho_0} = \frac{\rho_c(z)}{N_c} \ln(\rho_c(z)). \quad (3.26)$$

The last equation takes into account the entropy of mixing of the entire copolymer chain with the surrounding. The term which arises from the interactions between monomers in different blocks is absent in this equation. Inserting Eq.(3.26) into Eq.(3.25) yields

$$\frac{\mu_c(z)}{N_c k_B T} = \frac{1}{N_c} \{ \ln(\rho_c(z)) + (1 - \rho_c(z)) \}. \quad (3.27)$$

Combining the above results, we arrive at the following equation for the reduction of the interfacial tension

$$\Delta\gamma_c = -\frac{z_c^* \rho_0}{N_c} \int_{-\infty}^{+\infty} \frac{d\mu_c(z)}{dz} dz. \quad (3.28)$$

Finally, the reduction of the interfacial tension is obtained as

$$\Delta\gamma_c = -\frac{z_c^* \rho_0}{N_c} \int_{-\infty}^{+\infty} \frac{\partial \rho_c(z)}{\partial z} \left\{ \frac{1}{\rho_c(z)} - 1 \right\} dz. \quad (3.29)$$

In the above treatment the only interaction contribution comes from the monomer-interface interaction. This interaction plays an important role in determining the density of the diblock copolymer, and therefore affects the other interfacial properties.

The results for the density profiles, mean square end-to-end distance, and the reduction in the interfacial tension upon adding the diblock copolymer at the interface are exact. The results can be compared with the previous theoretical and experimental studies. In general the interface between two immiscible homopolymer A and B is weak and can be strengthened by adding a small amount of diblock copolymer. As a consequence of this adding the interfacial tension can be reduced dramatically to a small value. The stretching of the diblock into their own rich phase can be describe by compatibilizing effects which drive each block into A-rich phase and B-rich phase. The theory can be used to model and explore this behavior for a diblock copolymer between two solvents in the absence of the monomer-monomer interaction. The results of the various interfacial parameters calculated using this theory will be discussed in chapter 5.

# 4. Adsorption of a Semiflexible Polymer onto Penetrable Interfaces

In this chapter the adsorption properties of the semiflexible polymer chain near an attractive penetrable interfaces will be discussed. The importance of understanding the behavior of semiflexible polymers onto surfaces or interfaces is due to their wide range relevance in different physical phenomena. The different types of interactions adopted between the polymer chain and the interface lead to a different scenarios for the adsorption strength. The stiffness character of the semiflexible chain which can be controlled via the persistence length  $l_p$  shows a systematic effects on the adsorption behavior of the chain.

## 4.1. Introduction

Adsorption of polymers onto interfaces plays a major role in polymer adhesion, stabilization of colloidal suspensions, and also in processes including biological macromolecules such as protein adsorption on membranes. Indeed, macromolecules of various biopolymers ( nucleic acids, polysaccharides, and others) play an important role in all biological phenomena. Many molecular-biological phenomena are associated with quite ordinary properties and characteristics of polymers (chain structure, flexibility, *etc.*). For many applications including the biopolymers were the stiffness of the polymers is important. Central issues are originate as a result of the stiffness. For example the adsorption of the polymer chain onto membranes. The analysis of phenomena associated with the stiff-character of the polymer are rather a difficult task, even for the free chains.

However many facts are discovered many years ago, there is still no consensus on their theoretical explanations. Moreover, the more dominate models (or theories) [9], [63], and [79] which describe the adsorption of the semiflexible polymers onto surfaces or interfaces, still suffer from drawbacks. One of the difficulties of such theories have to make specific assumption about the microscopic mechanisms of adsorption. As it is difficult to probe these processes directly in an experiment, the main test for the theories

has been a comparison of their predictions with macroscopic properties, such as interfacial width, adsorption amount, segment orientation and density profiles. Simulation studies can potentially play an important role in this direction by providing insight into the microscopic processes involved in semiflexible polymer adsorption. Thus helping in assessment and refinement of the current theories and perhaps in development of new theories. However, there have been simulation studies [41], [90], and [91] which have attempted to investigate the basic process in the adsorption of the semiflexible polymers on surfaces or interfaces. For example Kramarenko *et al.* [78] applied the continuous Molecular dynamics simulations to the adsorption problem of semiflexible interface for different chains lengths and stiffness. They found that stiffer chains adsorb more easily. In addition to computer simulations intensive analytical calculations (*i.e.*, scaling arguments, mean-field approach *etc.*) have been performed. As an example Morse *et al.* [70] applied the self-consistent-field theory to analyze the equilibrium properties of two immiscible semiflexible polymers. The theory predicts a strong orientational order of the polymer chain in the large rigidity limit, and reduces to the well-know Edwards theory of flexible polymers [92].

Birshtein *et al.* [54] have discussed the conformation of biopolymer molecules (*e.g.*, polypeptides) near an attractive interface (*e.g.*, membranes). They have taken into account the effect of a short-range interactions between the semiflexible polymer chain and the interface. They developed a theory of adsorption of the semiflexible polymer chains of different stiffness. It predicted that the adsorption-desorption phase transition of second order. They found that the chain stiffness favors adsorption : the critical adsorption energy decreased and the transition sharpened when the chain stiffness increased. Semiflexible living polymers studied by Menon and Pandit [93]. In the framework of the a  $d$ -dimensional lattice model, they showed of possibilities of these living polymers (*i.e.*, polymers whose lengths fluctuate and attain an equilibrium length distribution at given temperature  $T$ ) to exhibit both equilibrium crystallization and glass formation. It is well know that in some biological macromolecules with intrinsic stiffness ( *e.g.*, *DNA* or synthetic polypeptides) crystallization occurs when a polymeric melt is cooled very slowly. They have demonstrated that in semiflexible melts and living polymers exist a phase transition from disorder to order phase. However, the statistical mechanics of polymeric melts is a complex problem. Schick *et al.* [94] presented a self-consistent field theory in studying the phase behavior of melts of semiflexible diblock copolymers for different bending rigidity. These semiflexible diblock copolymers melts considered under the action of anisotropic external fields and interactions. They have found that the repulsion interaction between incompatible blocks is the responsible about microphase separations, while anisotropic external field and interactions between polymers induce liquid-crystalline phases.

The work of Carignano and Szleifer [95] has addressed the surface segregation of athermal conformationally asymmetric alloys using a single chain mean field theory. They found that the local entropic effect drive the stiffer binary blends to segregate to the surface. However, for a diblock copolymers in the strong microphase segregation limit they found nonuniversal behavior, *i.e.*, either the more flexible or the more stiffer block can segregate to the surface depending on factors such as molecular density. Also Kumar *et al.* reported the results of calculations on athermal liquidlike mixtures of stiff and flexible molecules of short to moderate length ( $N \leq 100$ ) which suggested that the segments of the stiffer molecule always partition to neutral surface. This preliminary work has been extended by the same authors [96]. They have used the same simulation method of the polymer reference interaction site model (*PRISM*) to more longer chains which is relevant in experimental work ( $N \approx 500$ ) to verify that the earlier results were not merely a short chain effect. Their results showed that, at liquidlike densities, the stiffer polymer partitioned to the surface in a manner that is apparently independent of the chain lengths of the polymers. Further, the observed segregation of the stiff chains to the surface at liquidlike densities is shown to be primarily a consequence of the layering of molecules near surface, with stiffer chain packing better at this surface.

In the present chapter we consider the behavior of a semiflexible chain subject to an external attractive potential. The choice of the external potential plays an important role in determining the interfacial properties of the semiflexible chain. In particular, we have considered the effect of the type of interactions and the stiffness onto the adsorption strength of the polymer chain. Also the distribution function of the free ends of the polymer chain as a function of a distance from the interface is discussed for different  $l_p$  and  $v_c$ .

The chapter is organized as follows. In section 4.2 the integral equation of the Green's function of the semiflexible chain is derived. An analytical calculations of the adsorption strength as a function of the crossover length for different types of interaction (interactions which depend on the orientation as well as the spatial coordinates) are presented. Also the connection of the problem with Quantum Mechanics of a potential well of depth  $W_0$  and width  $a$  is discussed.

## 4.2. Theory

As it is well-known that the flexible polymers are described in terms of a non differentiable ‘trajectory’  $\mathbf{r}(s)$ , ( $0 \leq s \leq L$ ,  $L$  is the arc length of the polymer), while a semi-flexible polymer is described by trajectories  $\mathbf{r}(s)$  with well defined tangent  $\mathbf{u}(s) = d\mathbf{r}(s)/ds$ . The differential equation for the Green’s function of the semi-flexible polymer can be written as follows [63], [88], and [97]

$$\partial_L G(\mathbf{r}, \mathbf{u}, L; \mathbf{r}_0, \mathbf{u}_0, 0) = \partial_{\mathbf{u}}(l_p^{-1} \mathbf{u} + D_v \partial_{\mathbf{u}}) G(\mathbf{r}, \mathbf{u}, L; \mathbf{r}_0, \mathbf{u}_0, 0) - \mathbf{u} \partial_{\mathbf{r}} G(\mathbf{r}, \mathbf{u}, L; \mathbf{r}_0, \mathbf{u}_0, 0) - V(\mathbf{r}, \mathbf{u}) G(\mathbf{r}, \mathbf{u}, L; \mathbf{r}_0, \mathbf{u}_0, 0), \quad (4.1)$$

where  $\mathbf{r}$  and  $\mathbf{u}$  are the position and the tangent,  $d\mathbf{r}(L)/dL$ , of the free end of the polymer chain, respectively,  $l_p$  is the persistence length of the polymer, and  $D_v = l_p^{-1}$ . Note that the term which contains the potential energy  $V(\mathbf{r}, \mathbf{u})$  is absent in Eq.(2.3). Therefore in order to describe the semiflexible polymer chain in an external field, the interaction energy must be added to equation (2.3). Another important note is that the main difference between the semiflexible chain and flexible chain is the existence of orientation-dependent interactions. Imposing the constraint,  $|\mathbf{u}| = 1$  Eq.(4.1) gives the Fokker-Planck equation on sphere, which is expected to be equivalent to the Kratky-Porod model [9]. Notice that this model (*i.e.*, 4.1) is more general than the two models presented in [63], [66], and [69] since it takes into account the term linear  $\partial_{\mathbf{u}}$ . The absence of this term may lead to incorrect description of the adsorption of the semiflexible polymer chains at interfaces or surfaces.

Equation(4.1) can be rewritten as an integral equation as follows

$$G(\mathbf{r}, \mathbf{u}, L; \mathbf{r}_0, \mathbf{u}_0) = G_0(\mathbf{r}, \mathbf{u}, L; \mathbf{r}_0, \mathbf{u}_0) - \int_0^L ds \int d\mathbf{r}' \int d\mathbf{u}' G_0(\mathbf{r}, \mathbf{u}, L - s; \mathbf{r}', \mathbf{u}') V(\mathbf{r}', \mathbf{u}') G(\mathbf{r}', \mathbf{u}', s; \mathbf{r}_0, \mathbf{u}_0), \quad (4.2)$$

where  $G_0(\mathbf{r}, \mathbf{u}, L; \mathbf{r}_0, \mathbf{u}_0)$  is the solution of (4.1) with  $V(\mathbf{r}, \mathbf{u}) = 0$ . The Fourier transform of the transition probability density  $G_0(\mathbf{r}, \mathbf{u}, L; \mathbf{r}_0, \mathbf{u}_0)$  is obtained in [59] as

$$\begin{aligned}
G_0(\mathbf{p}, \mathbf{k}, \mathbf{k}', L) &= \delta(\mathbf{k}' - \mathbf{k}e^{-L/l_p} - \mathbf{p}l_p(1 - e^{-L/l_p})) \\
&\exp\left(-\frac{D_v p^2 l_p^3}{2} [2L/l_p + 4e^{-L/l_p} - e^{-2L/l_p} - 3] - \right. \\
&\quad \left. \frac{D_v k^2 l_p}{2} (1 - e^{-2L/l_p}) - D_v l_p^2 \mathbf{p} \mathbf{k} (1 - e^{-L/l_p})^2 \right), \tag{4.3}
\end{aligned}$$

where the wave vectors  $\mathbf{p}$ ,  $\mathbf{k}$ , and  $\mathbf{k}'$  are respectively conjugated to  $\mathbf{r} - \mathbf{r}_0$ ,  $\mathbf{u}$ , and  $-\mathbf{u}_0$ .

The integration of  $G_0(\mathbf{r}, \mathbf{u}, L; \mathbf{r}_0, \mathbf{u}_0, 0) \exp(-(d/2)\mathbf{u}_0^2)$  over  $\mathbf{u}$  and  $\mathbf{u}_0$  gives the distribution function of the chain end-to-end distance  $G_0(\mathbf{r} - \mathbf{r}_0, L) = (1/(4\pi l_p^2 h(L/l_p)))^{d/2} \exp(-(\mathbf{r} - \mathbf{r}_0)^2/4l_p^2 h(L/l_p))$  with  $h(x) = \exp(-x) + x - 1$  and  $l_p$  being the persistence length of the polymer chain ( see Appendix B). The mean-square end-to-end distance of the polymer chain computed by using the latter is obtained as  $\langle (\mathbf{r}(L) - \mathbf{r}(0))^2 \rangle = 2l_p^2(\exp(-L/l_p) + L/l_p - 1)$ , which coincides exactly with the result predicted by the Kratky and Porod model.

We now will consider the case of the isotropic interaction potential,  $V(\mathbf{r}, \mathbf{u}) = v(z)$ . In this case the potential energy does not depend on  $\mathbf{u}$  or  $\mathbf{r}_{tr}$ , then we can easily obtain an integral equation for the Green's function which depends only on  $r_z$ . In order to simplify (4.2) we multiply it by  $\exp(-(d/2)\mathbf{u}_0^2)$  and integrate over  $\mathbf{r}_{tr}$ ,  $\mathbf{u}$ , and  $\mathbf{u}_0$ .

$$G(z, L; z_0) = \int d\mathbf{r}_{tr} \int d\mathbf{u} \int d\mathbf{u}_0 G(\mathbf{r}, \mathbf{u}, L; \mathbf{r}_0, \mathbf{u}_0) \exp(-(d/2)\mathbf{u}_0^2),$$

this implies that

$$\begin{aligned}
G(z, L; z_0) &= \int d\mathbf{r}_{tr} \int d\mathbf{u} \int d\mathbf{u}_0 \exp(-(d/2)\mathbf{u}_0^2) [G_0(\mathbf{r}, \mathbf{u}, L; \mathbf{r}_0, \mathbf{u}_0) - \\
&\int_0^L ds \int d\mathbf{r}' \int d\mathbf{u}' G_0(\mathbf{r}, \mathbf{u}, L - s; \mathbf{r}', \mathbf{u}') V(\mathbf{z}) G(\mathbf{r}', \mathbf{u}', s; \mathbf{r}_0, \mathbf{u}_0)].
\end{aligned}$$

After approximating the quantity  $u'_z$  in  $G_0(\mathbf{r}, \mathbf{u}, L - s; \mathbf{r}', \mathbf{u}')$  in (4.2) by  $u'_z = (r_z - r'_z)/(L - s)$  we get an integral equation for the reduced Green's function which can be written as

$$G(z, p; z_0) = G_0(z, p; z_0) - \int dz' \overline{G}_0(z, p; z') v(z') G(z', p; z_0), \quad (4.4)$$

where  $z \equiv r_z$  and  $G(z, p; z_0)$  is the Laplace transform of  $G(z, L; z_0)$  with respect to  $L$  and  $\overline{G}_0(z, p; z')$  is the Laplace transform of the function  $\int du_z G_0(r_z, u_z, L; r'_z, u'_z, L) = (r_z - r'_z)/L$  with respect to  $L$ . Notice that the approximation  $u'_z = (r_z - r'_z)/(L - s)$  is exact for small  $L - s$  and will become unimportant for large  $L - s$ . This is the only approximation in reducing the integral equation (4.2) to the form (4.4).

The integral equation (4.4) can be easily solved for the delta potential  $v(z) = -v\delta(z)$  to give

$$G(z, p; z_0) = G_0(z, p; z_0) + \frac{v\overline{G}_0(z, p; 0)G_0(0, p; z_0)}{1 - vG_0(0, p; 0)}, \quad (4.5)$$

where we took into account that  $\overline{G}_0(0, p; 0) = G_0(0, p; 0)$ . For detailed calculations see Appendix B. This equation can be used to study the adsorption of both flexible and semiflexible polymer chains. The unperturbed Green's function for a flexible polymer is given by  $G_0(z, L; z_0) = (1/(4\pi lL)^{1/2} \exp(-(z - z_0)^2/4lL)$  ( $l$  is the statistical segment length), while for a semi-flexible polymer the appropriate approximation (see Appendix B) for the unperturbed Greens' function is  $G_0(z, L; z_0) = (1/(4\pi l_p^2 h(L/l_p))^{1/2} \exp(-(z - z_0)^2/4l_p^2 h(L/l_p))$ . Notice that replacing  $1/2$  in  $G_0(z, L; z_0)$  by  $d/2$  enables one to study the adsorption of a polymer onto an interface ( $d = 1$ ), a cylinder ( $d = 2$ ), and a sphere ( $d = 3$ ). The adsorption condition corresponds to the pole  $1 - vG_0(0, p; 0) = 0$  in Eq.(4.5) which can be written for a semiflexible polymer as

$$1 - v/\sqrt{2\pi} \int_0^\infty dt \exp(-t/x)/(\exp(-t) + t - 1)^{1/2} = 0, \quad (4.6)$$

The above expression is divergent at the lower integration limit (*i.e.*,  $t = 0$ ). This divergency is due to the stiffness nature of the polymer chain at small distances. Therefore it is necessary to introduce a cutoff  $t_0$  to prevent divergences at the lower limit by the integration over  $t$ . Then Eq.(4.6) becomes

$$1 - v/\sqrt{2\pi} \int_0^\infty dt \exp(-t/x)(1/(\exp(-t) + t - 1)^{1/2} - \sqrt{2}/t) -$$

$$v\sqrt{2}/\sqrt{2\pi}\Gamma(0, t_0/x) = 0, \quad (4.7)$$

where  $\Gamma(0, x)$  is the incomplete Gamma function ( $\Gamma(a, x) = \int_x^\infty e^{-t} t^{a-1} dt$ ). Notice that for  $d < 1$  the integral is convergent. Another possible distribution function is the one found by Wilhelm and Frey ( see Eq.(2.9)). The adsorption condition for this Green's function subject to the delta potential  $v(z) = -v_f \delta(z)$  is simply given by Eq.(4.5). This Green's function can be written in 1-dimension as

$$G(z, t) = \int G(\mathbf{r}_{tr}, z, t; 0) d\mathbf{r}_{tr} \quad (4.8)$$

performing out the integration over  $r_{tr}$  and by setting  $z = 0$  gives the normalized Green's function in one-dimension as

$$G(0, t) = \frac{2\pi \sum_{l=1}^{\infty} (-1)^{l+1} \left( \frac{t}{\pi^2 l^2} + \frac{t^2}{\pi^4 l^4} (-1 + \exp(\frac{\pi^2 l^2}{t})) \right) l^2}{\frac{4}{\pi} \sum_{l=1}^{\infty} (-1)^{l+1} \left( \frac{-2\pi^2 t^2}{l^2} + \pi^4 t + \frac{2t^3}{l^4} (-1 + \exp(\frac{\pi^2 l^2}{t})) \right)}. \quad (4.9)$$

Substituting the above equation in Eq.(4.5), therefore the pole condition reads

$$1 - v_f \int_0^\infty \left[ \frac{2\pi \sum_{l=1}^{\infty} (-1)^{l+1} \left( \frac{t}{\pi^2 l^2} + \frac{t^2}{\pi^4 l^4} (-1 + \exp(\frac{\pi^2 l^2}{t})) \right) l^2}{\frac{4}{\pi} \sum_{l=1}^{\infty} (-1)^{l+1} \left( \frac{-2\pi^2 t^2}{l^2} + \pi^4 t + \frac{2t^3}{l^4} (-1 + \exp(\frac{\pi^2 l^2}{t})) \right)} \right. \\ \left. - \frac{4}{\pi} \sum_{l=1}^{\infty} (-1)^{l+1} t \right] \exp(-t/x) dt - v_f \int_{t_0}^\infty \frac{4}{\pi} \sum_{l=1}^{\infty} (-1)^{l+1} t \exp(-t/x) dt = 0. \quad (4.10)$$

Therefore the above equation becomes

$$1 - v_f \int_0^\infty \left[ \frac{2\pi \sum_{l=1}^{\infty} (-1)^{l+1} \left( \frac{t}{\pi^2 l^2} + \frac{t^2}{\pi^4 l^4} (-1 + \exp(\frac{\pi^2 l^2}{t})) \right) l^2}{\frac{4}{\pi} \sum_{l=1}^{\infty} (-1)^{l+1} \left( \frac{-2\pi^2 t^2}{l^2} + \pi^4 t + \frac{2t^3}{l^4} (-1 + \exp(\frac{\pi^2 l^2}{t})) \right)} \right. \\ \left. - \frac{4}{\pi} \sum_{l=1}^{\infty} (-1)^{l+1} t \right] \exp(-t/x) dt - v \frac{2}{\pi} x(x + t_0) \exp(-t_0/x) = 0. \quad (4.11)$$

This circumstance legitimates us to consider (4.6) as an analytical continuation from  $d < 1$ . The strength of the attraction  $v$  can be expressed through the depth  $W_0$  and the width  $a$  of the potential well as  $v \rightarrow W_0 a^d$ . The cutoff  $t_0$  in (4.6) is given in units of  $a/l_p$ . Notice that the dependence of the adsorption condition (4.6) on  $a$  is similar to the situation for flexible polymers at  $d = 2$ . The adsorption of a flexible polymer onto an interface can be mapped onto the problem of the existence of a bound state for a quantum

mechanical particle in a potential well. It is known from the Quantum Mechanics [98] that in  $d = 1$  only the quantity  $W_0 a$  is relevant, while for  $d \geq 2$  the quantities under consideration (localization length etc.) depend on both the strength of the potential  $W_0 a^d$  and the width  $a$  of the potential. For semi-flexible polymers the border dimension, where the explicit dependence on the width  $a$  appears, is  $d = 1$ . Eq.(4.5) can be used to study the adsorption of a semiflexible polymer chain onto a penetrable cylinder or a sphere. It is known from Quantum Mechanics that for adsorption of a flexible polymer onto a penetrable sphere ( $d = 3$ ) a minimal depth  $W_c$  of the potential well is necessary [98]. The pole in Eq.(4.5) can be written in the case of adsorption of a semiflexible polymer onto a penetrable sphere as

$$1 - vl_p^{-2}/(4\pi)^{3/2} \int_0^\infty dt \exp(-t/x)/(\exp(-t) + t - 1)^{3/2} = 0$$

The above equation is divergent at the lower integration limit. Then, employing the same argument as in the previous case, one gets

$$0 = 1 - vl_p^{-2}/(4\pi)^{3/2} \int_0^\infty dt \exp(-t/x)(1/(\exp(-t) + t - 1)^{3/2} - \sqrt{2}(2t^{-3} + t^{-2} + t^{-1}/6)) - vc_{as} \quad (4.12)$$

with  $c_{as}$  given by

$$\begin{aligned} c_{as} &= l_p^{-2} \sqrt{2}/(4\pi)^{3/2} \int_{t_0}^\infty dt \exp(-t/x)(2t^{-3} + t^{-2} + t^{-1}/6) = \\ & l_p^{-2} \sqrt{2}/(4\pi)^{3/2} \Gamma(0, t_0/x)(1/(x^2 - 1/x + 1/6) + \\ & l_p^{-2} \sqrt{2}/(4\pi)^{3/2} \exp(-t_0/x)(t_0^{-2} - (xt_0)^{-1} + t_0^{-1}). \end{aligned} \quad (4.13)$$

We now will consider the adsorption of a semi-flexible polymer chain onto an interface in the case of an anisotropic attraction potential to the interface, *i.e.*, the potential depends both on  $\mathbf{r}(s)$  and  $d\mathbf{r}(s)/ds$ . As an first example we will consider the potential  $V(\mathbf{r}(s), d\mathbf{r}(s)/ds) = -v\delta(z(s))\delta(dx(s)/ds - 1)$ . This interaction gives an example of a structured interface. We are aware that the adsorption of semiflexible polymers onto structured surfaces is of more practical importance. However, the latter case is much more difficult. While the distribution function  $G_0(\mathbf{r}, \mathbf{u}, L; \mathbf{r}_0, \mathbf{u}_0)$  is a product over Cartesian components, the integrations over  $r_y$  and  $u_y$  can be performed straightforwardly for the potential under consideration. In order to simplify (4.2) we multiply it

with  $\exp(-(1/2)u_{z0}^2)$  and integrate over  $r_x$ ,  $u_z$ , and  $u_{z0}$ . After approximating the quantity  $u'_z$  in  $G_0(r_z, u, L-s; r'_z, u'_z)$  in (4.2) by  $(r_z - r'_z)/(L-s)$  we get an integral equation for the reduced Green's function  $G(z, u_x, p; z_0, u_{0x})$ . Following the same steps in Appendix B, Eq.(4.2) can be easily solved exactly for the above pseudopotential as

$$G(z, u_x, p; z_0, u_{0x}) = G_0(z, u_x, p; z_0, u_{0x}) + \frac{vG_0(z, u_x, p; 0, u_{0x} = 1)G_0(0, u_x = 1, p; z_0, u_{0x})}{1 - vG_0(0, u_x = 1, p; 0, u_{0x} = 1)}. \quad (4.14)$$

Due to the fact that any boundary conditions on the tangent at the interface reduce the number of states, which is proportional to  $G_0$ , the adsorption of a semiflexible polymer with an anisotropic interaction with the interface is expected to be more difficult in comparison to the isotropic case. The quantity  $G_0(0, u_x = 1, p; 0, u_{0x} = 1)$  entering Eq.(4.14) can be obtained from Eq.(4.3), so that finally the adsorption condition, which corresponds to the pole in (4.14), results in

$$0 = 1 - v \frac{1}{2\sqrt{2\pi}} \int_0^\infty dt (\exp(-t/x) (\exp(-(1/2)(1 - \exp(-t))) / (1 + \exp(-t))) (1 - \exp(-2t))^{-1/2} (\exp(-t) + t - 1)^{-1/2}). \quad (4.15)$$

The divergency of the above equation at the lower limit, force us to rewrite it as

$$0 = 1 - v \frac{1}{2\sqrt{2\pi}} \int_0^\infty dt (\exp(-t/x) (\exp(-(1/2)(1 - \exp(-t))) / (1 + \exp(-t))) (1 - \exp(-2t))^{-1/2} (\exp(-t) + t - 1)^{-1/2} - t^{-3/2} - (5/12)t^{-1/2}) - v \frac{1}{2\sqrt{2\pi}} c_{xs}, \quad (4.16)$$

where  $c_{xs}$  is given by

$$c_{xs} = \int_{t_0}^\infty dt (t^{-3/2} + 5/12t^{-1/2}) \exp(-t/x) = -2\sqrt{\pi}x^{-1/2} + \frac{5}{12} \sqrt{\pi}\sqrt{x} + 2t_0^{-1/2} \exp(-t_0/x + 2\sqrt{\pi}x^{-1/2} \operatorname{erf}(\sqrt{t_0/x}) - \frac{5}{12} \sqrt{\pi}\sqrt{x} \operatorname{erf}(\sqrt{t_0/x}). \quad (4.17)$$

The second example which we will consider of the adsorption of a semi-flexible polymer chain onto an interface in this case is  $V(\mathbf{r}(s), d\mathbf{r}(s)/ds) = -v\delta(z(s))\delta(dz(s)/ds)$ .

The same procedure as in the first example is applicable also here, therefore Eq.(4.2) is solved exactly as

$$G(z, u_z, p; z_0, u_{0z}) = G_0(z, u_z, p; z_0, u_{0z}) + \frac{vG_0(z, u_z, p; 0, u_{0z} = 0)G_0(0, u_z = 0, p; z_0, u_{0z})}{1 - vG_0(0, u_z = 0, p; 0, u_{0z} = 0)}. \quad (4.18)$$

Thus the adsorption condition, which corresponds to the pole in Eq.(4.18) reads

$$0 = 1 - v \frac{\sqrt{2}}{4\pi} \int_0^\infty dt (\exp(-t/x)) ((1 - \exp(-t))(t - 2 + t \exp(-t) + 2 \exp(-t))^{-1/2} \sqrt{6}(t^{-2} + 1/2t^{-1})) - v \frac{\sqrt{2}}{4\pi} c_{zs}, \quad (4.19)$$

where  $c_{zs}$  is given by

$$c_{zs} = \sqrt{6} \int_{t_0}^\infty dt (t^{-2} + 1/2t^{-1}) \exp(-t/x) = \sqrt{6} (\exp(-t_0/x)/t_0 - \text{Ei}(1, t_0/x)/x + \text{Ei}(1, t_0/x)/2). \quad (4.20)$$

It is clear from the above theory that due to different types of interactions the behavior of the semiflexible chain near attractive interfaces is affected. The results of the attraction strength  $v$  are totally depend on the type of ineractions experinced by the polymer chain and its stiffness. It should be also noted that the density profiles are affectd by the type of interactions. The discussion of the above results will be presented in chapter (5).

# 5. Results and Discussion

## 5.1. Interfacial properties of the copolymer chain

In this section, we will discuss the density profile of the diblock copolymer, the mean square end-end distance of the copolymer chain from the interface, and the reduction of the interfacial tension.  $N = 32$  is used in obtaining the density profiles for the copolymer chains in Figures (5.1)-(5.7). Distances are scaled in units of the interfacial width in the strong segregation limit  $w_{SSL}$ . The radius of gyration in these units is  $R_g = 4.2 w_{SSL}$ . Our discussion will be limited to the case where no ordered mesophases are formed by the polymer system, and a comparison with the Monte Carlo Simulations (MCS) [99] is also presented.

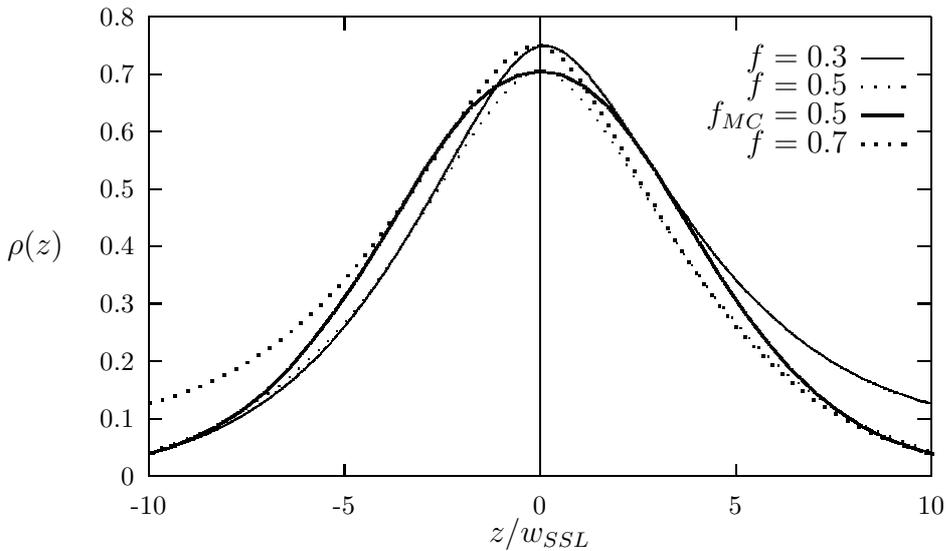


Figure 5.1.: The density profile as a function of the distance from the interface  $z$ , in units of  $w_{SSL}$ , the density distribution of the  $AB$  copolymer are shown for different values of  $f$  for  $\chi = 0.54$ , the case  $f = 0.5$  is compared with the MC results.

### 5.1.1. The density profiles for the copolymer chain

Fig.(5.1) shows the density profiles of the  $AB$ -block copolymer for different compositions  $f$ . As expected, the density profile is symmetric for  $f = 0.50$  with respect to the position of the interface  $z = 0$  and it is asymmetric for compositions  $f = 0.30$  or  $0.70$ . The copolymer chain prefers the region where the concentration of one kind of the monomers is rich. As a consequence of this rearrangement of the monomers, the peak of the distribution no more coincides with the interface position at  $z = 0$ . In the most transparent symmetric case a comparison with the prediction of MCS shows a very good agreement.

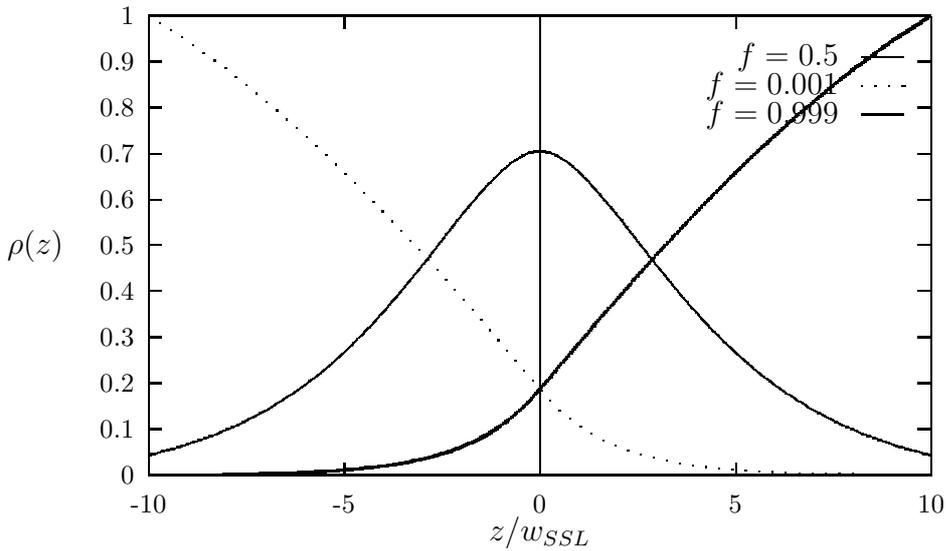


Figure 5.2.: The density profile as a function of the distance from the interface  $z$ , in units of  $w_{SSL}$ , the density distribution of the  $AB$  copolymer are shown for the symmetric and in the dilute regimes for  $\chi = 0.54$ .

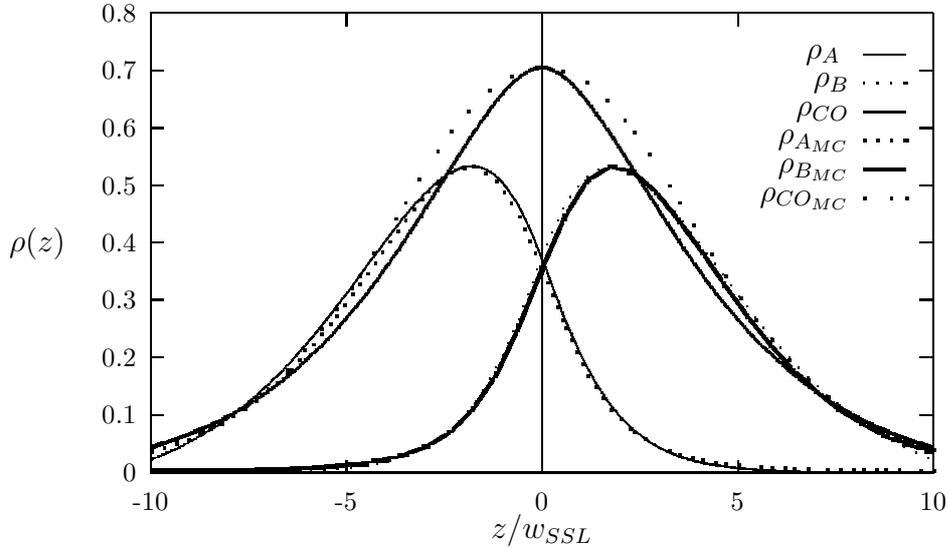


Figure 5.3.: The density profile as a function of the distance from the interface  $z$ , in units of  $w_{SSL}$ , the density distribution of the  $AB$  copolymer are shown as well as the individual copolymer blocks, and compared with the prediction of the MC results for the symmetric case for  $\chi = 0.54$ .

On the other hand Fig.(5.2) shows the profiles of the  $A$  and the  $B$  sequences of the monomers of the copolymer for strongly asymmetric composition ( $f = 0.999$  or  $0.001$ ), and the density profile of the copolymer with symmetric composition ( $f = 0.50$ ). Another comparison of the symmetric case between the numerical evaluations of the analytical results and the simulation is illustrated in Fig.(5.3). The density profile of the whole copolymer as well as the individual copolymer blocks in the symmetric case are presented. The density profiles of the MCS are slightly broader than the other density profile, nevertheless the agreement is very good. The density profiles of the whole copolymer and of the individual copolymer blocks for different compositions ( $f = 0.50$ ,  $0.40$ , and  $0.60$ ) are shown in Fig.(5.4). The above figures show that the asymmetry of the composition plays an important role in determining the character of the behavior of the copolymer chain at interfaces. For example, in the regime of strongly asymmetric composition the longer part of copolymer chain affects the density profile dramatically. In this case the whole profile appears to be very similar to a profile of a pure homopolymer chain [28], [30].

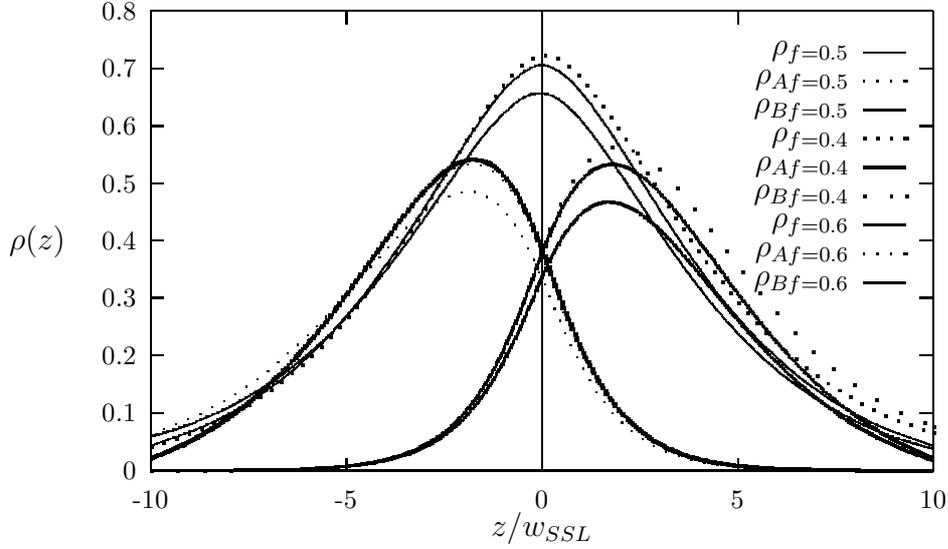


Figure 5.4.: The density profile as a function of the distance from the interface  $z$ , in units of  $w_{SSL}$ , the density distribution of the whole  $AB$  copolymer and the individual copolymer blocks for  $f=0.5, 0.4$ , and  $0.6$  for  $\chi = 0.54$ .

The dependence of the interfacial profile on the interaction parameter  $\chi$  is illustrated in Fig.(5.5). The profiles are shown for  $\chi = 0.54, 0.75$  and  $0.85$  at symmetric composition  $f = 0.50$ . It shows how the distribution profile of the copolymer chain is affected by the variation of the interaction between the monomers and interface. Increasing the value of  $\chi$  making distribution narrower and vice versa. This can be interpreted due to the effect of localization of the copolymer at the interface. A common feature of all the above profiles is that the peak of the distributions are broader than the gyration radius. The above results agree with the experiments of [3], [48], and [85], with the simulations of Werner *et al.* [25], and [99], and with the mean field theory [28], [30].

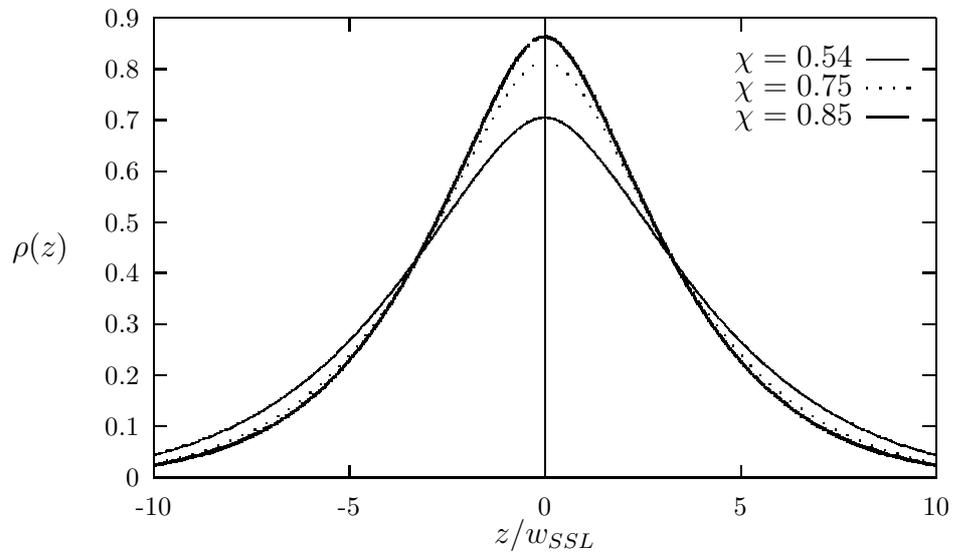


Figure 5.5.: The density profile as a function of the distance from the interface  $z$ , in units of  $w_{SSL}$ , the density distribution of different values of  $\chi$ , for  $f = 0.5$ .

### 5.1.2. The stretching properties of the copolymer chain

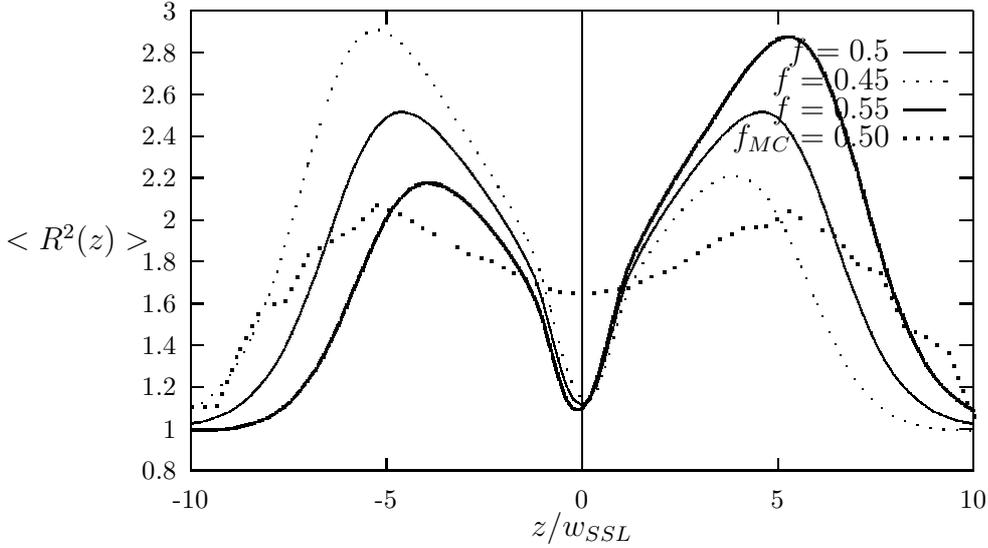


Figure 5.6.: The mean square end-to-end distance in unites of  $a^2N/3$ , plotted vs.  $z/w_{SSL}$ . The results are shown for different values of  $f$  for  $\chi = 0.54$ , the symmetric case is compared with the MC results.

Next we consider the stretching properties of the copolymer chain. Fig.(5.6) illustrates the copolymer coil stretching in the direction perpendicular to the interface. This figure shows the  $z$ -component of the mean square end-to-end distance. Different compositions ( $f = 0.50, 0.45$ , and  $0.55$ ) are considered. It is clear that the copolymer coil stretches in the direction perpendicular to the interface. In the symmetric case the agreement with MCS is qualitatively good. This picture was confirmed in many previous investigations: by scaling theory [42], experiments [101], and by simulations [25], [84], and [99]. The effect of the stretching is very strong for copolymers centered at about two to three gyration radii away from the interface, but it almost disappears for copolymers centered at the interface. The effect of the interaction of the monomers with the interface is illustrated in Fig.(5.7) for three different values of the interaction parameter  $\chi = 0.54, 0.65$  and  $0.75$  for two compositions  $f = 0.50$  and  $0.40$ . As it is clear from this figure, the central region, and the wings of the copolymer profile are hardly affected by increasing the value of the interaction parameter between the monomers and the interface. On the other hand the amount of the copolymer located at about two to three gyration radii is more affected by this variation of the interaction parameter. Increasing the value of  $\chi$  results in stretching the copolymer coil in its rich phase. These results support the picture that the copolymer behaves as it would consist of two independent homopolymers.

The stretching of the block copolymer chains in diblock copolymer melts was studied previously by different authors[20], [70], and [87]. The results obtained above show that one of the effects of the interface is the stretching of the copolymer chain. Both theo-

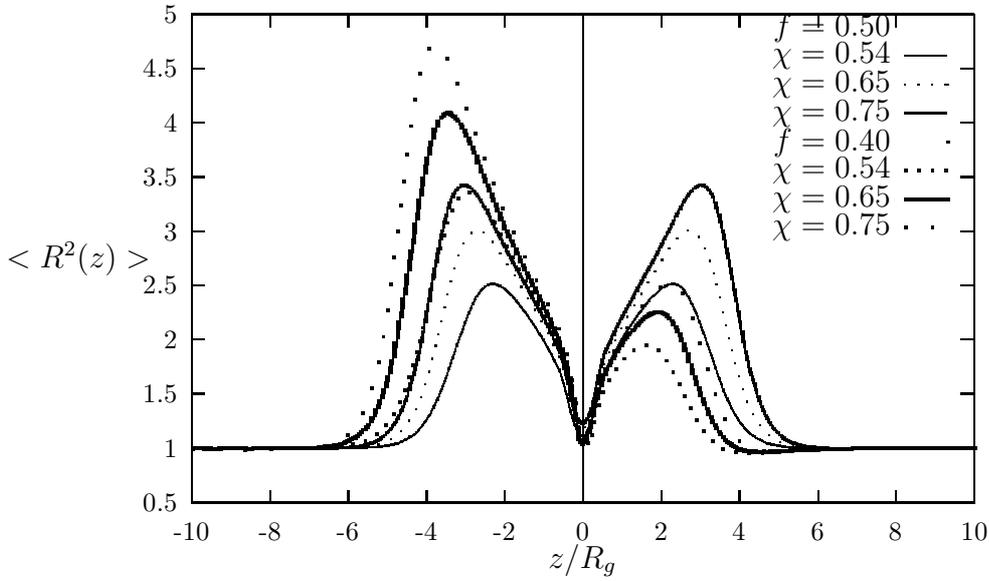


Figure 5.7.: The mean square end-to-end distance in unites of  $a^2N/3$ , plotted vs.  $z/w_{SSL}$ . The results are shown for different values of  $\chi$  for  $f = 0.5$  and  $0.4$ .

retical and experimental work, confirm the stretching of copolymers at interfaces. The Leibler's theory of the microphase separation [38] predicts that the copolymer chains do not stretch in the weak segregation regime, while the theories of the strong segregation regime [100] predict stretching of the copolymers.

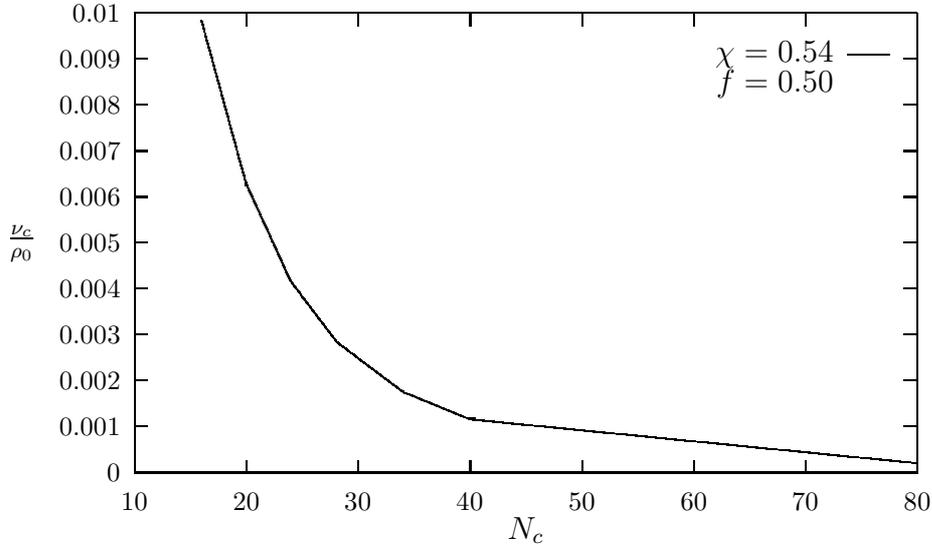


Figure 5.8.: The molecular surface excess of the copolymer, plotted vs.  $N_c$ .

### 5.1.3. The interfacial tension of the copolymer chain

Finally the dependance of the molecular surface excess and the reduction of the interfacial tension on the degree of polymerization is plotted in figures (5.8) and (5.9). Here we examine the importance of the degree of polymerization  $N_c$  on the tendency for a block copolymer to segregate onto the interface and reduce the interfacial tension. However, as shown in figures(5.1& 5.5), the copolymer chains are localized at the interface, with the two blocks extending into their respective rich phase. This localization of the copolymer chain in the central region is accompanied by an increase in the density of the copolymer chain at the interface, and therefore a decrease in the interfacial tension. Fig.(5.8) shows the molecular surface excess of the copolymer chain as a function of the degree of polymerization and Fig.(5.9) shows the reduction of the interfacial tension as a function of the degree of polymerization. At a given value of  $\chi$ , the ability of a block copolymer to reduce the interfacial tension is higher for smaller block copolymer. However, Noolandi *et al.* [30] computed the reduction of the interfacial tension as a function of the copolymer molecular weight. Their results shows that  $\Delta\gamma_c$  decreases as the molecular weight increases. The calculations of the mean field theory by Shull *et al.* [31], of the interfacial tension as well as the interfacial excess on dependence on the degree of polymerization of one block of the copolymer shows that, the interfacial parameters vary only slightly when the degree of polymerization of the shorter block is altered but vary significantly when the degree of polymerization of the longer block is altered. A close look on the experiment of Hu *et al.* [46], shows that the reduction of the interfacial tension of the ternary system,  $PS4K/[PDMS4.5K + P(S - b - DMS)]$  decreases as a function of the copolymer concentration. At a critical value of the copolymer concentration the reduction of the interfacial tension is limited. This limitation could be due either to saturation of the interface or micelle formation by the diblock copolymer. As one expect

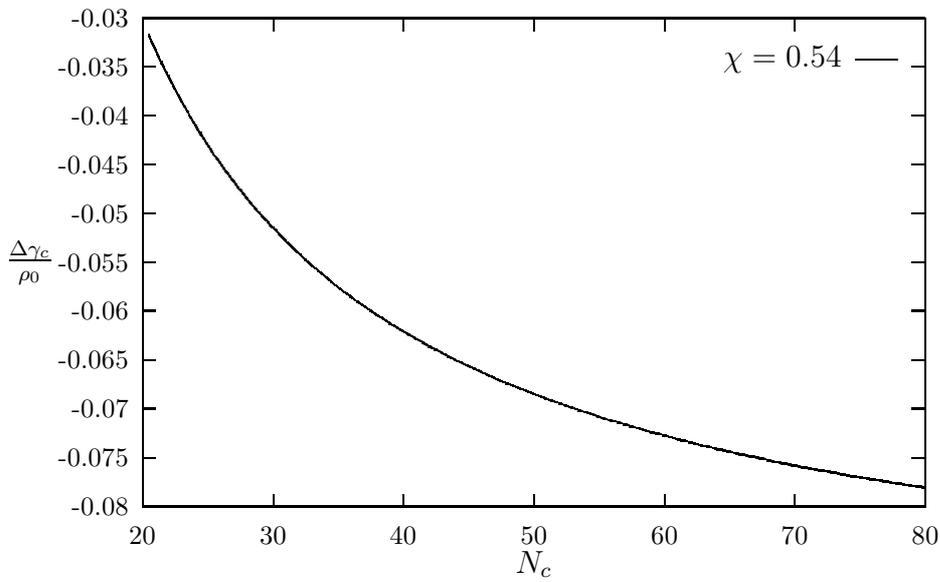


Figure 5.9.: The reduction in the interfacial tension of the copolymer, plotted vs.  $N_c$ .

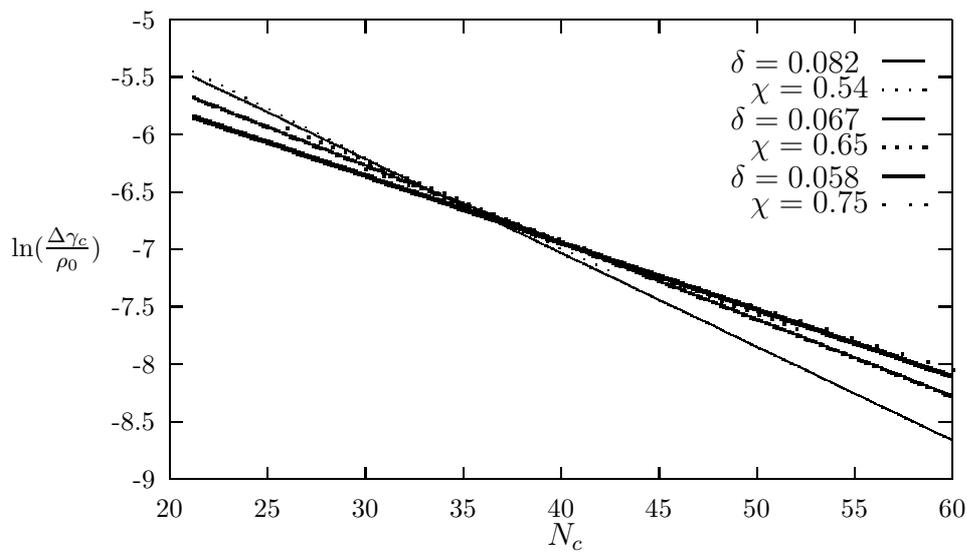


Figure 5.10.: The natural logarithm of the reduction in the interfacial tension as a function of  $N_c$  and its corresponding straight line,  $\delta$  is the slope of the line. The results are shown for different values of  $\chi$  and the corresponding exponent  $\delta$  for  $f = 0.50$ .

a small amount of diblock copolymer can reduce the interfacial tension significantly. On the other hand the above figures shows that the reduction of the interfacial tension obeys the following simple scaling law  $\Delta\gamma_c \sim N_c^{-\delta}$  where  $\delta$  is an exponent. For example the value of  $\delta = 0.067$  when  $\chi = 0.54$ . Fig.(5.10) shows the logarithm of the reduction of the interfacial tension as a function of the degree of polymerization for different values of  $\chi$ . The value of  $\delta$  is obtained by fitting the logarithm of the reduction of the interfacial tension by a straight line. This fit shows that the value of  $\delta$  decreasing with increasing the value of  $\chi$ .

## 5.2. Adsorption of a semiflexible polymer onto interfaces

### 5.2.1. Isotropic interaction

The adsorption of a flexible polymer onto an interface can be mapped onto the problem of the existence of a bound state for a quantum mechanical particle in a potential well. It is known from the Quantum Mechanics [98] that in  $d = 1$  only the quantity  $W_0 a$  is relevant, while for  $d \geq 2$  the quantities under consideration (localization length *etc.*) depend on both the strength of the potential  $W_0 a^2$  and the width  $a$  of the potential. For semi-flexible polymers the border dimension, where the explicit dependence on the width  $a$  appears, is  $d = 1$ . The dependence of the crossover length  $x$  (measured in units of  $l_p$ )

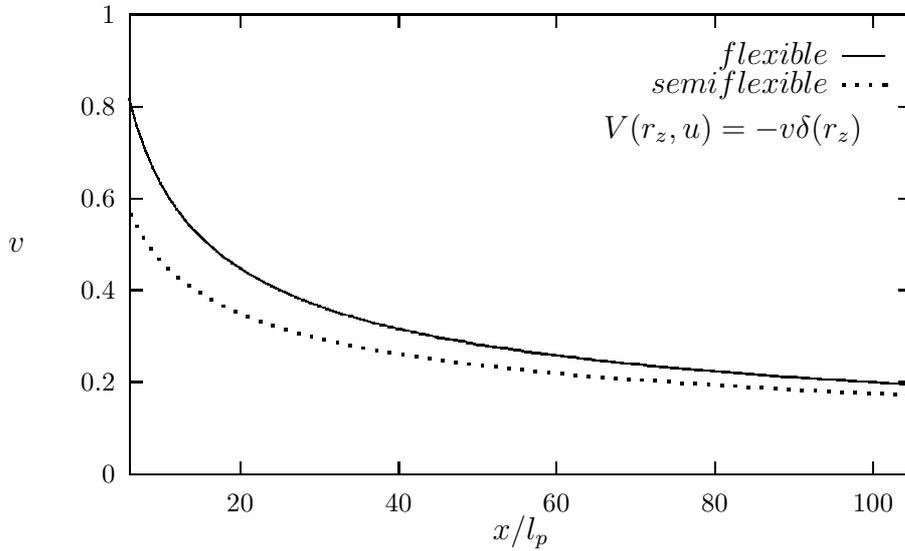


Figure 5.11.: The crossover length  $x$  vs. strength of adsorption  $v$  for both flexible and semiflexible polymers.

on the strength of attraction  $v$  is plotted in Fig.(5.11) for a particular value of  $t_0 = 0.1$ . As a comparison the  $v - x$ -dependence for a flexible polymer is also plotted. Fig.(5.11) shows that the semiflexible polymers adsorb easily than the flexible one. This is due to the fact that the entropy of the semiflexible polymer is less than for flexible one. This result has been confirmed in many previous studies. On one hand Leermakers *et al.* [80] found that the adsorption of semi-flexible polymers at liquid-liquid interface is largely affected by the rigidity of the polymer chain. They considered a semi-flexible polymer dissolves equally well in both liquids. A self-consistent field model in the dilute regime is used in studying this system. They were able to show that the interfacial width, the persistence length, and the chain length are relevant parameters in the adsorption behavior. The stiffness of the polymer chain plays a an essential role in determining the adsorbed amount at the interface and the density profiles. Increasing the stiffness of the polymer

chain implies an increase in the adsorption amount and consequently making the adsorption easier at the interface. On the other hand Monte Carlo simulations on a mixture of

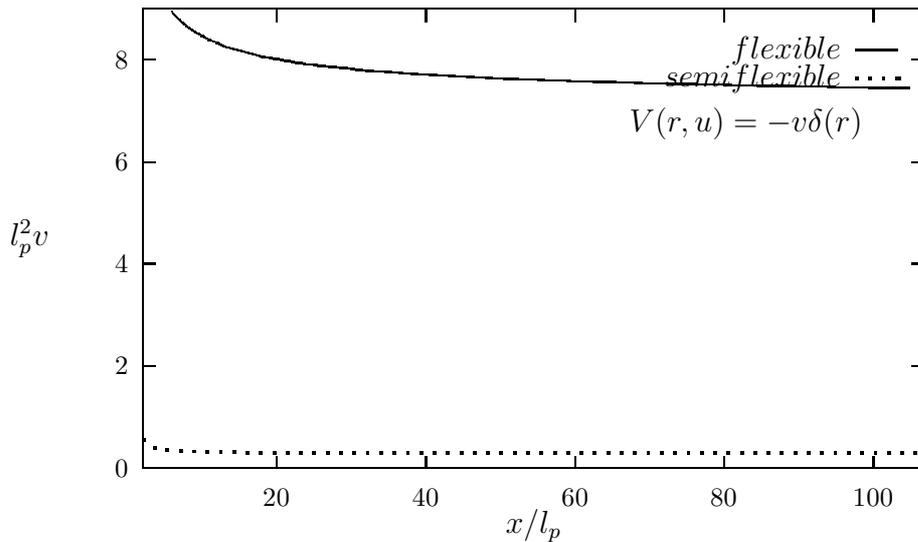


Figure 5.12.: The crossover length  $x$  vs. strength of adsorption  $v$  for both flexible and semiflexible polymers.

flexible and semiflexible chains show that the stiff chains near a Fresnel interface (*i.e.*, infinitely sharp) adsorb easier than the flexible ones [75], [96]. The above studies were concerned with studying the adsorption of the semiflexible polymers applying theoretical treatments, and they attributed their results by a pure entropic effects. However Hariharan *et al.* [77] reported the neutron reflectivity experimental measurements of the isotopic effect in the surface behavior of binary polystyrene blends of symmetric and disparate molecular weight near an air surface. They found that the segments of the deuterated polymer (typical miscible polymer blends) are always partitioned preferentially to the free sharp interface when nearly symmetric polymer blends are considered. This interfacial segregation is driven by a purely energetic effects, specified by the interaction parameter  $\chi$ . Kuznetsov and Sung [73] considered the homogeneous semiflexible polymers attracted by a field from a flat surface. This field is characterized by the range  $b$  and depth  $U$  as a hard square-well potential, neglecting intersegmental interactions (including *excluded volume* interactions). Using the scaling theory and the Green's function perturbation theory they were able to show that there is a desorption-adsorption transition and the semiflexible polymer adsorption energy decreasing with increasing the persistence length. In context of polymer blends, Fredrickson and Donley [102] have implemented a phenomenological density functional theory. Their analysis showed that the surface segregation in a related system, an athermal long chain mixture of purely Gaussian macromolecules with different statistical segment lengths can be driven by nonlocal entropic effects. They concluded that when a blend of polymers with different stiffness are placed near surface the less flexible component will segregate to the sur-

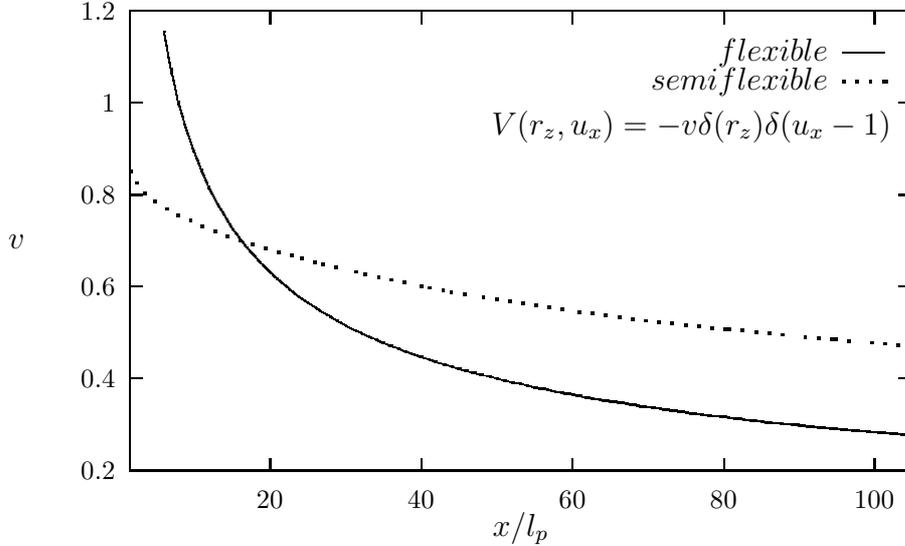


Figure 5.13.: The crossover length  $x$  vs. strength of adsorption  $v$  for both flexible and semiflexible polymers.

face. The possible relevance of this work the experiment on microphase separated block copolymers has implied by Sikka *et al.* [103] by identifying the more flexible polymer in the theory with the block that has more flexibility will segregate to the surface. The study of adsorption of a semiflexible polymer chain is not restricted to the use of the approximate Gaussian distribution function given above. Instead of it one can use in Eq.(4.5) the exact distribution function (*i. e.*, Eq.(2.9)) found recently by Wilhelm and Frey [62] or an approximate distribution function, which correctly describe the peak of the distribution function at  $r = l_p$  [104] (see Fig.(5.15)). One can also attempt to solve approximately the integral equation (4.2) for a potential well with finite  $W_0$  and  $a$ . Fig.(5.12) shows the dependence of the crossover length  $x$  on the strength of the attraction potential  $v$  for the adsorption of a semiflexible polymer onto a penetrable sphere. The  $v - x$ -dependence for a flexible chain is also plotted for a comparison. For both flexible and semiflexible polymers the critical strength of attraction,  $W_c$ , is necessary. This is due to the fact that the integral in (4.12) converges for  $x \rightarrow \infty$ . While for a flexible polymer the threshold value of the strength of adsorption  $v_c$  is proportional to  $t_0^{1/2}$ , for a semiflexible polymer it is proportional to  $t_0^2$ .

### 5.2.2. Isotropic-anisotropic interaction

In the last subsection, we have investigated the strength of attraction  $v$  as a function of the crossover length  $x$ , for the case where no anisotropic interaction is presented. Here we will consider the effect of the anisotropic interaction on the adsorption behavior of the semiflexible chain near an attractive interface. Fig.(5.13) shows the  $v - x$ -dependence for the anisotropic interaction. In the present case the anisotropy of the interaction align the

semiflexible polymer parallel to the interface ( which is assumed to be in the  $xy$ -plane) with slope equal to one with respect to the  $x$ -direction. This means that for a polymer adsorb at the interface it should leave the interface with slope equal to one and return back with the same slope. It is clear from Fig.(5.13) that adsorption of the semiflexible polymer chain onto the structured interface is more difficult in comparison with the case where no anisotropy is present. Another possible case when the anisotropy derive the semiflexible polymer to adsorb to the interface but using different kind of anisotropic interaction. In this case the polymer is attracted to the interface by a potential of the form  $-v\delta(z)\delta(v_z)$ . Lässig *et al.* [81] considered this type of interaction in the framework of field–theoretical method. In this work, they considered a fluid membranes or semi–flexible polymers subject to a field which makes the contacts of the polymer system always has a preferred orientation parallel to the defect. The perturbation theory calculations imply that the system undergoes a delocalization transition. Fig.(5.14)

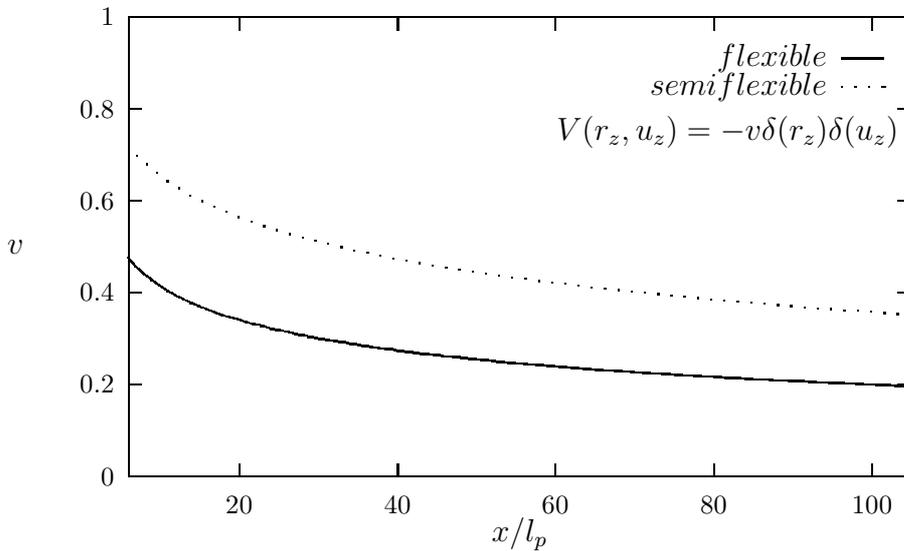


Figure 5.14.: The crossover length  $x$  vs. strength of adsorption  $v$  for both flexible and semiflexible polymers.

shows the adsorption behavior of the chain due to this potential. As it is expected the semiflexible polymer chains adsorb easier than the flexible ones. A clear picture which shows the adsorption strength of the semiflexible polymer chain for different interaction potentials given in Fig.(5.15). Using the distribution proposed by S. Stepanow [88], the easier adsorption is the case of isotropic interactions. While in the case of Wilhelm and Frey [62] distribution function it is much easier for the semiflexible polymer chain to adsorb than the previous case. This is because in obtaining the latter distribution function no restriction was made on the magnitude of the tangent vector. The other two anisotropic interactions plotted in the same figure show that in the case  $u_x$  dependent anisotropic interaction the polymer is harder to adsorb at the interface. This is due to the fact that it reduces the possible number of adsorption states of the polymer

chain more than in the other two cases. Therefore the coupling way between the spatial isotropic and orientational anisotropic interactions can affect the adsorption of the chain and consequently affect the adsorption density profiles at the interface ( for example see Fig.(5.16)).

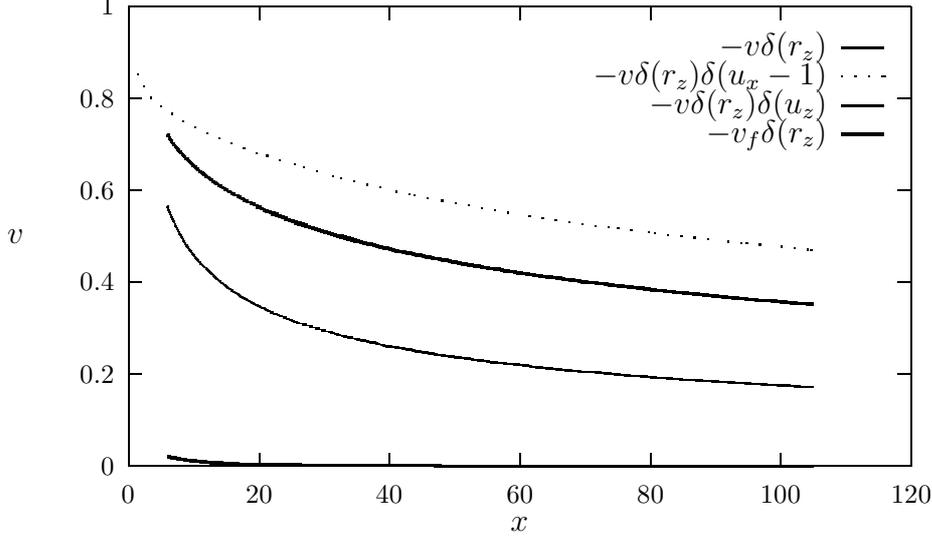


Figure 5.15.: comparison of the strength of adsorption  $v$  of semiflexible polymers with different interaction potentials.

### 5.2.3. Distribution function: Isotropic interaction

The distribution function of the adsorbed polymer chain and therefore the localization length can be obtained from the inverse Laplace transform of Eq.(4.5). The main contribution of the inverse Laplace transform for a large chain is due to the pole, which is given by  $p = 1/x$  with  $x$  being the solution of adsorption condition (4.5). Thus, the  $z$ -dependence of the distribution function is given by  $G_0(z, 1/x; 0)$ . Notes that taking into account only the pole in Eq.(4.5) in performing the inverse Laplace transform corresponds to the ground state dominance approximation. For a flexible chain the  $z$ -dependence is obtained as  $\exp(-|z|/\xi)$ , with the localization length  $\xi$  given by  $\xi = \sqrt{x}$ . The  $z$ -dependence of the distribution of the free end of the semiflexible polymer is shown in Fig.(5.16), and Fig.(5.17) for critical adsorption strength  $v_c = 0.10463$ , and  $0.50463$  respectively. Different values of  $l_p$  (or alternatively  $x_c$ ) which correspond to the same critical adsorption strength have been displayed in the graphs. In both figures the deviation from the exponential decay is more pronounced with increasing the persistence length  $l_p$  ( or decreasing the crossover length  $x_c$ ). Also it is clear that increasing the strength of the adsorption increasing the localization of the semiflexible polymer

chain into the interface. These results in agreement with [73], also this behavior can be interpreted as tendency for a first order liquid–crystalline phase transition. However our study gives no evidences for the first order liquid–crystalline phase transition predicted by Kuznetsov and Sung [73] for a polymer chain with finite persistence length  $l_p$ . Also we have studied the behavior of the distribution function for different values of  $v_c$ . Fig.(5.18), and Fig.(5.19) show the non–exponential decay is more pronounced as the  $v_c$  increases. Comparing both figures as  $l_p$  increases the polymer chain becomes more localized at the interface. Finally we have shown the phase diagram ( $l_p - x$ ) for different values of  $v_c$ . For all values of  $v_c$  the persistence length decreasing as the crossover length increasing. Also one should notes that decreasing the value of  $v_c$  implying that an increase in the value of  $l_p$  at one particular crossover length.

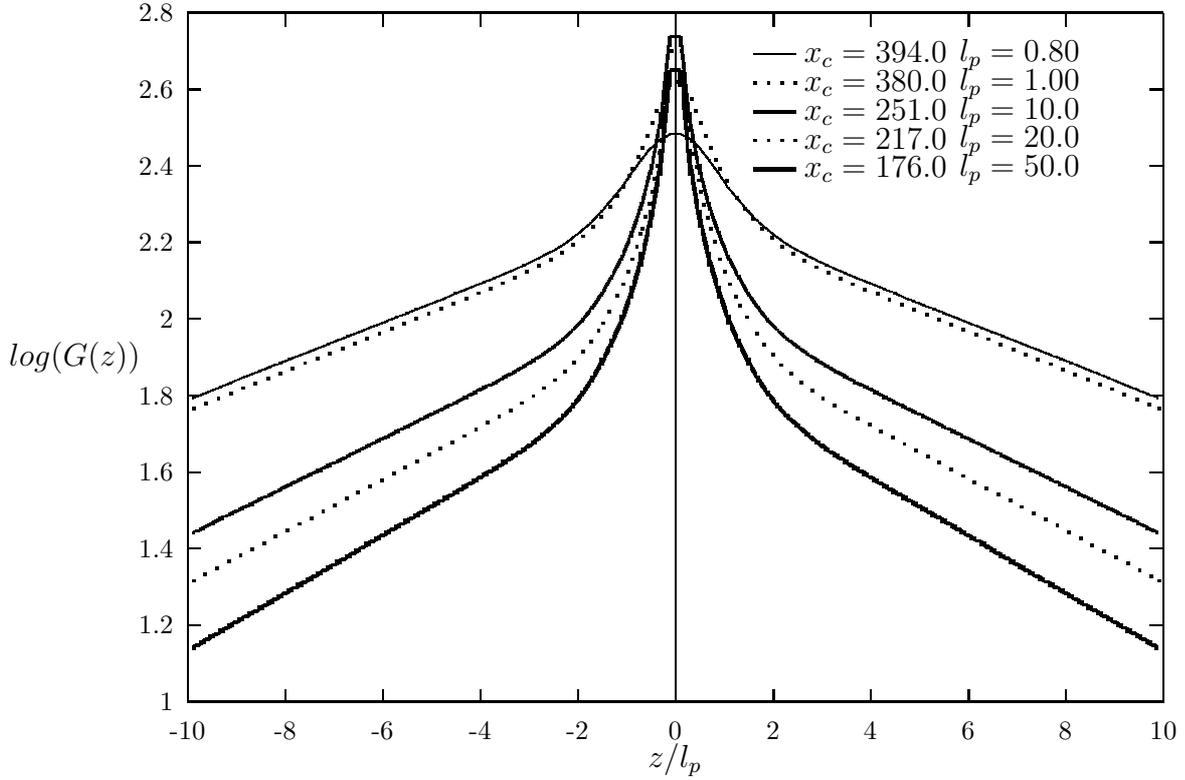


Figure 5.16.: The logarithmic of the distribution function, plotted as a function of the distance from the interface  $z$  for the potential  $V(r_z) = -v\delta(r_z)$ .

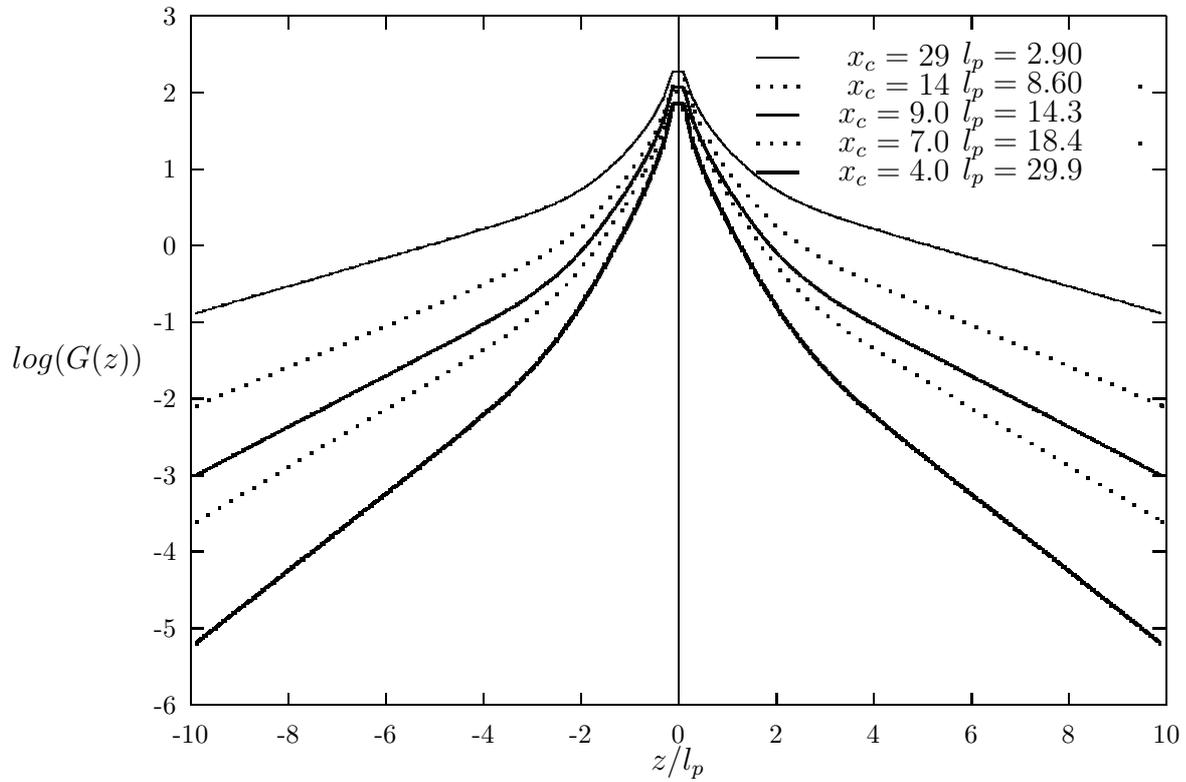


Figure 5.17.: The logarithmic of the distribution function, plotted as a function of the distance from the interface  $z$  for the potential  $V(r_z) = -v\delta(r_z)$ .

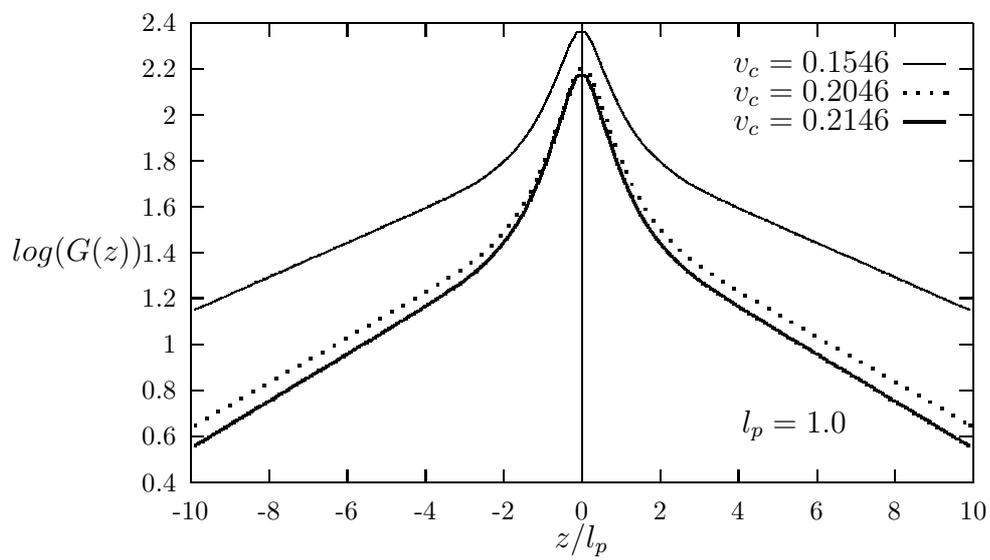


Figure 5.18.: The logarithmic of the distribution function, plotted as a function of the distance from the interface  $z$  for the potential  $V(r_z) = -v\delta(r_z)$ .

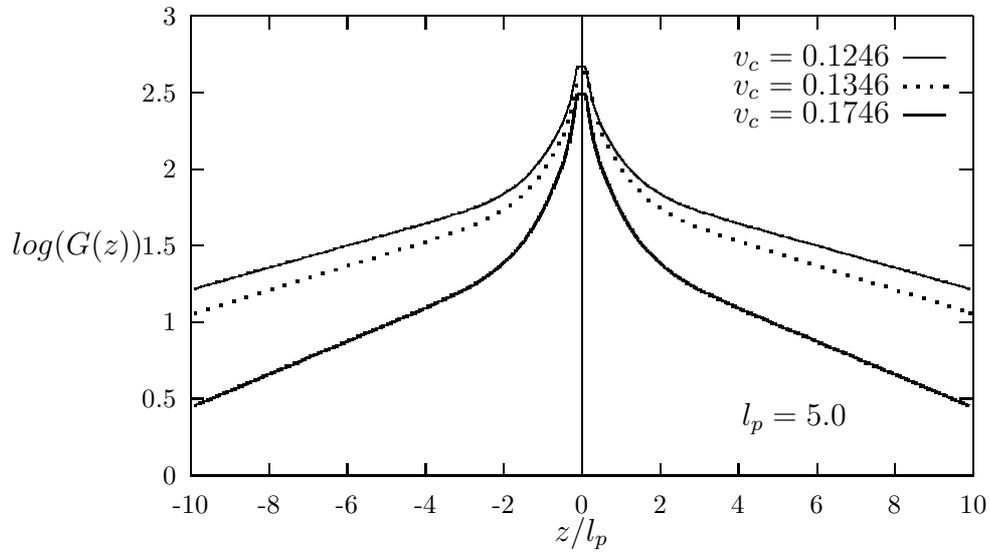


Figure 5.19.: The logarithmic of the distribution function, plotted as a function of the distance from the interface  $z$  for the potential  $V(r_z) = -v\delta(r_z)$ .

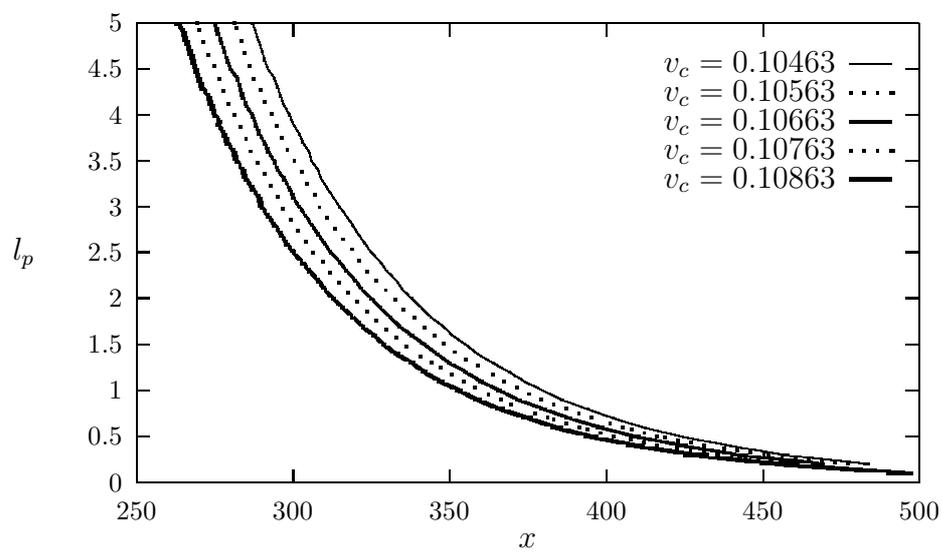


Figure 5.20.: The persistence length, plotted as a function of the crossover length  $x$  for different strength of adsorption  $v$  for the potential  $V(r_z) = -v\delta(r_z)$ .

## 6. Conclusions

The central aim of this work is to answer and address the question what is the influence of an attractive interface on the interfacial properties of a polymer chain. In particular we have studied the adsorption properties of diblock copolymer chain and semiflexible polymer chain in the presence of an attractive interface. Studying and understanding such polymer systems is a challenge for theoretical and experimental scientist and it's a growing field in polymer physics. Interest in such studies comes from vastly different fields ranging from industrial to biological applications. On one hand understanding the behavior of flexible polymeric materials is important in several practical applications including adhesion, catalysis, lubrication, and polymer processing. For these processes, the structure and the properties of the material within a certain width from the interface are critical. For example, in isotopic blends of similar molecular weight, the slightly weaker intermolecular interactions of the deuterated polymer causes this component to segregate preferentially to the interface. On the other hand the wide range of the applications (*e.g.*, liquid–crystalline ordering) of semiflexible polymeric materials stem from the crucial importance of elasticity. Biopolymer macromolecules such as spectrin, actin, *DNA* and other biological materials have provide physicists with the most practical models to test their theories of soft matter. For example, recently the concept of normal modes in dynamics of polymeric macromolecules has been verified experimentally, that *DNA* can be stretched up to 30% of its initial end–to–end distance of its contour length [105].

The presence of *AB* copolymers at an interface between two immiscible fluids or homopolymers is crucial to properties such as interfacial tension, stretching, and density profiles. However the copolymers diffuse to interface between the two liquids. Subsequently, the *A*–blocks will extend into the *A* solvent and the *B*–blocks will stretch into the compatible *B* solution. Through this phenomena, diblock copolymers serve as compatibilizers, and therefore reduce the interfacial tension between the two fluid phases. For oil–water interface, the copolymers that are utilized in these applications are amphiphilic in nature: one component is soluble in the oil phase, while the other is water–soluble. This difference in solubilities drives the copolymers to adsorb at the boundary of the two fluid phases. In other words, the localization of the copolymer chain at penetrable interface stabilizes the boundary and enhances the efficiency of the

mechanical properties of the interface. Therefore the diblocks that constitute the most effective additives "compatibilizers" contain blocks that have a specific affinity for one of the solution phases. This behavior arises mainly from the energetically preferred orientation of the blocks at the interface into their respective compatible rich phase. Since the copolymers confinement at the interface is associated with a reduction in the interfacial tension, the mean counter term in this process is the entropy loss of the copolymers which localize at the interface.

Studying the adsorption properties of semiflexible polymers at penetrable interfaces has been of considerable interest since many years ago. Different Adsorption behavior may be seen in a variety of long-chain systems at low temperature, such as some biological macromolecules with intrinsic stiffness (*e.g.*, *DNA*). The backbone stiffness, one of the basic characteristics of polymer properties, which is governed by the persistence length  $l_p$  is of course of practical use. The stiffness (or rigidity) character of the polymer chain can induce an order-disorder phase transition at a critical temperature. This transition temperature depends preliminarily on the chemical structure of the macromolecular compound. Among the many significant phenomena induced by polymer stiffness is the nematic liquid-crystalline (A state of matter that is sometimes observed intermediate between a solid crystal and isotropic liquid.) ordering of semiflexible segments near attractive surfaces and interfaces. In general this liquid-crystalline ordered phases due to anisotropic interactions between semiflexible polymeric materials. However, polymers with different stiffness near attractive surfaces or interfaces, show that the segments of the stiffer polymer always partition to the interface. This segregation of the polymer chain to the interface is purely entropic effect: the stiffer chain losses less entropy when adsorbs into the interface. However, in this context one should also be aware of the fact that it is in practice difficult to change the stiffness of molecules without changing other interaction. Related to this drawback, some recent neutron reflectivity experiments reported that enthalpic effects play a more important role than entropic ones. In other words, when one tries to change the stiffness of a polymer chain, it is possible to change its energetic interactions with its surroundings.

In the first part of the thesis we discussed the interfacial properties of a single diblock copolymer chain near an attractive interface between two solvents [106]. The interaction between the interface and the monomers of the diblock chain is modulated by a constant external potential strength  $\chi$ . In contrast to the self-consistent field theory in which the mean field potential is related to the composition of the polymer system, the potential acting on the diblock copolymer chain is considered as an external one and it is not subject to the self-consistent procedure. The advantage of such a simplified approach is that it makes possible to use the exact analytical solution for the Green's function in a present of an penetrable attractive interface. We considered an *AB*-block copolymer chain, which is composed of *A*-block of length  $N_A$ , and *B*-block of length  $N_B$ . The copolymer interacts with the interface in such a way that *A*-monomers prefer to be in

the right half plane, while the  $B$ -monomers prefer to be in the left half plane. In other word, the diblock copolymer chain that are utilized in this application are amphiphilic in nature. Therefore, a set of equations describing the interfacial properties of the diblock copolymer near a penetrable interface are derived. These equations give the exact results of the various physical quantities of the diblock copolymer chain. We have studied the mean-square end-to-end distance of the copolymer chain  $\langle R^2(z) \rangle$ , as a function of the distance of the join point of the copolymer to the interface (*i.e.*,  $z$ ), the segment density distribution  $\rho(z)$ , and the reduction of the interfacial tension in the presence of the diblock copolymer chain  $\Delta\gamma_c$ .

The density profiles of the  $AB$ -block copolymer chain for different compositions  $f$ , and interaction parameter  $\chi$  have been explored. In studying the density profiles for different  $f$  with fixed  $\chi$ , and in contrast to the symmetrical composition (*i.e.*,  $f = 0.50$ ) in which the copolymer density profile is symmetric with respect to the position of the interface at  $z = 0$ , we have found that the density profile is asymmetric for  $f = 0.30$  or  $0.70$ . The general trend of them is that the copolymer chain prefers the region where the concentration of one kind of monomers is rich. The case of symmetrical composition shows a very good agreement with the prediction of the Monte Carlo Simulations. In the case of strongly asymmetrical compositions ( $f = 0.999$  or  $f = 0.001$ ) the whole profile appears to be very similar to a profile of a pure homopolymer chain. Also the density profile of the individual copolymer blocks for different compositions are presented (see Fig.(5.4)), and it confirms the picture that the polymer chain prefers to extend into its own rich phase. As one can see the asymmetry in the copolymer chain plays an important role in determining the character of the behavior of the chain at the interface. Also, the dependence of the interfacial profile on the interaction parameter  $\chi$  is discussed. At symmetrical composition and for different values of  $\chi$ , the density profile of the copolymer chain is affected by the variation of the interaction parameter between the monomers and the interface. We have found that increasing the value of  $\chi$  tends the monomers to segregate into the interface making the density profile narrower and vice versa. This phenomenon can be interpreted as a localization of the copolymer at the interface. Also we have predicted that the peak of the distribution are broader than the gyration radius. A good agreement was found between our results and the results of experimental data and the simulations.

The stretching properties of the diblock copolymer chain are discussed in this context. The copolymer coil stretching in the direction perpendicular to the interface investigated via studying the  $z$ -component of the mean-square end-to-end distance. We considered different compositions and we have demonstrated that the copolymer coil is stretched in the direction perpendicular to the interface. In the case of symmetrical composition, we have compared our results with Monte Carlo Simulations. The agreement is found to be qualitatively good. The effect of the stretching is very strong for blocks centered at about two to three gyration radii away from the interface, but almost

disappears for copolymers centered at the interface (*i.e.*,  $z = 0$ ). In addition, we have studied the effect of changing the strength of the interaction parameter on the stretching property of the diblock chain. We have found that the central region and the wings of the copolymer profile are hardly affected by increasing the values of  $\chi$  for any value of  $f$ . On the other hand the amount of the copolymer located at about two to three radii of gyration is more affected by this variation of the interaction parameter. Increasing the value of  $\chi$  results in stretching the copolymer coil in its own rich phase. These results support the picture that the copolymer behaves as it would consist of two independent homopolymer blocks, which hardly feel the effect of being linked together at the joint point.

Finally we made predictions on the dependence of the molecular excess and the reduction of the interfacial tension on the degree of polymerization  $N_c$  for  $f = 0.50$  and  $\chi = 0.54$ . Here we examined the influence of the degree of polymerization on the tendency for a copolymer to segregate onto the interface and reduce the interfacial tension. However, as discussed above the copolymer chains are localized at the interface, with the two blocks extending into their respective rich phase. This localization of the copolymer chain in the central region is accompanied by an increase in the density of copolymer chain at the interface, and therefore a decrease in the interfacial tension. The reduction of the interfacial tension is higher for smaller block copolymer, so that a small amount of diblock copolymer can reduce the interfacial tension significantly. Also we have derived a scaling law for the reduction of the interfacial tension as a function of the polymerization degree as  $\Delta\gamma_c = N_c^{-\delta}$ . The value of  $\delta$  is obtained by fitting the logarithm of the reduction of the interfacial tension by a straight line. We have predicted that the value of  $\delta$  is decreasing with increasing the value of the interaction parameter  $\chi$ .

In the second part of this work we discussed the adsorption properties of a semiflexible polymer chain near an attractive penetrable interface [107]. As it is well known the importance of the semiflexible polymer emerges from its application in different physical phenomena. Here we considered different types of interactions between the polymer chain and interface. Such interactions lead to different adsorption behavior of the chain onto a penetrable interface. In particular we examined the effect of isotropic interaction (in one- and three-dimensions) as well as anisotropic ones. We have studied the adsorption of the semiflexible polymer chain onto a penetrable sphere and structured interface. Also the effect of changing the persistence length  $l_p$  is investigated. We have introduced a Green's function for the semiflexible chain by solving an integral equation for all types of interactions. In fact we have mapped our problem onto the problem of the existence of a bound state in the quantum mechanical particle in a potential well. The strength of the attraction  $v$  can be expressed through the depth  $W_0$  and the width  $a$  of the potential well as  $v \rightarrow W_0 a^d$ . Due to the stiffness of the semiflexible polymer chain, a cutoff  $t_0$  is introduced as  $t_0 = a/l_p$ . The border dimension of the semiflexible polymer chain is  $d = 1$ . Therefore the explicit dependence on  $a$  appears at this dimension, and

the only relevant quantity is the strength of the potential  $W_0a$ . For  $d \geq 2$  the relevant physical quantities depend on both the strength of the potential  $W_0a^d$  and the width  $a$ . Consequently, we found and studied different relations between the adsorption strength  $v$  and the crossover length  $x$ . In the case of isotropic interaction the distribution function of the free end of the semiflexible polymer chain is studied as a function of a distance from the interface for different persistence length  $l_p$ , and critical adsorption  $v_c$ . Also the phase diagram of  $l_p$  as a function of  $x$  for different  $v$  is presented.

The adsorption of the semiflexible polymer chain onto an interface and penetrable sphere in the case of isotropic interactions is studied. The dependence of the crossover length (measured in units of  $l_p$ ) on the strength of the attraction for flexible and semiflexible chains is investigated. We have found that the semiflexible polymer chain adsorbs easier than the flexible one when they are under the influence of an attractive penetrable interface. This is because when the semiflexible polymer adsorbs onto the interface it loses less entropy in comparison with the flexible one. In other words, an increase of the stiffness of the polymer chain makes the adsorption at the interface easier. Such behavior has been confirmed by previous theoretical and experimental studies. The adsorption of the semiflexible polymer chain in the presence of isotropic–anisotropic interaction is studied. This case can be thought to model the behavior of the polymer chain near a structured interface. It shows that the adsorption becomes more difficult in comparison with the isotropic case. In fact two types of anisotropic interactions were considered. The one which has the  $v_x$ –component dependence tends to make the adsorption more difficult than the one which has the  $v_z$ – component dependence. Also when using the distribution function proposed by Wilhelm and Frey, we found that it is easier for the semiflexible polymer to adsorb at the interface.

The study of the adsorption of the semiflexible polymer chain at penetrable interfaces enables one to obtain the distribution function of the chain employing the inverse Laplace transform technique. The main contribution of the inverse Laplace transform comes from the pole of the Green’s function of the semiflexible polymer chain. This is equivalent to the ground state dominance approximation. We have found that increasing the value of  $l_p$  making the non-exponential decay more pronounced, and therefore tends the polymer chain to be more localized at the interface. This behavior can be interpreted as tendency for the semiflexible polymer chain to form liquid–crystalline phase.

# A. Computation of the first and second moments

The expression of the normalization constant  $\Omega$  can be written as

$$\Omega = \int_{-\infty}^{+\infty} \rho(z) dz. \quad (\text{A.1})$$

Using Eqs.(3.10,3.11 and 3.12) , then Eq.(A.1) becomes

$$\Omega = \int_{-\infty}^{+\infty} [I_-(z, f)I_+(-z, 1-f)\Theta(-z) + I_-(-z, 1-f)I_+(z, f)\Theta(z)] dz \quad (\text{A.2})$$

where  $I_-(z, f)$ , and  $I_+(z, f)$  are given in Eqs.(3.13, 3.14) respectively.

Simple and straightforward calculations lead to

$$\begin{aligned} \Omega = & 4\sqrt{\frac{3R_g^2}{\pi f(1-f)}} \frac{1 - e^{-f\chi N}}{N} + \frac{2}{\pi} \sqrt{\frac{3R_g^2}{\pi}} \int_0^1 \frac{\arctan(\frac{1-f}{f}w)}{\sqrt{(1-w)/(1-f)}} (e^{\chi(1-f)Nw - \chi N} + e^{\chi(1-f)Nw}) dw \\ & + \frac{2}{\pi} \sqrt{\frac{3R_g^2}{\pi}} \int_0^1 \frac{\arctan(\frac{f}{1-f}u)}{\sqrt{(1-u)/f}} (e^{\chi f N u - \chi N} + e^{-\chi f N u}) du \\ & + \frac{1}{\pi} \sqrt{\frac{3R_g^2}{\pi N}} \int_0^1 \int_0^1 \frac{1}{N(1-u)(1-w)(fu + (1-f)w)} \\ & [e^{-\chi N f + \chi N(fu - (1-f)w)} + e^{-\chi N(1-f) - \chi N(fu - (1-f)w)}] dw du. \end{aligned}$$

The expressions of the moments  $z_0^2$  , and  $z_0$  are given by the following

$$\begin{aligned} \langle z_0^2 \rangle &= \frac{1}{\Omega(z)} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} z_0^2 G_\chi(z', N_A; z) G_\chi(z, N_B; z_0, 0) dz_0 dz' \\ \langle z_0 \rangle &= \frac{1}{\Omega(z)} \int_{-\infty}^{-\infty} z_0 G_\chi(z', N_A; z) G_\chi(z, N_B; z_0, 0) dz_0 dz'. \end{aligned}$$

After a tedious but straightforward calculations we obtained

$$\langle z_0^2 \rangle = J_-(z, N_B)\Theta(-z) + J_+(z, N_B)\Theta(z), \quad (\text{A.3})$$

$$\langle z_0 \rangle = L_-(z, N_B)\Theta(-z) + L_+(z, N_B)\Theta(z), \quad (\text{A.4})$$

where  $J_-(z, N_B)$  can be calculated as follows

$$J_-(z, N_B) = \frac{1}{\Omega(z)} \int_{-\infty}^0 \int_{-\infty}^0 z_0^2 G_\chi(z', N_A; z) G_\chi(z, N_B; z_0, 0) dz_0 dz',$$

since the variables  $z_0$ , and  $z$  are independent, then we can rewrite the above equation as

$$= \frac{1}{\Omega(z)} I_-(z, f) \int_{-\infty}^0 z_0^2 G_\chi(z, N_B; z_0, 0) dz_0,$$

hence

$$J_-(z, 1-f) = \frac{I'_-(z, 1-f)}{I_-(z, 1-f)}, \quad (\text{A.5})$$

where

$$\begin{aligned} I'_-(z, 1-f)/R_g^2 &= (6(1-f) + z^2/R_g^2) \operatorname{erf}\left(\frac{-z/R_g}{\sqrt{12(1-f)}}\right) - \\ &\sqrt{\frac{3(1-f)}{\pi}} (z/R_g) e^{\left(\frac{-(z/R_g)^2}{12(1-f)}\right)} + \frac{12(1-f)}{\pi} \int_0^1 \sqrt{\frac{1-u}{u}} e^{-\chi N(1-f)(1-u)} \\ &e^{\left(\frac{-(z/R_g)^2}{12(1-f)u}\right)} du - 6(1-f) \int_0^1 e^{-\chi N(1-f)(1-u)} \operatorname{erf} c\left(\frac{-z/R_g}{\sqrt{12(1-f)u}}\right) + \\ &\frac{6(1-f)}{\sqrt{\pi}} \int_0^1 e^{-\chi N(1-f)(1-u)} \left\{ \frac{z/R_g}{\sqrt{3(1-f)}} \operatorname{erf} c\left(\frac{z/R_g}{\sqrt{12(1-f)u}}\right) + 2\sqrt{\frac{u}{\pi}} e^{\left(\frac{-(z/R_g)^2}{12(1-f)u}\right)} \right\}. \end{aligned} \quad (\text{A.6})$$

The expression of  $J_+(z, N_A)$  can be obtained in a similar way as,

$$\begin{aligned} J_+(z, N_A) &= \frac{1}{\Omega(z)} \int_0^\infty \int_0^\infty z_0^2 G_\chi(z', N_A; z) G_\chi(z, N_B; z_0, 0) dz_0 dz', \\ &= \frac{1}{\Omega(z)} I_+(z, f) \int_0^\infty z_0^2 G_\chi(z, N_B; z_0, 0) dz_0, \end{aligned}$$

therefore

$$J_+(z, 1-f) = \frac{I'_+(z, 1-f)}{I_+(z, 1-f)}, \quad (\text{A.7})$$

where

$$I'_+(z, 1-f)/R_g^2 = (6(1-f) + z^2/R_g^2) \operatorname{erf}\left(\frac{z/R_g}{\sqrt{12(1-f)}}\right) e^{-\chi N(1-f)} +$$

$$\begin{aligned}
& \sqrt{\frac{3(1-f)}{\pi}} (z/R_g) e^{\left(\frac{-z/R_g}{12(1-f)}\right)^2} e^{-\chi N(1-f)} + \frac{12(1-f)}{\pi} \int_0^1 \sqrt{\frac{1-u}{u}} e^{-\chi N(1-f)u} \\
& e^{\left(\frac{-z/R_g}{12(1-f)u}\right)^2} du - 6(1-f) \int_0^1 e^{-\chi N(1-f)u} \operatorname{erf} c\left(\frac{z/R_g}{\sqrt{12(1-f)u}}\right) + \frac{6(1-f)}{\sqrt{\pi}} \\
& \int_0^1 e^{-\chi N(1-f)u} \left\{ \frac{-z/R_g}{\sqrt{3(1-f)}} \operatorname{erf} c\left(\frac{z/R_g}{\sqrt{12(1-f)u}}\right) + 2\sqrt{\frac{u}{\pi}} e^{\left(\frac{-z/R_g}{12(1-f)u}\right)^2} \right\}. \quad (\text{A.8})
\end{aligned}$$

Similarly the expressions of  $L_-(z, N_B)$  and  $L_+(z, N_B)$  can be calculated, and hence

$$\begin{aligned}
L_-(z, 1-f)/R_g &= z/R_g + \sqrt{\frac{3(1-f)}{\pi}} \int_0^1 \sqrt{\frac{1}{u}} e^{-\chi N(1-f)(1-u)} e^{\left(\frac{-z/R_g}{12(1-f)u}\right)^2} du - \\
& \sqrt{\frac{3(1-f)}{\pi}} \int_0^1 \sqrt{\frac{1}{1-u}} e^{-\chi N(1-f)(1-u)} \operatorname{erf} c\left(\frac{-z/R_g}{\sqrt{12(1-f)u}}\right) du, \quad (\text{A.9})
\end{aligned}$$

and

$$\begin{aligned}
L_+(z, 1-f)/R_g &= z/R_g e^{-\chi N(1-f)} - \sqrt{\frac{3(1-f)}{\pi}} \int_0^1 \sqrt{\frac{1}{u}} e^{-\chi N(1-f)u} e^{\left(\frac{-z/R_g}{12(1-f)u}\right)^2} du + \\
& \sqrt{\frac{3(1-f)}{\pi}} \int_0^1 \sqrt{\frac{1}{1-u}} e^{-\chi N(1-f)u} \operatorname{erf} c\left(\frac{z/R_g}{\sqrt{12(1-f)u}}\right) du \quad (\text{A.10})
\end{aligned}$$

## B. Solving the Integral Equation

The Green's function of the semiflexible polymer is given by Eq.(2.4) in chapter 2. This function depends on the space and orientational coordinates. By employing this function, one can obtain the Green's function of the polymer chain as a function of the distance perpendicular (*i.e.*, the  $z$ -component) to the interface only.

The Green's function (2.4) is a quadratic function of its variables. Therefore it can be written in the following form

$$G_0(\mathbf{r}, \mathbf{u}, L; \mathbf{r}_0, \mathbf{u}_0) = G_0(\mathbf{r}_{tr}, \mathbf{u}_{tr}, L; \mathbf{r}_{tr0}, \mathbf{u}_{tr0})G_0(z, u_z, L; z_0, u_{z0}), \quad (\text{B.1})$$

where  $G_0(\mathbf{r}_{tr}, \mathbf{u}_{tr}, L; \mathbf{r}_{tr0}, \mathbf{u}_{tr0})$  is the transversal Green's function, and  $G_0(\mathbf{z}, \mathbf{u}_z, L; \mathbf{z}_0, \mathbf{u}_{z0})$  is the longitudinal Green's function of the polymer chain, which is given by

$$\begin{aligned} G_0(z, u_z, L; z_0, u_{z0}) &= \left( \frac{1}{2\pi[1-\exp(-2L/l_p)]} \right)^{1/2} \\ &\times \left( \frac{1}{4\pi/l_p^2} \frac{1+\exp(-L/l_p)}{L/l_p-2+L/l_p \exp(-L/l_p)+2 \exp(-L/l_p)} \right)^{1/2} \\ &\times \exp \left[ -\frac{1}{2[1-\exp(-2L/l_p)]} [u_z - u_{z0} \exp(-L/l_p)]^2 \right. \\ &\left. - \frac{1}{4/l_p^2} \frac{1+\exp(-L/l_p)}{L/l_p-2+L/l_p \exp(-L/l_p)+2 \exp(-L/l_p)} \right. \\ &\quad \left. \left( z - z_0 + l_p \frac{1 - \exp(-L/l_p)}{1 + \exp(-L/l_p)} (u_z + u_{z0}) \right)^2 \right]. \end{aligned} \quad (\text{B.2})$$

In order to find  $G_0(z, L; z_0)$ , we multiply it by  $\exp(-u_{z0}/2)$  and integrate over  $u_z, u_{0z}$ , then the result is

$$G_0(z-z_0, L) = \int_{-\infty}^{-\infty} \int_{-\infty}^{-\infty} G_0(z, u_z, L; z_0, u_{z_0}) \exp(-u_{z_0}/2) du_z du_{0z}, \quad (\text{B.3})$$

then, we obtain

$$G_0(z-z_0, L) = (1/(4\pi l_p^2 h(L/l_p)))^{d/2} \exp(-(\mathbf{r} - \mathbf{r}_0)^2/4l_p^2 h(L/l_p)), \quad (\text{B.4})$$

where  $h(x) = \exp(-x) + x - 1$ , and  $x = L/l_p$ .

To find the solution of the integral equation (4.4), we use the perturbation expansion of the Green's function in powers of the external potential. Then

$$\begin{aligned} G(z, p; z_0) = & G_0(z, p; z_0) - \int dz' \overline{G}_0(z, p; z') V(z') G_0(z', p; z_0) + \\ & \int dz' dz'' \overline{G}_0(z, p; z'') V(z'') G_0(z'', p; z') V(z') G_0(z', p; z_0) + \\ & \int dz' dz'' dz''' \overline{G}_0(z, p; z''') V(z''') G_0(z''', p; z'') V(z'') G_0(z'', p; z') \\ & V(z') G_0(z', p; z_0) + \end{aligned} \quad (\text{B.5})$$

Inserting  $V(z) = -v\delta(z)$  in the last equation, and by carrying out the integration over the internal coordinates  $(z', z'', \dots)$ . Then the  $\delta$  function sets the internal coordinates to zero. Thus

$$G(z, p; z_0) = G_0(z, p; z_0) + v\overline{G}_0(z, p; 0)G_0(0, p; z_0)[1 + vG_0(0, p; 0) + v^2G_0^2(0, p; 0) + \dots]. \quad (\text{B.6})$$

Therefore, the final result is

$$G(z, p; z_0) = G_0(z, p; z_0) + \frac{v\overline{G}_0(z, p; 0)G_0(0, p; z_0)}{1 - vG_0(0, p; z_0)} \quad (\text{B.7})$$

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# *Erklärung*

Ich erkläre hiermit, dass die Dissertation selbständig verfasst wurde und nur die angegebenen Hilfsmittel benutzt wurden. Die Dissertation wurde noch an keiner anderen Universität oder Hochschule eingereicht.

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3. Ph.D. research focus on the adsorption properties of the diblock copolymer. In my current research, the adsorption as well as the other interfacial properties such as stretching, and interfacial tension of the copolymer onto an interface for both flexible and semiflexible polymer are under consideration. They are interesting in polymer physics, because of their commercial application.

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