Molecular modeling of microstructure and thermodynamics of bulk and inhomogeneous polymer systems

by

Shekhar Jain

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APPROVED, THESIS COMMITTEE:

Walter G Chapman, Chair, William W. Akers Professor
Chemical and Biomolecular Engineering

Sibani L Biswal, Assistant Professor
Chemical and Biomolecular Engineering

Kenneth R Cox, Professor-in-the-practice
Chemical and Biomolecular Engineering

Enrique V Barrera, Professor
Mechanical Engineering and Materials Science

Houston, Texas

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Abstract

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Modeling of thermodynamics and microstructure of polymer systems is important in their production, processing, and applications. Success in modeling these systems is contingent upon the ability of the molecular model to describe specific interactions, and capture the size and shape effects. Molecular models for polymers are divided into areas that separately focus on the bulk and inhomogeneous aspects of polymer systems.

In current work, a new equation of state (EOS) based on Wertheim’s thermodynamic perturbation theory (TPT1) has been developed for bulk polymer systems. Treating the polymeric fluid as a fluid mixture of associating spheres in the limit of complete association, the EOS more accurately accounts for the architecture and interactions of the polymer molecules. The EOS accurately predicts the phase behavior of bulk polymer systems over the whole range of polymer weight fractions in comparison to previous theoretical approaches, and the improvement is significant near the critical region.

For inhomogeneous polymer systems, a new density functional theory (DFT) based on TPT1 has been developed. The DFT derived in terms of the segment density, offers
accuracy comparable to the previous molecular density-based, simulation-dependent
theories at a computational expense comparable to atomic DFTs. Comparisons with
molecular simulations for the microstructure of the heteronuclear (model lipids and
block copolymers) and star-like branched polymer melts near a surface, demonstrate
the capability of the theory to accurately capture the effects of the polymer chain
architecture, segment-segment, and segment-surface interactions.

The DFT has been applied to analyze the lamellar morphologies of symmetric
diblock copolymers in bulk melts and ultra-thin films confined between two surfaces.
Effects of the chain length of the copolymer, incompatibility between the two blocks,
surface-block interactions, and film thickness on the microstructure are investigated.

Finally, the DFT has also been applied to predict the microstructure of the mono-
layers formed by grafted polymers (on a planar surface) and the force of interaction
between two such monolayers. The theory successfully accounts for the difference in
the segment sizes of the grafted polymer and the free polymer solvent. This has not
been investigated with the previous theoretical approaches for grafted polymers.
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Last but not the least, I am indebted to my family for supporting and encouraging me to keep focus on my goals even during the toughest time of my life. I would like to dedicate this thesis to them.
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Chapter 1

Introduction

This dissertation presents the development of molecular models based on statistical mechanics to predict the

- thermodynamics and phase behavior of bulk polymer systems, and

- microstructure, phase behavior and other thermodynamic properties of inhomogeneous polymer systems.

Bulk polymer systems include polymer melts, polymer solutions and polymer blends while inhomogeneous polymer systems include self-assembling polymers, polymers near a surface or an interface, and confined polymers. The current chapter explains the motivation, challenges, specific objectives, basis, and the scope of this research.
1.1 Motivation

Polymers are ubiquitous in our day-to-day life in the form of plastics, resins, adhesives, rubber, cellulose, and so on. Some of these like natural resins and rubber have been in use for centuries. Biopolymers like proteins and nucleic acids play crucial roles in biological processes. A polymer molecule or macromolecule is a species of high molecular weight composed of several repeating structural units connected by covalent bonds. These structural units represent residues from small molecular compounds called “monomers” which are employed in the preparation of the polymer. For example, a common plastic material polyethylene (PE) is produced by reacting (or “polymerizing”) ethylene molecules to form chain-like macromolecules consisting of thousands of ethylene residues. The structural units can be connected in any conceivable pattern leading to linear or branched polymers. The presence of branching results in a number of polymer chain architectures such as star, comb or cascade polymers. These molecular topologies are sought after, because they impart desired macroscopic properties to the polymeric material. For example, short chain branches on linear low density polyethylene (LLDPE) confer great flexibility to the resulting material, thus making it suitable for manufacturing plastic bags and sheets.

Another broad classification of polymers depends upon their internal chemical composition. Polymers derived from a single type of monomers are referred to as homopolymers, while others produced by linking two or more types of chemically distinct monomers are designated as copolymers. One common example of copolymer
is the styrene butadiene rubber (SBR), widely used in tires, shoe heels and soles, and gaskets. SBR is classified as a random or statistical copolymer owing to the random distribution of styrene and butadiene monomers along the polymer chain. Another important class of copolymers is the block copolymers in which monomers of a given type are grouped into polymerized sequences, or “blocks”, along the polymer chain. For example styrene-butadiene-styrene (SBS) is a triblock copolymer with three blocks: polystyrene block followed by a central block of polybutadiene followed by another polystyrene block. Interestingly, random and block copolymers have very different properties, even when composed of the same two monomers. For example, SBS has far superior elastic recovery characteristics than SBR. This feature has been highly exploited in the current polymer R&D.

The progress in polymer science and technology has made possible the design of polymers at the molecular level. It is possible to create polymers with a variety of chain topologies and sequence of monomers along the chain. Hence, rather than seeking advanced polymeric materials based on new monomers, scientists are creating new polymeric materials from commodity/low-cost monomers just by varying the molecular architectures. This rapid development of new synthetic techniques to create wide varieties of polymer architectures and new types of block copolymers, leads to the problem of handling a large design space. Although, experimental methods are a powerful tool to tackle this design space and test if the new materials meet the required mechanical and thermodynamic properties, experimental screening is
expensive. Polymer theories can aid in identifying the most important experimental parameters to be varied, thus supporting the new perspective that theory and simulation can be effectively applied in tandem with the high-throughput experimentation to accelerate the material design process. With a powerful theoretical model in hand, it is comparatively inexpensive to tackle the large parameter space and explore the physical and thermodynamic properties of the new polymeric materials. However, this is possible only when the theoretical model provides an accurate description of the physical system, includes the details of the polymer architecture at the molecular level, and the model parameters reconcile with experimentally realizable parameters. The aim of this research is to develop such powerful theoretical models to probe the properties of both bulk and inhomogeneous polymers. However, the primary focus is only the microstructure, phase behavior and thermodynamics of these systems.

1.1.1 Molecular modeling of the thermodynamics and phase behavior of bulk polymer systems

Understanding the phase behavior of the polymeric materials is an important requirement of modern polymer science and technology. The phase state of polymeric systems determines their properties and subsequently their applications. For example, according to the properties desired, polymer blends as used may be either homogeneous polymer “alloys” or partially miscible, more or less finely dispersed two-phase materials. Polymer blends show substantial improvements in performance
characteristics such as rigidity, toughness, abrasion resistance, chemical and flame resistance, heat resistance, and ease of processing. In addition, they offer possible economic bonuses such as lower cost, easier recycling, relatively rapid commercialization when based on already available constituents, and greater versatility of tailoring to match users' needs. The blend of polycarbonate (PC) and acrylonitrile butadiene styrene (ABS) is a plastic material, which combines the strength of PC with the flexibility of ABS. It is extensively used in the production of parts for automotive, electronic, telecommunication, and toy industries. One of the biggest problems concerning the development of new polymer blends is that only a few polymer pairs are miscible, thermodynamically. The entropic driving force towards miscibility is too small for polymer mixtures. Polystyrene/polyphenylene is one of the few polymer blends that are miscible. One of the ways of preventing the polymer blends from demixing/destabilizing is to add a third component that acts much like a surfactant. It resides at the interface of the polymer domains and reduces the interfacial tension or the driving force towards macro-phase separation. It also improves the adhesion between the immiscible polymer domains and thus the mechanical properties of the blend. These compatibilizers are often block copolymers. Thermodynamics and phase behavior of the constituent polymers is used to search for the suitable compatibilizer of the polymer blend.

The production and processing of polymers are also influenced by the presence of phase separation and segregation, which may be either necessary or highly unde-
sirable. For example, proper orientation and crystallization conditions are needed to secure useful fibers and films; on the other hand, segregation of highly viscous phases may lead to catastrophic consequences like plugged lines or overheated reactors. Folie and Radosz [1] presented a review on the relationship between polymer processing and the phase equilibria of the system in the commercial high-pressure polyethylene process (HPPE). HPPE is used to produce low density polyethylene (LDPE) by free-radical polymerization [2, 3] and LLDPE by using single-site homogeneous metallocene catalysts [4, 5]. The process is carried out in supercritical ethylene, which is both the reactant and the solvent for the polymer. The production of LDPE is carried out in a single-phase region to facilitate the heat removal from the exothermic polymerization reaction and ensure adequate reaction temperature control. Efficient temperature control is required to avoid forming cross-linked materials. Again, segregation of the viscous polymer rich phase increases the probability of forming hot spots in the reactor and initiating the explosive runaway reactions [6, 7].

On the other hand, polymerization reaction to produce LLDPE is carried out in a two-phase region. Phase separation in the autoclave reactor is achieved by lowering the pressure or adding an anti-solvent, such as N₂ to the reaction mixture. LLDPE produced this way exhibits superior film properties because of narrower molecular weight distribution (MWD) and less long chain branches [8]. An undesirable phase transition is the polymer precipitation due to the cooling of the reaction mixture. This leads to the deposition of polymer films, which impairs heat transfer and re-
quires continuous line defouling. Therefore, in order to choose the optimal operating conditions for the reactor, it is necessary to know the temperature, pressure, and mixture compositions corresponding to the demixing points. Demixing or the cloud points depends to a large extent on the polymer size, structure, MWD, and interactions with the solvent.

Another important plastic material, high impact polystyrene (HIPS), is generally produced by reactive processing. The styrene monomer is polymerized in the presence of an elastomer like polybutadiene (PB). The starting phase is homogeneous system of PB in styrene, in which increasing amount of PS is generated as the polymerization progresses. At a characteristic concentration of PS, phase separation occurs and the graft copolymer (PS backbone with PB branches) called HIPS is formed simultaneously in the system by a chain transfer reaction. HIPS is stronger than PS and PB branches give it the elastic properties making it less brittle than PS. HIPS is commonly used in fridge liners, food packaging, vending cups, and toys.

Hence, understanding the phase behavior of the polymer systems is of critical importance for both polymer scientists and engineers. Many of the qualitative features of (fluid-fluid) phase equilibria in polymer mixtures and blends can also be found in mixtures of small molecules, and all the basic thermodynamic relations apply. Yet, there are significant quantitative differences, mainly due to the large size of the polymer molecules. Some of the common features that pose a challenge while modeling the phase behavior of these systems are:
• Fully atomistic modeling of polymer molecule with more than a thousand atoms is computationally intractable. Hence, the model polymer molecule is “coarse-grained” so that groups of atoms are lumped into larger entities referred to as “segments”. Although, this coarse-graining procedure may ignore the atomic details of the polymer molecules, it must preserve their large-scale features, such as chain connectivity, space-filling characteristics, and architecture.

• In a polymer/solvent system, as the difference in the molecular sizes of the components increases, the miscibility gaps becomes highly symmetric, with the critical points shifting towards lower mass fractions of polymer. This leads to numerical complexities like convergence (due to very low polymer mass fraction in the polymer-lean phase), while modeling these systems.

• Polymers are branched, with the branch points being regular or random, leading to different chain architectures. These branches significantly affect the phase behavior of polymer systems.

• In addition to branching, polymer chains can have functional groups, such as polar groups in poly(ethylene-co-methacrylate) or hydrogen bonding groups in poly(ethylene-co-acrylic acid).

• Polymer samples are often polydisperse in molecular weight, chain branching, and comonomer content (and therefore polarity and hydrogen-bonding strength). Consequently, a polymer solution is de facto a multi-component
• Variations in the polymer chain length alone (at a fixed chemical composition, temperature, and pressure) can bring about marked changes in phase behavior, thus furnishing an additional parameter.

• The phase boundary in polymer solutions is situated at elevated pressures and temperatures. Hence, experimental measurements are costly and require very sophisticated apparatuses. Consequently, data on phase behavior of polymer solutions is limited.

• Concentrated polymer solutions and blends are very viscous even at high temperatures. Kinetic hindrances to the achievement of an equilibrium state may therefore limit the applicability of the equilibrium models. Moreover, phase behavior experiments are difficult to carry out in this concentration regime.

Hence, polymer systems are very challenging to model. Nevertheless, there have been a number of theoretical developments in the field of polymer thermodynamics that somehow incorporate the molecular description of the polymers. The earliest of these is the Flory-Huggins theory [9, 10]. In this approach, a molecular lattice model is proposed with the polymer and solvent occupying all the available sites of the lattice. Each of the segments of the polymer molecule occupies one lattice site, and the rest of the sites are filled with the solvent molecules, each of which also occupies a single lattice site. The lattice is thus incompressible. The entropy
of mixing is obtained by counting the number of all the possible configurations of
the polymer-solvent system on the lattice, while the enthalpy of mixing is obtained
by accounting for all the nearest neighbors' interactions, with $\chi$ being the interac-
tion parameter. The entropy of mixing is always positive and thus always favors
mixing, however it is small for large polymer molecules. For certain values of $\chi$ corre-
sponding to unfavorable interactions between the polymer and solvent molecules, the
enthalpy of mixing becomes sufficiently positive, and the system exhibits liquid-liquid
(L-L) immiscibility characterized by a upper critical solution temperature (UCST).
Another interesting liquid-liquid immiscibility is commonly observed in polymer sys-
tems, where the single liquid phase becomes unstable on increasing the temperature
in the direction of the critical point of the solvent. The lowest temperature at which
the two-phase (L-L) region appears is referred to as the lower critical solution tem-
perature (LCST). LCST behavior occurs in polymer solutions due to the difference
in free volume or compressibility of the polymer and solvent molecules [11, 12, 13].
Consequently, Flory-Huggins theory, which assumes incompressibility, cannot predict
the LCST behavior in polymer solutions. Phenomenological approaches have been
introduced to describe polymer solutions with a LCST in Flory-Huggins approach
by defining an empirical temperature, composition, and even pressure dependence on
the $\chi$ parameter [14, 15, 16, 17, 18].

Other more fundamental approaches, such as the lattice cell models and lattice
hole models, aim to incorporate compressibility in the lattice model. In lattice cell
models, the polymer segments are allowed to vibrate around their equilibrium position, and the partition function of the polymer chain is written in terms of its degrees of freedom. Prigogine [19] introduced an empirical $c$ factor corresponding to the degrees of freedom of the polymer chain. Using Prigogine-Flory cell theory, Patterson [12] was able to explain the LCST type phase behavior in polymer systems. However, an important issue regarding the individual roles of 'excluded volume' and 'attractive' interactions on these systems, remained unanswered. The perturbed hard chain theory (PHCT) of Prausnitz and co-workers is also based Prigogine's partition function [20, 21]. Although, it has been successful in describing LCSTs in polyethylene solutions in hydrocarbons [22], PHCT is not widely applied due to its great sensitivity to the empirical $c$ factor. The lattice hole approach was followed by Sanchez and Lacombe [23, 24] in which the mixing-volume effects are incorporated via vacant lattice sites. Thus, the description of polymer solutions with the Sanchez-Lacombe equation of state can lead to both LCST and UCST behavior depending upon the intermolecular interactions [25].

Continuum statistical mechanics models provide an effective route to include the compressibility effects in the description of the phase behavior of polymer systems. These equations of state (EOS) separate out the effects of 'excluded volume' and 'attractive' interactions, which help understand the effects of each of them on the phase behavior, individually. But the most important feature of these continuum models is the accurate definition of density. In lattice models, the definition of density is rather
nebulous and consequently, the density dependence of the thermodynamic functions is often inadequate and can lead to the wrong conclusions about the nature of the phase behavior. Broadly, continuum models include three approaches: extension of Flory-Huggins theory in continuum space, integral equation theories, and theories based on Wertheim's first order thermodynamic perturbation theory (TPT1) [26, 27, 28, 29]. These theories are generally developed for hard chain fluids. In another step, attractive interactions can be added as a perturbation to the hard chain reference fluid.

Dickman and Hall [30] were the first one to develop an EOS for hard chain fluids by extending the Flory-Huggins treatment of configurational probabilities of chain molecules to continuous space. In this Generalized Flory (GF) theory, the probability of inserting of a polymer chain into the system is approximated from the probability of inserting a monomer (a single segment of the chain) into a fluid of monomers. Comparisons with Monte Carlo simulation results show that the theory does not yield accurate thermodynamic properties of chain fluids [31] as the effect of chain connectivity is underestimated. Based on these conclusions, Honell and Hall [32] developed an improved Generalized Flory-Dimer (GFD) theory. Now, the probability of inserting the chain is obtained from the probabilities of inserting a monomer into a monomer fluid and a dimer into a dimer fluid. GFD theory has been extended to attractive [33] and heteronuclear [34, 35] chains.

Standard integral equation theories from statistical mechanics can be used to determine the correlations between the segments forming the chains. This information
is availed to obtain the thermodynamic properties of chain fluids [36]. Based on these concepts, the reference interaction site mode (RISM) [37, 38], originally developed for small molecules was extended to polymers (polymer reference interaction site model or PRISM) by Curro and Schweizer [39, 40, 41]. PRISM provides a good representation of the segment-segment structure of the chain fluid, however, the description of the thermodynamics are often poor [42]. In addition, there are ambiguities regarding the closure equations to be used for specific systems. Other integral equation approaches for hard chain fluids have been developed by Chiew [43] (using Percus-Yevick closure together with chain connectivity constraints) and Chang and Sandler [44] (by solving Wertheim’s integral equation theory [26, 27, 28, 29]). Recently, the polymer mean spherical approximation (PMSA) integral equation theory has been used by Kalhuzhnyi et. al. [45] to obtain the thermodynamic properties of chains of Yukawa spheres.

One of the most accurate descriptions of the phase behavior of polymer systems had been achieved with EOS based on Wertheim’s TPT1 [26, 27, 28, 29] for associating atomic fluids. The molecules of these associating atomic fluids have spherical hard cores with off-centered associating sites on them. TPT1 accurately describes the phase behavior and thermodynamics of associating atomic fluids with multiple association sites. Chapman et. al. [46, 47] extended TPT1 to mixtures of associating atomic fluids and derived an EOS for hard chain fluids by taking the limit of complete association between the associating spheres. The EOS labeled as statistical associ-
ating fluid theory (SAFT) is found to be in excellent agreement with the simulation results for the thermodynamic properties of hard-chain fluids. The ‘attractive’ interactions can be added as a perturbation to the reference hard-chain term, to mimic real polymer systems. Different variants of SAFT have developed based on the way these ‘attractions’ are added. A brief review of the different versions of SAFT can be found in chapter 2, along with their strengths and shortcomings. One common shortcoming is that neither of them is able to provide an accurate description of the phase behavior of polymer solutions over the whole range of polymer weight fractions [48]. Hence, one of the specific objectives of this research is the development of an improved EOS based on SAFT for polymer systems, which can accurately predict the phase behavior of polymer solutions over range of polymer weight fractions.

Discussion of SAFT based EOS is incomplete without a description of TPT1, which is at the heart of this work and other variants of SAFT. Hence, section 2 of this chapter gives a brief description of TPT1.

1.1.2 Molecular modeling of the microstructure and thermodynamics of inhomogeneous polymers

As mentioned in the previous section, polymers are often immiscible. When two polymers A and B are mixed together, the different chemical nature of the two polymers and low entropy of mixing causes them to separate into A-rich and B-rich do-
mains. With time, these domains coarsen leading to 'macro-phase' separation, where the individual domain sizes are comparable to the volume of the container in which the fluid is held. The driving force is the interfacial energy of the two phases. Hence at equilibrium, the interface between the two macro-phases A and B will be minimum subject to the mass conservation of the species and boundary conditions that reflect the container. In addition to the two bulk phases, the interfacial region and thereby the interfacial properties are of fundamental interest.

On the contrary, if the polymers A and B are joined together to form a A-B diblock copolymer, they can no longer macro-phase separate. Instead, melts of diblock copolymers show an ordering phenomenon known as 'micro-phase' separation. At the local (~ 10 nm) level, A and B blocks phase separate by the same microscopic interactions that led to macro-phase separation. However, these local domains cannot coarsen since this would require breaking the bonds between the two blocks of the copolymer molecules. Indeed, microphase separation of a pure block copolymer melt is more properly viewed as an ordering phenomenon similar to the crystallization of a one component molecular fluid, rather than a spatially limited type of phase separation. Thermodynamic equilibrium corresponds to mesophases consisting of defect-free, periodic patterns with compositional order in one, two, or three dimensions. Defect states such as lattice dislocations and grain boundaries, however, are relatively low in energy and easily populated. Nevertheless, under certain circumstances, it is possible to obtain mesophases that are nearly defect-free and have a high degree of long-range
order. The microstructure of these mesophases depend mainly depend upon relative compositions of the A and B blocks in the copolymer and the degree of incompatibility between the two blocks, as shown in fig. 1.1. In the figure, $\chi$ parameter quantifies the degree of incompatibility between the blocks, $N$ is the degree of polymerization of the copolymer, and $f$ is the ratio of the degree of polymerization of the A block to that of the B block. As shown in the figure, there is a critical value of the parameter $\chi N$ at a particular $f$, where the order-disorder transition (ODT) takes place. For example, for $f$ equals to 1/2 (symmetric diblock copolymer), the ODT takes place at $\chi N \sim 10.5$ [49]. The microstructure of the mesophases vary from cubic at low degrees of polymerization of one of the blocks to lamellar for symmetric diblock copolymers.

Figure 1.1: Schematic of the phase diagram and microstructures of diblock copolymers. Figure from http://www.physics.nyu.edu/pine/research/nanocopoly.html
The interfacial region in homopolymer blends and the mesophases in diblock copolymer melts are examples of inhomogeneous polymer systems, which are characterized by non-uniformity in density with respect to spatial co-ordinates (on the order of molecular diameter), despite being in a state of equilibrium. To better understand this concept, a simpler example of a polymeric fluid adsorbed on to a (flat) planar surface, is considered. Since the surface is planar, the inhomogeneity is only in one dimension, which is normal to the surface. Figure 1.2 shows the 1-D microstructure in terms of the total segment density \( \rho(z) \) of the polymeric fluid as a function of the normal distance \( z \) away from the wall. Note that the normal distance is scaled by the segment diameter \( \sigma \) and the total segment density is scaled by its value in the bulk fluid \( \rho_{\text{bulk}} \), far away from the surface. The figure shows an enhancement in the total segment density at the surface, oscillations near the surface and finally a flat uniform profile away from the surface. The uniform region defines the bulk fluid which in equilibrium with the inhomogeneous fluid.

Many polymer systems are inhomogeneous, often encountered in biological, interfacial, and confined systems. Self-assembled lipid bilayers and micelles are classical examples, which are ubiquitous in all biological systems. Interfacial systems are of great industrial significance in areas like paints and coatings (polymer adsorption), detergents and shampoos (surfactants), food production (emulsions and colloids), pharmaceuticals (suspensions), lithographic templates for semiconductors (copolymer films), and microfluidic devices (hydrophobic films). Confined systems are of
fundamental interest to many practical processes, such as lubrication, membrane separations, chromatography, and enhanced oil recovery.

The major challenge in modeling the thermodynamics and phase-behavior of inhomogeneous systems is to obtain the microstructure of the fluid. Once the microstructure is obtained, other thermodynamic properties can be obtained using standard thermodynamic relations. The challenge of accurately predicting this structure multiplies manifold for a polymeric fluid, mainly due to both intra- and inter-molecular correlations between the segments of the polymer molecules. For example, a modest surface-fluid interaction per segment translates to a large surface-fluid interaction per molecule. Again, conformational entropy due to the intramolecular correlations of the polymer chains plays a predominant role in determining the microstructure of
(inhomogeneous) polymeric fluids. Another aspect while modeling inhomogeneous polymers, can be explained in terms of the example depicted in fig. 1.2. The range of oscillations in the total segment density profile is about 3 - 6 segment diameters, which is considerably smaller than the size of the polymer molecule. Hence, it is clear that a polymer molecule could at the same time be in the inhomogeneous as well as the bulk region. So the very notion of 'local' molecular density in the inhomogeneous region loses its significance. Since, bulk polymer theories analyze the system in terms of molecular density, any extension of their arguments to inhomogeneous systems cannot be expected to paint an accurate picture.

Short-range variations in the local density, along with the long-range structure, plays an important role in determining the macroscopic properties of the inhomogeneous polymers. For example, thin films of confined symmetric diblock copolymer form different lamellar phases (parallel/perpendicular to the confining surfaces with different number of lamella) between the two confining surfaces. The total segment density profiles of these lamellar phases show variations in the densities near to the confining surfaces. These variations influence the relative stability of the different lamellar morphologies [50]. Hence, to successfully model inhomogeneous polymer systems, the model must incorporate molecular features on all length scales, and yet remain computationally tractable.

Apart from modeling, fundamental challenge lies in understanding the new physics that emerges from finite-size effects, varying dimensionality, and surface forces. The
introduction of surface forces, and the competition between fluid-surface and fluid-fluid forces, can lead to interesting surface-driven phase changes. These include new kinds of phase transitions not found in the bulk phases, such as layering and wetting, as well as shifts in transitions (e.g. freezing, gas-liquid, liquid-liquid) that are familiar from bulk behavior.

Experimental techniques to study the microstructure of these systems are hampered by the molecular scale. Molecular simulations are computationally expensive and even with all the given computational advancement, are limited to short chain molecules with simple interactions. Hence, a number of theoretical models have been developed to study inhomogeneous systems. The earlier ones such as scaling/mean field theories were limited to a particular system, such as scaling theory of Alexander [51] and de Gennes [52] for polymer brush. Moreover, the scaling theories do not calculate the detailed structure, accurately. A more systematic theoretical approach for the equilibrium properties of inhomogeneous polymers, has been the self consistent field theory (SCFT). Using statistical mechanics, the Gaussian chain model [53] for long polymer chains can be solved using the self-consistent field theory (SCFT) introduced by Edwards [54]. In this approach, the molecular interactions are treated by a mean field which has to be evaluated numerically.

Another important class of theories that have recently been applied to study inhomogeneous polymer systems are the density functional theories (DFTs) [55]. These theories include more physics than mean field theories and SCFTs, as they retain
monomer or statistical segment length-level information rather the coarse-grained representation of the polymers. Thus, DFT provides an approach that is intermediate between macroscopic thermodynamic approaches and truly microscopic simulation-based methods. The theory incorporates molecular-level detail but is simple enough that calculation time is modest and physical insight is retained even in complex situations. Again, all the mean field theories and SCFTs neglect compressibility and the fluctuations in the local composition from an average value. However, as with bulk polymer systems, compressibility effects play an important role in inhomogeneous systems. The natural formalism of the DFTs is the grand canonical ensemble where fluctuations in the number of polymer chains in the system keep the chemical potential constant. Thus the system is compressible and phase transitions can include fluctuations in density/composition of the system. In addition, DFTs provide a single framework for modeling both interfacial and bulk properties. A thorough review of classical DFT is given by Evans [56] while many applications of DFT to interfacial systems are described by Davis [57] and Wu [55].

Owing to its success for homogeneous systems, several DFTs based on TPT1 have been proposed. As noted by Chapman [58] and Kierlik and Rosinberg [59], Wertheim’s theory is written in general for inhomogeneous associating (atomic) fluids. The central approximation of any density functional theory is an expression for the intrinsic Helmholtz free energy of the system. Considering the polyatomic system as a mixture of associating spherical segments in the limit of complete association,
the intrinsic Helmholtz free energy functional can be derived from Wertheim's TPT1. A review of the DFTs based on TPT1 is given in chapter 3 of this dissertation. As will be discussed in this chapter, these theories are in general not applicable to a range of inhomogeneous polymer systems. For example, the DFT by Tripathi and Chapman [60] is not applicable to heteropolymers, or the DFT by Yu and Wu [61] cannot be applied to study the lamellar microstructures in bulk copolymer melts. Hence, the second specific objective of this research is the development of a DFT based on TPT1 which in general can be applied to a range of inhomogeneous polymeric systems, and demonstrate few of its applications.

1.2 Basis: Wertheim’s first order thermodynamic perturbation theory for associating fluids

Wertheim [26, 27, 28, 29] proposed a first order perturbation theory (TPT1) for hydrogen-bonding atomic fluids. The molecules of the hydrogen-bonding/associating fluid are modeled as hard spheres with off-centered, short-ranged and highly directional associating sites on them, as shown in fig. 1.3. The theory was initially developed for molecules with one associating site, and later generalized to account for the presence of any number of associating sites on the molecules. Chapman [58] extended Wertheim’s TPT1 to mixtures of associating fluids, by introducing a simpler notation. A brief background of TPT1 is presented here using his notation.
The potential of interaction between two associating fluid molecules 1 and 2, is the sum of the spherically symmetric, hard core contribution, and the anisotropic, association contribution.

\[ u_{12}(r_1, \omega_1, \omega_2) = u_{12}^R(r) + \sum_{A \in \Gamma^{(1)}} \sum_{B \in \Gamma^{(2)}} u_{AB}^{\text{assoc}}(r, \omega_1, \omega_2), \tag{1.1} \]

where \( u_{12}^R \) is the pair potential of the hard core reference fluid, \( u_{AB}^{\text{assoc}} \) is the pair potential due to association between site A on the molecule 1 and site B on molecule 2, \( \Gamma^{(i)} \) is the set of all the associating sites on molecule \( i \), \( r \) is the magnitude of the vector \( r \) connecting the centers of the molecules 1 and 2, and \( \omega_1 \) and \( \omega_2 \) are the sets of angles defining the orientations of molecules 1 and 2 relative to vector \( r \). The pair...
potential due to association is given by

\[ u_{AB}^{assoc}(r, \omega_1, \omega_2) = \begin{cases} -\epsilon_{as} & \text{if } r < r_c; \theta_{A1} < \theta_c; \theta_{B2} < \theta_c, \\ 0 & \text{otherwise} \end{cases} \]  

(1.2)

Eqn. 1.2 essentially means that if the molecules 1 and 2 are close enough and their associating sites are oriented towards each other, they associate with the strength of the association potential given by \( \epsilon_{as} \). These positional and orientational constraints are prescribed by the parameters, \( r_c \) and \( \theta_c \), respectively. Wertheim introduced separate singlet densities for each possible associating state of a molecule. For example, for molecules with one associating site, the individual singlet densities are the densities of associated molecules and the non-associated molecules. For molecules with multiple associating sites, the associating state of a molecule increases depending upon the number of sites that are associated. Using graph theory in statistical mechanics, Wertheim derived the thermodynamic variables as functionals of the singlet densities. Additional constraints on the associating molecules were introduced to reduce the number of graphs, as shown in fig. 1.4.

- If two molecules are associated at their sites A and B respectively, then other molecules cannot associate at either A or B.

- A site on a molecule cannot associate with two sites on another molecule, simultaneously.

- Two sites on a molecule cannot associate with two sites on another molecule,
Finally, the free energy functional of a fluid mixture of these 'm' associating species can be written as a perturbation to the reference hard sphere fluid. Truncating the free energy to first order gives [58],

$$ A = A^{\text{ref}} + A^{\text{assoc}}, $$

(1.3)

where $A^{\text{ref}}$ is the free energy functional of the reference fluid and $A^{\text{assoc}}$ is given by

$$ \frac{A^{\text{assoc}}}{kT} = \frac{\int d\mathbf{r}d\omega \sum_{l=1}^{m} \rho_l(\mathbf{r}) \sum_{A \in \Gamma^0} \left( \ln X^l_A(\mathbf{r}, \omega) - \frac{X^l_A(\mathbf{r}, \omega)}{2} + \frac{1}{2} \right)}{\int d\omega}, $$

(1.4)

where $k$ is the Boltzmann constant, $T$ is the temperature, $\rho_l$ is the density of molecules.
of species ‘i’, and the singlet densities are replaced by the fraction of non-associated segments \(X_A^i\) as prescribed by Chapman [58]. To be precise, \(X_A^i\) is the fraction of molecules of species ‘i’ that are not associated at their site ‘A’. This fraction is given by the law of mass action [58, 62].

\[
X_A^i(r, \omega) = \frac{1}{1 + \sum_{j=1}^{m} \sum_{B \in \Gamma^{(j)}} \int d\Gamma' d\omega' \rho_j(\Gamma') X_B(\Gamma', \omega') g^{ref}(\Gamma - \Gamma') f_{AB}(\Gamma - \Gamma'|\omega, \omega')}.
\]  

(1.5)

where \(g^{ref}\) is the radial distribution function of the reference hard sphere fluid, and \(f_{AB}\) is the Mayer f-function for the association potential given as \(f_{AB} = \exp(-\beta u_{assoc}^A) - 1\).

It has to be noted that these equations are written for a potentially inhomogeneous associating atomic fluid - the densities are position dependent. The expressions for the free energy of a homogeneous fluid can be obtained by ignoring the dependence of densities on position. Thus a common basis can be used to develop theories for both homogeneous and inhomogeneous associating atomic fluids or its extension to chain-like molecules by imposing the limit of complete association between the different species in the mixture of associating atomic fluids. The extension in case of homogeneous polymeric fluids is popularly known as statistical associating fluid theory (SAFT) while the inhomogeneous version leads to the new density functional theory (DFT) called modified interfacial-SAFT (or iSAFT) developed in this research work.

Few assumptions are made while extending TPT1 to the limit of complete association/bonding, when the associating atomic molecules become the segments of the chain. The chain molecules that are formed are freely-jointed chains where the
segments bonded tangentially to each other. Since, these are fully flexible chains, the angular dependence of the sites on the segments is relaxed and the site-site structural properties of the segments such as Mayer-f function are averaged over all possible orientations. Hence, eqs. 1.4 and 1.5 reduces to

$$\frac{A^{\text{assoc}}}{kT} = \int dr \sum_{i=1}^{m} \rho_i(r) \sum_{A \in \Gamma(i)} \left( \ln X_A^i(r) - \frac{X_A^i(r)}{2} + \frac{1}{2} \right),$$

where

$$X_A^i(r) = \frac{1}{1 + \sum_{j=1}^{m} \sum_{B \in \Gamma(j)} \int dr' \rho_j(r')X_B^j(r') \Delta^{A,B_j}(r,r')}.$$  

and

$$\Delta^{A,B_j}(r,r') = f_{AB}(r,r')g^{r_{ef}}(r,r')K^{A,B_j}. $$  

$K^{A,B_j}$ is a constant geometric factor resulting from averaging the orientation constraints that the segments must satisfy to form a bond. Another assumption is that bonding at a site of a segment is independent of bonding at its other sites. The derivation of SAFT as an EOS for homogeneous polymeric systems is the focus of next chapter while the development of modified iSAFT as a new DFT for a range of inhomogeneous polymeric systems is the crux of the rest of this dissertation. It has to be pointed out that a remarkable characteristic of these theories based on perturbation is their flexibility for adding contributions to the free energy to explicitly account for all the interactions present in the fluid mixtures, such as dispersion, polar or induced dipole interactions. For example, the free energy of a chain-fluid with
dispersion interactions is simply

\[ A = A^{\text{ref}} + A^{\text{assoc}} + A^{\text{dispersion}}. \] (1.9)

Obtaining the expressions for these contributions, however, is another task. This is a substantial advantage over lattice-based theories where all the interactions are included in the \( \chi \) interaction parameter. The incorporation of an accurate description of the physical state and chemical nature of the fluid into a thermodynamic model is a necessary condition to the obtention of a predictive model with physically meaningful parameters.

A particularly challenging task in the area of thermodynamic modeling is to represent interfacial and bulk properties in the same framework, and Wertheim's TPT1, being originally formulated for inhomogeneous fluids, is potentially applicable in both regions.

### 1.3 Scope of this work

Thermodynamic modeling of polymer systems is important for both industrial applications and fundamental research. It has two major components: bulk homogeneous systems and inhomogeneous systems. This dissertation is motivated towards developing a single framework for modeling both homogeneous and inhomogeneous polymer systems. The basis of this research work is Wertheim's first order thermody-
namic perturbation theory (TPT1). For the homogeneous polymer systems, a number of engineering equations of state based on TPT1 have been developed. These EOS depict the polymer molecule as a fully flexible chain of tangentially bonded spheres. Such a model, albeit simple, capture the essential features of polymer systems, namely excluded volume, and chain connectivity. One of the shortcomings of these EOS is that neither of them are able to provide an accurate description of the phase behavior of polymer solutions over the whole range of polymer weight fractions. Chapter 2 proposes a new improved EOS based on TPT1, and validates it by comparisons to experimental data for \( n \)-alkanes, and polymer solutions.

The success of TPT1 for bulk homogeneous polymer systems has triggered the interest of researchers to formulate TPT1 in a density functional theory (DFT) formalism for inhomogeneous polymer systems. Chapter 3 presents a brief background on DFTs based on TPT1. Rather than rigorously forming polymer chains starting from associating atomic fluids in the inhomogeneous conditions, these DFTs use the final expression for the homogeneous free energy of polymer chains (from SAFT), which only accounts for indirect intramolecular interactions due to volume exclusion. Thus, the intramolecular interactions due to direct bonding between the segments are included into the ideal chain term. This ideal chain term is based on multi-point-based molecular density, \( \rho_M(R) \) \( (R = \{r_1, r_2, \ldots, r_m\}) \) where \( r_i \) is the position of segment \( 'i' \) in the polymer chain with \( 'm' \) segments), which makes the computations expensive. In the current research work, the rigorous approach of starting from inhomogeneous
associating atomic segments and bonding them to form chains allows the derivation of
the free energy functional of polymer chains only in terms of segment densities. This
segment-density based DFT labeled as modified interfacial-SAFT (iSAFT) has the
computational efficiency of atomic DFTs while it is comparable in terms of accuracy
to multi-point-based, simulation dependent polymeric DFTs. Chapter 4 presents
the derivation of modified iSAFT along with its validation by comparing the theoretical results with the available simulation results for model lipids, and copolymers near selective surfaces.

The rigor and computational efficiency of modified iSAFT makes it in general applicable to a range of inhomogeneous polymer systems. Chapter 5 presents one of its application to symmetric diblock copolymers. As shown in fig. 1.1, melts of symmetric AB diblock copolymers form lamellar structures of almost pure A and B, at mesoscopic length scales, typically ~100 nm. Understanding of these lamellar structures is relevant in many industrial applications of copolymer thin films.

Another important inhomogeneous system are the tethered polymers. Tethered polymers are polymer chains with one of their ends attached to a solid surface/interface. The chain end can be a special functional group on the chain that can be either chemically bonded or strongly adsorbed onto the surface/interface. These have numerous industrial applications in colloid stabilization, adhesives, lubricants, micro-fluidic devices, introducing specialized functional groups onto the conventional surfaces, modification of surface hydrophobicity, and so on. Chapter 6 presents the extension of
modified iSAFT to tethered polymers.

In these chapters, modified iSAFT is formulated only for linear polymer chains. Polymer chain architecture plays an important role in determining the structural and thermodynamic properties of inhomogeneous polymer systems. For different architectures such as linear and branched, different structures and properties are expected. Chapter 7 extends modified iSAFT to branched polymer chains. To test the theory, it is applied to star-like branched polymers and again, the results are compared with the available simulation results.

As mentioned earlier, self consistent field theory (SCFT) is another approach that has been applied to inhomogeneous polymer systems. Chapter 8 presents a brief review of SCFT and discusses its merits and drawbacks in comparison to modified iSAFT.

Chapter 9 summarizes this dissertation and outlines some of the future directions that can be taken in terms of further development and/or applications of modified iSAFT.
Chapter 2

SAFT-D: a new equation of state
for polymers based on SAFT

2.1 Introduction

As mentioned in the previous chapter, SAFT was developed by Chapman et. al. [46, 47] as an extension of Wertheim’s TPT1 [26, 27, 28, 29] for associating atomic fluids to chain-like molecules. This original derivation of SAFT is for hard chain fluids, where all the segments in the chains are purely repulsive hard spheres. Thus, the reference fluid is the fluid of hard spheres. The hard chain EOS, which will be referred to as SAFT-HS in this dissertation, accounts for two most important interactions among the segments of chain molecules: chain connectivity and excluded volume. Comparisons with simulation results show that SAFT-HS is an excellent EOS for hard chain fluids. However, to develop an EOS for real systems, attractive
interactions need to be included. Hence, many variants of SAFT have been developed depending upon the way attractive interactions/dispersions are included in the model.

In the original SAFT publication, Chapman et. al. [46] included a generalized van der Waals mean field term to account for the dispersive forces. Such a simple dispersion term is, however, not suitable for modeling the properties of real polymeric fluids. Huang and Radosz [63, 64] developed the first widely applied version of SAFT, known as HR-SAFT. The dispersion term is based on a power series fitted to accurate PvT, internal energy, and second viral coefficient data for argon, by Chen and Kreglewski [65]. Huang and Radosz obtained pure component parameters for over 100 non-associating and associating components. The fitted parameters are well-behaved, and for a homologous series such as n-alkanes, they follow a trend. This allows users to estimate the pure component parameters for larger molecules. This is the main reason for HR-SAFT being widely used in the 1990's, and it is still applied today.

Another approach that has been followed is to use Lennard-Jones (LJ), Square Well (SW) or Yukawa potential to define the attractive (spherical) reference fluid and bond them to form chain fluids. Chapman [66] proposed a EOS for LJ chain fluids (LJ-SAFT) which has been extended and applied to real fluids by Blas and Vega [67, 68] and Kraska and Gubbins [69, 70]. The EOS developed by Blas and Vega is labelled as soft-SAFT and has subsequently been applied to mixtures of hydrocarbons [71], perfluoroalkanes [72], and recently to polymers [73]. Similar ideas were employed by Banaszak et. al. [74] to propose an EOS for SW chain fluids.
Yet, another variant (SAFT-VR) using attractive potentials of variable range was developed by Gill-Villegas et. al. [75]. The free energy and radial distribution function for the attractive reference (spherical) fluid are obtained using a high temperature expansion up to the second order. The resulting EOS was analyzed for different attractive potentials such as SW or Yukawa with variable ranges given by the parameter $\lambda$. However, this includes an additional parameter to be fitted.

The strength of these different variants of SAFT depends upon the way chain connectivity is included into the attraction term. Chain connectivity reduces both repulsive and attractive intermolecular interactions between the segments of the chains as compared to a system of unbonded spheres. This chain connectivity effect which is due to the shielding of chain segments by other segments of the same chain depends on system density as well as on chain length. Both mean field and HR-SAFT dispersion term do not account for chain connectivity, only the hard chain (or repulsive) term includes chain connectivity. Other variants such as LJ-SAFT, soft-SAFT, SAFT-VR, etc. include chain connectivity in both the repulsive and attractive interactions by bonding a reference fluid which includes attractive interactions. The properties of these attractive reference (spherical) fluids are obtained again by applying a perturbation to the hard sphere reference fluid. For example, Barker and Henderson [76, 77] perturbation theory can be used to obtain the properties of SW or LJ spherical fluid using the reference hard sphere fluid. On the contrary, Gross and Sadowki [78] followed a different approach to first form the hard chain molecules using SAFT-HS and
then applying perturbation to hard-chain reference fluid to obtain an EOS for SW chain fluids. These two different approaches to develop an EOS for attractive chains is depicted in fig. 2.1.

Figure 2.1: Schematic of the associating molecules as modeled in TPT1.

The EOS for SW chain fluids developed by Gross and Sadowski has been extended to real fluids [48, 79]. This EOS, labelled as perturbed-chain SAFT (or PC-SAFT), accurately describes the phase behavior and thermophysical properties of pure long chain molecules and their mixtures. Comparisons with HR-SAFT showed that PC-SAFT is clearly superior. Hence, PC-SAFT is now recognized as being more accurate and versatile engineering EOS. However, as with the HR-SAFT, PC-SAFT is not able
to provide an accurate description of the phase behavior of polymer solutions for the whole range of polymer weight fractions, as pointed out by Gross and Sadowski [48]. They found that the EOS significantly underestimated the cloud point pressure of polymer solutions at polymer concentrations greater than 10wt.%. This is significant since the polymer concentration in systems of industrial interest is typically between 10 and 20wt.%.

As evident from previous discussion, all variants of the SAFT including PC-SAFT have used the chain term originally proposed by Chapman et al. [46, 47]. Hence, a possible reason for the inaccuracy in polymer phase behavior prediction is inaccuracy in this chain term. The chain term was developed from Wertheim’s theory for associating fluids by forcing spheres to bond, to form a mixture of chain fluids. For hard chain fluid, although the results are in good agreement with molecular simulation results, the SAFT-HS EOS becomes less accurate as the molecular chain length increases [47, 80]. Ghonasgi and Chapman [80], and independently Chang and Sandler [81], demonstrated that a SAFT Dimer EOS for hard-chain fluids, created by bonding hard-sphere dimers (or diatomics) together to form chain-like molecules is in excellent agreement with molecular simulation results for long chain molecules [80].

In this work, a new EOS for real fluids based on the SAFT Dimer hard-chain term has been proposed. The new EOS, labeled as SAFT-D, describes the phase behavior of polymer solutions accurately over the whole range of polymer concentrations. Moreover, a better representation of the coexistence curves for long chain molecules
is obtained, and the predictions are in better agreement with experimental data for asymmetric mixtures of n-alkanes than PC-SAFT. The next section of this chapter provides a detailed description of SAFT-D. The results obtained for the homologous series of n-alkanes, long chain alkanes, and polymers are discussed in the subsequent section. SAFT-D predictions are compared with results obtained from the PC-SAFT model for both monodisperse and polydisperse polymer solutions.

2.2 SAFT-D equation of state

Consider a mixture of chain fluids such that the chain fluid of type 'i' has 'mᵢ' number of segments, \( \sigma_i \) is the size of their segments (i.e. homonuclear polymer chains), and \( x_i \) is their (number) fraction in the mixture. For total 'N' number of chains in the mixture, the Helmholtz free energy is given in terms of a perturbation expansion as

\[
A = A^{id} + A^{hs} + A^{chain} + A^{disp},
\]

(2.1)

where, \( A^{id} \) is the ideal free energy of segments, and the various excess contributions to the free energy are: \( A^{hs} \) due to volume exclusion/repulsive interactions, \( A^{chain} \) due to chain formation, and \( A^{disp} \) due to the dispersive/attractive interactions. It is clear from eqn. 2.1 that there are two perturbations involved. First one (chain term) derives the free energy of hard-chain fluid using perturbation from a reference fluid of hard spheres in case of SAFT-HS and hard dimers in case of SAFT-D, while the second one (dispersion term) derives the free energy of the attractive chain fluid using
perturbation from the reference hard-chain fluid.

### 2.2.1 Chain term

From eqn. 2.1, the Helmholtz free energy of a mixture of hard-chain fluids is given by

\[ A^{hc} = A^{id} + A^{hs} + A^{chain}. \]

The ideal free energy of the segments is given by

\[ \frac{A^{id}}{NkT} = \sum_i m_i x_i (\ln \rho_i - 1) + C, \]

where the term 'C' includes the term involving the De Broglie wavelength. For repulsive interactions, instead of using a purely repulsive hard sphere potential, softly-repulsive potential suggested by Chen and Kreglewski [65] is used.

\[ u_i^{\text{repulsion}}(r) = \begin{cases} 
\infty & r < (\sigma_i - s_1) \\
3\epsilon_i & (\sigma_i - s_1) \leq r < \sigma_i \\
0 & r \geq \sigma_i 
\end{cases}, \]

where \( \epsilon \) is the depth of the potential well that quantifies the square-well attractive interactions between the segments of the chains (as will be discussed in the dispersion term), and \( s_1 = 0.12\sigma \). Following Barker and Henderson perturbation theory [77], this soft repulsion between spheres can be described using a purely repulsive hard-sphere
potential with a temperature dependent segment diameter, \( d_i \), given by

\[
d_i(T) = \int_0^\sigma_i \left[ 1 - \exp \left(-\frac{\mathcal{u}_{i,\text{repulsion}}(r)}{kT}\right) \right] \, dr = \sigma_i \left[ 1 - 0.12 \exp \left(-\frac{3\zeta_i}{kT}\right) \right]. \tag{2.5}
\]

Thus, the excess contribution to the free energy due to repulsive interactions is given by [82, 83]

\[
\frac{A_{hs}}{N_sKT} = \frac{1}{\zeta_0} \left[ \frac{3\zeta_1\zeta_2}{1-\zeta_3} + \frac{\zeta_2^3}{(1-\zeta_3)^2} + \left( \frac{\zeta_3^3}{\zeta_3^2 - \zeta_0} - \zeta_0 \right) \ln (1 - \zeta_3) \right], \tag{2.6}
\]

where \( N_s \) is the total number of spheres (or segments of the chains) in the system, \( N_s = \sum_i x_i m_i \), and

\[
\zeta_n = \frac{\pi}{6} \rho \sum_i x_i m_i d_i^n, \quad n \in \{0, 1, 2, 3\}. \tag{2.7}
\]

\( \rho (= N/V) \) is the total density of the chains formed by bonding these segments.

\[\begin{array}{c}
\text{Figure 2.2: Schematic of chain formation from associating spherical molecules.}
\end{array}\]

All previously published versions of SAFT include the term accounting for chain connectivity (\( A_{\text{chain}} \)) derived by Chapman et al. [46] on the basis of Wertheim's theory for associating atomic fluids. To form chains of type 'i', the starting point is a
stoichiometric mixture of ‘m‘ segments labeled from 1 till m, such that segments ‘1‘ and ‘m‘ have only one associating site, A or B, while the other segments have two associating sites, A and B. This is depicted in fig. 2.2. Similarly, chains of other types are formed. Using eqn. 1.6 in the bulk homogeneous limit, the free energy of association between the segments of the chains is given by

$$\frac{A_{assoc}}{NkT} = \sum_i \sum_{\alpha=1}^{m_i} x_i \sum_{A \in \Gamma^{(\alpha)}} \left( \ln X_A^\alpha - \frac{X_A^\alpha}{2} + \frac{1}{2} \right), \quad (2.8)$$

where the first sum is over all the chain species, second over all the segments of a chain ‘i’, and the third over all the associating/bonding sites on segment ‘\alpha’ of chain ‘i’. $X_A^\alpha$ denotes the fraction of segments $\alpha$ that are not bonded at their associating site A. The expressions for $X_A^\alpha$ are given by eqn. 1.7 in the bulk homogeneous limit. To form chain molecules, the segments are bonded at contact. Furthermore, for chains of type ‘i’, mid-segments $\alpha$ only bond to segments $\alpha - 1$ and $\alpha + 1$ of the same type, and end-segments 1 and 2 only bond to segments 2 and $(m - 1)$, respectively. Hence for chain ‘i’,

$$X_A^\alpha = \frac{1}{1 + \rho_i X_B^{(\alpha+1)} \Delta^i}, \quad (2.9)$$

where $\Delta^i = K[\exp(-\epsilon_{assoc}/kT) - 1]g_{ji}^{\delta}(d_i)$, $\rho_i$ is the density of chains of type ‘i’, and

$$X_B^\alpha = \frac{1}{1 + \rho_i X_A^{(\alpha-1)} \Delta^i}. \quad (2.10)$$

Chains are formed by increasing the strength of association such that $\epsilon_{assoc} \rightarrow$
In this complete bonding limit, $X_A$ and $X_B$ would vanish throughout the system. Also, $X_A = X_B (= X)$ for all the segments of chain ‘i’ since each site on the segments reaches its complete bonding limit at the same rate. This leads to the simplification

$$\frac{(X^i)^2}{\rho_i \Delta^{ii}} = \frac{1 - X^i}{\rho_i \Delta^{ii}}, \quad (2.11)$$

and the excess free energy due to formation of the bonds is

$$\frac{A_{\text{chain}}}{NkT} = -\frac{1}{2} \sum_i \sum_{\alpha=1}^{m_i} x_i \sum_{A \in \Gamma^{(\alpha)}} \left( \ln \rho_i + \ln g_{ii}^{hs}(d_i) - 1 \right), \quad (2.12)$$

where the constant term containing the energy of association and the bonding volume has been dropped. The second and third sum over all the segments of chain ‘i’ and their bonding sites yield $2(m_i - 1)$. Therefore,

$$\frac{A_{\text{chain}}}{NkT} = -\sum_i x_i (m_i - 1) \left( \ln \rho_i - 1 \right) - \sum_i x_i (m_i - 1) \left( \ln g_{ii}^{hs}(d_i) \right). \quad (2.13)$$

The first term in this equation accounts for the decrease in the ideal free energy or the loss in the translation degrees of freedom due to decrease in the number of molecules (from $N_s$ spheres to $N$ chains), while the second term accounts for the decrease in the excluded volume as the chains are formed. Substituting eqs. 2.3, 2.6, and 2.13 in
eqn. 2.2 gives

$$
\frac{A_{hc}}{NkT} = \sum_i m_{i} x_i (\ln \rho_i - 1) + \sum_i x_i m_{i} \frac{A_{hs}}{N kT} - \sum_i x_i (m_{i} - 1) (\ln \rho_i - 1) - \sum_i x_i (m_{i} - 1) (\ln g_{ii}^{hs}(d_i)) ,
$$

or simply,

$$
\frac{A_{hc}}{NkT} = \sum_i x_i (\ln \rho_i - 1) + \sum_i x_i m_{i} \frac{A_{hs}}{N kT} - \sum_i x_i (m_{i} - 1) (\ln g_{ii}^{hs}(d_i)) .
$$

In eqn. 2.15, the first term is the ideal free energy of the mixture of chain fluids. Hence, the residual helmholtz free energy of a mixture of hard chain fluids from SAFT-HS is given as

$$
\frac{A_{hc,res}}{NkT} = \sum_i x_i m_{i} \frac{A_{hs}}{N kT} - \sum_i x_i (m_{i} - 1) (\ln g_{ii}^{hs}(d_i)) .
$$

Ghonasi and Chapman [80] and independently Chang and Sandler [81] proposed a modification of the expressions for the free energy contribution due to chain connectivity [80]. Ghonasgi and Chapman labeled the resulting equation of state SAFT-Dimer (or SAFT-D for short). The change to the chain term ($A_{chain}^{hs}$) is schematically illustrated in figure 2.3, and consists in the addition of an extra step in the derivation of the expression for the free energy contribution due to chain connectivity. In SAFT-HS, all the bonds between segments are formed simultaneously, and are thus equivalent. In SAFT-D, dimers are formed in a first step from the mixture of hard
spheres, and the change in free energy upon dimerization is written out, labeled here $A^{\text{monomer-dimer}}$. A second step consists of forming bonds between dimers to obtain chains; the change in free energy due to chain formation from dimers, labeled as $A^{\text{dimer-chain}}$, is also derived using TPT1. The total contribution to the free energy due to chain connectivity is thus the sum of the two contributions $A^{\text{monomer-dimer}}$ and $A^{\text{dimer-chain}}$. When this path towards chain formation is taken, any segment on a given chain is “aware” of the presence of its two nearest neighbors and of the presence of the segments next to them, as opposed to the chain term in the original SAFT-HS. This implies that more detailed information about the chain formation is incorporated into the chain EOS, thus improving the predictive abilities of the equation of state. The new chain free energy contribution has the following form [80]

$$\frac{A^{hc,\text{res}}}{NKT} = \sum_i x_i m_i \frac{A^{hs}}{N_s kT} - \sum_i x_i \left( \frac{m_i}{2} - 1 \right) \ln g^{hd}_i (\sigma_{ii}) - \sum_i x_i \frac{m_i}{2} \ln g^{hs}_i (\sigma_{ii}),$$

(2.17)

where $g^{hd}_i (\sigma_{ii})$ is the site-site correlation function at contact for a mixture of hard dispheres. The form of the site-site correlation function proposed by Ghonasgi and Chapman [80, 84] is used in this work.

$$g^{hd}_{ij} (\sigma_{ij}) = \frac{1 + 2 \zeta_2 \sigma_i \sigma_j / \sigma_{ij} + c \zeta_2^{6.17} (\sigma_i \sigma_j / \sigma_{ij})^{6.17}}{2(1 - \zeta_3)^2},$$

(2.18)

where, $c = 26.4503$. 

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2.2.2 Dispersion term

Now that the equation of state for hard chains is defined, the contribution that will account for the dispersive interactions between molecules is to be added. The model potential used to describe the attraction is given by the square-well potential.

\[
\varphi_i^{att}(r) = \begin{cases} 
0 & r < \sigma_i \\
-c_i & \sigma_i \leq r < \lambda_i \\
0 & r \geq \lambda_i 
\end{cases}
\]  

(2.19)

where \( \lambda \) is the width of the potential well, \( \lambda = 1.5\sigma \). An accurate expression for this attraction/dispersion contribution to the free energy was developed by Gross and Sadowski [48] based on the extension of the perturbation theory of Barker and Hen-
derson [76, 77] for atomic fluids to chain-like fluids. It is a second-order perturbation theory, in which the Helmholtz free energy is given as a sum of first- and second-order contributions, as

\[
\frac{A_{\text{disp}}^{\text{disp}}}{NKT} = \frac{A_{\text{disp}}^{\text{disp}}}{NKT} + \frac{A_{\text{disp}}^{\text{disp}}}{NKT},
\]  

(2.20)

For chain-like molecules, the first and second term of the perturbation expansion have the following form

\[
\frac{A_{1}^{\text{disp}}}{NKT} = -2\pi \rho I_{1} \sum_{i} \sum_{j} x_{i}x_{j}m_{i}m_{j} \left( \frac{\epsilon_{ij}}{kT} \right) \sigma_{ij}^{3}, \tag{2.21}
\]

and

\[
\frac{A_{2}^{\text{disp}}}{NKT} = -\pi \rho I_{2} \bar{m} \left( 1 + Z^{hc} + \rho \frac{\partial Z^{hc}}{\partial \rho} \right)^{-1} \sum_{i} \sum_{j} x_{i}x_{j}m_{i}m_{j} \left( \frac{\epsilon_{ij}}{kT} \right)^{2} \sigma_{ij}^{3}, \tag{2.22}
\]

where \(Z^{hc}\) is the compressibility factor of the hard-chain fluid, the parameters \(\epsilon_{ij}\) and \(\sigma_{ij}\) are obtained by conventional Berthelot-Lorentz mixing rules, \(\bar{m}\) is the average chain length of the mixture defined as

\[
\bar{m} = \sum_{i} x_{i}m_{i}, \tag{2.23}
\]

and \(I_{1}\) and \(I_{2}\) are integrals given as

\[
I_{1} = \int_{1}^{\infty} \bar{u}^{\text{att}} g^{hc}(m; x^{2}d) x^{2}dx, \tag{2.24}
\]
and

\[ I_2 = \frac{\partial}{\partial \rho} \left[ \rho \int_{1}^{\infty} (\tilde{u}^{\text{att}})^2 g^{hc}(m; x \frac{\sigma}{d}) x^2 dx \right]. \quad (2.25) \]

In eqs. 2.24 and 2.25, \( x \) is the radial distance around a segment \((x = r/\sigma)\), \( \tilde{u}^{\text{att}} = u^{\text{att}}/\epsilon \) is the reduced potential function, and \( g^{hc} \) is the average segment-segment radial distribution function of the hard-chain fluid with temperature dependent segment diameter, \( d(T) \). The analytical evaluation of these integrals is tedious since the expressions for the average segment-segment radial distribution functions for hard chain fluid are lengthy. In addition these correlations become less accurate for long chains and polymers [85]. Thereby, these were approximated as a power series of the packing fraction, with the coefficients being a function of the average chain length of the mixture.

\[ I_1(\eta, \tilde{m}) = \sum_{i=0}^{6} a_i(\tilde{m}) \eta^i, \quad (2.26) \]

and

\[ I_2(\eta, \tilde{m}) = \sum_{i=0}^{6} b_i(\tilde{m}) \eta^i. \quad (2.27) \]

The coefficients are given by

\[ a_i(\tilde{m}) = a_{0i} + \frac{(\tilde{m} - 1)}{\tilde{m}} a_{1i} + \frac{(\tilde{m} - 1)}{\tilde{m}} \frac{(\tilde{m} - 2)}{\tilde{m}} a_{2i}, \quad (2.28) \]

and

\[ b_i(\tilde{m}) = b_{0i} + \frac{(\tilde{m} - 1)}{\tilde{m}} b_{1i} + \frac{(\tilde{m} - 1)}{\tilde{m}} \frac{(\tilde{m} - 2)}{\tilde{m}} b_{2i}. \quad (2.29) \]
where \( a_{0i}, a_{1i}, \) and \( a_{2i}, \) as well as \( b_{0i}, b_{1i}, \) and \( b_{2i}, \) are the model (universal) constants.

The new EOS has a different hard chain term than the PC-SAFT equation of state; therefore the first step was to obtain the universal constants from the experimental data of n-alkanes, following the method proposed by Gross and Sadowski for the estimation of the constants of the original PC-SAFT equation of state [48]. During the regression process, it was found that the sensitivity of the model to the values of \( b_{0i}, b_{1i} \) and \( b_{2i} \) was low, therefore the values of \( b_{0i}, b_{1i} \) and \( b_{2i} \) regressed by Gross and Sadowski [48] were not changed. The \( a_{0i}, a_{1i} \) and \( a_{2i} \) constants were regressed using the data for the n-alkane series from n-C3 to n-C10. The universal model constants are reported in Table 2.1. It should be noted that unlike the original work by Gross and Sadowski [48], methane was not used during the regression. This is because the chain length parameter of methane less than two. The hard chain term in SAFT-D is undefined for values less than two, as it includes a contribution from dimerization. The focus of this work being on long chain molecules and polymers, this problem is not addressed here.

<table>
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<th>( a_0 )</th>
<th>( a_1 )</th>
<th>( a_2 )</th>
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<th>( b_1 )</th>
<th>( b_2 )</th>
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**Table 2.1:** Universal model constants. The values of \( a_0, a_1 \) and \( a_2 \) were adjusted in this work; the values of \( b_0, b_1 \) and \( b_2 \) are from Gross and Sadowski [48].
2.3 Results and discussion

2.3.1 Pure components

The pure component data, namely, the vapor pressure, saturated liquid densities and liquid densities from PvT data were fitted to obtain the pure component parameters, chain length(m), segment diameter(σ) and the segment energy parameter(ε/k). These parameters were obtained for n-alkane series from n-C3 to n-C20. The regression was done using Levenberg-Marquardt algorithm by minimizing the objective function

\[ F(m, \sigma, \varepsilon/k) = \sum_{i=1}^{N_{\text{exp}}} \left( \frac{\theta_i^{\text{exp}} - \theta_i^{\text{calc}}}{\theta_i^{\text{exp}}} \right)^2, \]  

(2.30)

where \( \theta_i \) is the thermodynamic property, namely vapor pressure or saturated liquid density or PvT data, considered for regression. Once the parameters were obtained, the average absolute deviation (AAD%) was calculated for both vapor pressure and saturated liquid density data. The parameters along with the AAD% are presented in table 2.2.

The pure component vapor-liquid equilibria predictions of the new EOS are compared to experimental data in figure 2.4 for selected n-alkanes. The temperature range of the experimental data used for regression is the same as that used for determining the PC-SAFT parameters for these components [48]. ADD% for both \( P_{\text{sat}} \) and \( \rho_{\text{liq}} \) for the new EOS are smaller than PC-SAFT for the n-alkanes considered. Based on these parameters, the critical temperatures and pressures were computed.
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<th>m</th>
<th>$\sigma$ [Å]</th>
<th>$\epsilon/k$ [K]</th>
<th>AAD%</th>
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Table 2.2: Pure component parameters for n-alkane series. The data used for parameter regression were the same as in Gross and Sadowski [48].

Figures 2.5 a and b compare the critical temperatures and pressures for the n-alkane series from n-C3 to n-C20, predicted from the new EOS and PC-SAFT with the experimental critical constants. While both equations of state over-predict the critical temperature and pressure, the critical constants predicted by the new EOS are in better agreement with the experimental data, especially for longer n-alkanes. The improvement of density predictions over PC-SAFT in the critical region is also illustrated in figure 2.4. Like other classical equations of state, the new EOS cannot describe accurately the singular asymptotic behavior of fluids, which is marked by long-range density fluctuations. Several methodologies for incorporating critical scaling into different versions of SAFT have been recently proposed [86, 87] in order
to improve the predictions of the EOS in the critical region. The results have been promising, but further studies are necessary before an EOS including critical scaling can be used as a predictive tool for a wide range of systems. Consequently, the better performance of the new EOS near the critical region without introducing any new parameters is commendable, since correct prediction of the phase behavior near the critical region is of great industrial significance in a wide variety of fluid separation processes like supercritical extraction and fractionation of petroleum. The new EOS correlates pure component properties better than PC-SAFT (see figure 2.4). The deviations are low for higher alkanes, indicating the improvement over PC-SAFT for longer chain lengths. Although the low values of AAD% and better estimates of critical temperatures and pressures, demonstrate that the parameters describe the
properties of n-alkanes accurately, the tests for the robustness of the parameters are that they must follow a definite trend and when extrapolated to higher molecular weights, should predict the thermodynamics with reasonable accuracy.

Figure 2.6 shows the trend of the parameters with increasing molar mass. The parameters show a smooth course and tend to approach a constant value at large molecular weights. The pure component parameters can be correlated to the molecular weight using the following functional form,

\[
\text{parameter}(k) = q_{0k} + \frac{M_i - M_{C_3H_8}}{M_i} q_{1k} + \frac{M_i - M_{C_5H_{10}}}{M_i} \frac{M_i - 2M_{C_3H_8}}{M_i} q_{2k},
\] (2.31)
where parameter(k) is one of \((m_i/M_w, \sigma, \epsilon_i/k)\). The coefficients of the correlations are given in table 2.3. The correlations are also plotted in figure 2.6. These correlations are used to extrapolate the parameters for higher alkanes.

<table>
<thead>
<tr>
<th>parameter ((k))</th>
<th>units</th>
<th>(q_{0k})</th>
<th>(q_{1k})</th>
<th>(q_{2k})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(m/M_w)</td>
<td>mol/g</td>
<td>3.626670923</td>
<td>0.44366558</td>
<td>0.373239091</td>
</tr>
<tr>
<td>(\sigma)</td>
<td>Å</td>
<td>0.045349657</td>
<td>-0.021681925</td>
<td>-0.001005353</td>
</tr>
<tr>
<td>(\epsilon/k)</td>
<td>K</td>
<td>209.4657254</td>
<td>64.23483985</td>
<td>5.152948312</td>
</tr>
</tbody>
</table>

**Table 2.3:** Constants used in the correlation presented in Eq. (2.31) for the dependence of SAFT-D parameters on molecular weight of n-alkanes.

Figure 2.7 compares experimental saturated liquid densities of tetracosane(n-C24), triacontane(n-C30), and hexatriacontane(n-C36), with those calculated from PC-SAFT and the new equation of state using extrapolated parameters. The new EOS performs better than PC-SAFT and give reasonably accurate densities for all three components in the range of temperature considered.
Figure 2.7: Comparison of predictions from the new equation of state (solid lines) and PC-SAFT (dashed lines) with experimental data for saturated liquid density of n-C24, n-C30 and n-C36.

2.3.2 Mixtures

The new equation of state was applied to mixtures of non-associating fluids with the binary interaction parameter, $k_{ij}$ set to 0. The results were compared with PC-SAFT predictions as well as with experimental data. Figures 2.8a, 2.8b, 2.9a, and 2.9b show vapor-liquid equilibria diagrams of eicosane-propane, hexadecane-hexane, tetracosane-hexane and hexatriacontane-hexane mixtures, respectively, at various temperatures. Both EOS perform equally well for eicosane-propane mixture. For other mixtures, the new EOS is in better agreement with the experimental data. For these systems, the deviations of the predictions of the new EOS from the experimental data are low for n-C16 mixture, lower for n-C24 mixture and lowest for n-C36 mixture. This emphasizes the fact that the new EOS performs better for long chain...
Figure 2.8: (a) Vapor-liquid equilibrium of n-eicosane-propane mixture at \( T = 350 \text{ K} \). Comparison of the predictions from the new equation of state (solid lines) and PC-SAFT (dashed lines) with experimental data (symbols) from Gregorowicz et al. [88] (b) Vapor-liquid equilibrium of n-hexadecane-hexane mixture at \( T = 623 \text{ K} \). Experimental data is from Joyce and Thies [89].

Figure 2.10 compares the vapor compositions of the long chain alkanes, for three of these systems, hexadecane-hexane, tetracosane-hexane and hexatriacontane-hexane. As seen from the figure, the predictions from the new EOS are in better agreement with the experimental data. The parameters for long chain alkanes were extrapolated from the correlations from the alkane series for both the equations.
2.3.3 Polymer systems

The parameters from the \( n \)-alkane series on extrapolation to molecular weights corresponding to polymers, asymptotically tend to limiting values. Based on this extrapolation, the parameters obtained for high density polyethylene (HDPE) were \( m/M_w = 0.02268 \), \( \sigma = 4.4358 \text{Å} \) and \( \epsilon/k = 278.79 \text{ K} \). An average absolute deviation of 8% was obtained for the density data of HDPE in the pressure range from 1 to 2000 bar, and the temperature range from 410 to 473 K. With these parameters and \( k_{ij} = 0.0045 \), the phase behavior of HDPE-n-pentane mixture was calculated as shown by dot-dashed curve in figure 2.11a. These calculations show that the
extrapolated parameters can predict HDPE densities with reasonable accuracy along with predicting better phase behavior for HDPE-pentane system than PC-SAFT. As pointed out by Gross and Sadowski [79], extrapolated parameters do not account for high molecular effects such as entanglement, and shielding which are not observed in lower n-alkanes. Hence, the obtained parameters were modified slightly along with $k_{ij}$, to obtain a better fit for the phase behavior of HDPE-n-pentane system. Finally, the parameters for HDPE were fixed at $m/M_w = 0.02361$, $\sigma = 4.4357 \text{Å}$, and $\epsilon/k = 278.78 \text{ K}$. The parameters give better agreement for the density data of HDPE in the previous pressure and temperature range, with an average absolute deviation of 3.74%. The solid curve in figure 2.11a also shows the phase behavior of HDPE-pentane using these parameters in a cloud point pressure versus polyethylene (PE)
concentration diagram. The two phase region predicted by the new EOS is broader than PC-SAFT prediction (PC-SAFT parameters for HDPE are taken from [79]) and the phase envelope is in good agreement with the experimental data. The phase behavior of the HDPE-n-hexane system predicted from the new EOS is shown in figure 2.11b. The phase behavior is compared with the experimental data and PC-SAFT predictions. At low polymer concentrations ($W_P \leq 10\%$), both EOS predict similar phase behavior. At higher polymer concentrations the PC-SAFT pressure-composition curve becomes steeper. The new EOS predicts a broader two phase region.

In both the previous cases the polymer was assumed to be monodisperse. Kiran et. al. [93] studied the effect of polydispersity on the demixing pressure of polyethylene in $n$-pentane. The PE sample used for the analysis had a $M_w = 121\, kg/mol$ and a polydispersity index of 4.32. The molecular weight distribution of the sample was determined by gel-permeation chromatography (GPC) analysis. Based on the analysis the polymer was characterized by 10 pseudo-components (see table 2.4) for our calculations. The phase envelope predicted from the new EOS for this HDPE-n-pentane system is shown in figure 2.12a. The results are compared with the experimental data and the prediction from PC-SAFT. The new EOS shows significant improvement in the shape of the cloud point curve compared to PC-SAFT. The pressure composition slope is nearly the same as what is seen from the experimental data, hence the new EOS predicts the two phase region more accurately.
Figure 2.11: (a) Phase equilibrium of PE-n-pentane at T = 460 K. Comparison of the predictions from the new equation of state (solid line, $k_{ij} = 0.0065$) and PC-SAFT (dashed line, $k_{ij} = -0.005$) with experimental data from Kiran et al. [91] (PE: $M_w = 108$ kg/mol, $M_w/M_n = 1.32$). The dot-dashed line is the prediction from the new equation of state with parameters extrapolated from the alkane series ($k_{ij} = 0.0045$). PE was assumed to be monodisperse. (b) Phase equilibrium of PE-n-hexane at T = 500 K. Comparison of the predictions from the new equation of state (solid line, $k_{ij} = -0.004$) and PC-SAFT (dashed line, $k_{ij} = -0.01$) with experimental data from Schnell et al. [92] (PE: $M_w = 382.8$ kg/mol, $M_w/M_n = 1.19$). PE was assumed to be monodisperse.

Figure 2.12b compares the results from the new EOS with experimental liquid-liquid equilibrium (LLE) data for HDPE-n-hexane mixture. The experimental data was collected by Kennis et. al. [95] who studied the influence of nitrogen on the phase behavior of the system. The characterization of the molecular weight distribution of polyethylene was based on the three molecular weights: $M_n = 8$ kg/mol, $M_w = 177$ kg/mol, and $M_z = 1000$ kg/mol. This molecular distribution was modeled using six pseudocomponents (see table 2.5) computed by Tork et. al. [94]. For comparison, similar calculations were done using the PC-SAFT model with the same set of pseudo-
Table 2.4: Molecular weight distribution of HDPE as characterized by Gross and Sadowski [48]

<table>
<thead>
<tr>
<th>pseudocomponent ( j )</th>
<th>mol wt ( M_j ) [g/mol]</th>
<th>mass fraction of pseudocomponent ( w_{pj} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1000</td>
<td>0.025</td>
</tr>
<tr>
<td>2</td>
<td>9500</td>
<td>0.096</td>
</tr>
<tr>
<td>3</td>
<td>19500</td>
<td>0.115</td>
</tr>
<tr>
<td>4</td>
<td>32500</td>
<td>0.14</td>
</tr>
<tr>
<td>5</td>
<td>50000</td>
<td>0.128</td>
</tr>
<tr>
<td>6</td>
<td>80000</td>
<td>0.16</td>
</tr>
<tr>
<td>7</td>
<td>137500</td>
<td>0.13</td>
</tr>
<tr>
<td>8</td>
<td>212500</td>
<td>0.06</td>
</tr>
<tr>
<td>9</td>
<td>325000</td>
<td>0.1</td>
</tr>
<tr>
<td>10</td>
<td>900000</td>
<td>0.046</td>
</tr>
</tbody>
</table>

Table 2.5: Molecular weight distribution of HDPE as characterized by Tork et. al. [94]

<table>
<thead>
<tr>
<th>pseudocomponent ( j )</th>
<th>mol wt ( M_j ) [g/mol]</th>
<th>mass fraction of pseudocomponent ( w_{pj} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>432.23</td>
<td>0.043995541</td>
</tr>
<tr>
<td>2</td>
<td>27696</td>
<td>0.616896145</td>
</tr>
<tr>
<td>3</td>
<td>341590</td>
<td>0.317484536</td>
</tr>
<tr>
<td>4</td>
<td>2295800</td>
<td>0.021433497</td>
</tr>
<tr>
<td>5</td>
<td>11740000</td>
<td>0.000190184</td>
</tr>
<tr>
<td>6</td>
<td>55579000</td>
<td>9.73E-08</td>
</tr>
</tbody>
</table>

docomponents. The new EOS is in better agreement with the experimental data as compared to PC-SAFT. The liquid-liquid (LL) two phase domain is broader and the predicted phase envelope is significantly closer to the experimental data at higher PE concentrations. Thus the set of parameters for HDPE not only give better estimates of its liquid densities in a wide range of pressure and temperature but also predict better liquid-liquid phase behavior of HDPE in various solvents. This is a significant improvement considering the industrial importance of predicting accurate phase behavior of polymer systems.
2.4 Conclusions

A new equation of state is developed, based upon the hard chain equation of state developed by Ghonasgi and Chapman and by Chang and Sandler. The equation was applied to pure n-alkanes, as well as mixtures of long and short chain n-alkanes. For pure components, the critical temperatures and pressures predicted by the new EOS are closer to the experimental values than those predicted by PC-SAFT. The new EOS gives better estimates of liquid densities than PC-SAFT for long chain n-alkanes (C_{24} and higher) described with parameters extrapolated from those regressed
for the n-alkane series, emphasizing the robustness of its chain and dispersion terms for extrapolation. The new EOS also shows significantly improved predictions of phase behavior of asymmetric mixtures when compared to predictions from PC-SAFT. The results are also better in the critical region. Finally the model was applied to HDPE in various solvents, and it was found to accurately describe the phase equilibria of HDPE solutions. In particular, the model predictions of the demixing pressure are significantly closer to experimental data than the predictions of the PC-SAFT model at high polymer concentrations.
This chapter introduces the formalism of a density functional theory (DFT) and demonstrates how TPT1 or its extension for homogeneous polymer systems (SAFT) fit into this formalism. The chapter gives a brief review on the DFTs based on TPT1/SAFT.

3.1 Formalism of a density functional theory

The mathematical formulation of DFT stems from quantum mechanics. The approach was developed by Hohenberg and Kohn [96] to describe the electronic structure for a ground state of an inhomogeneous electronic field. Classical DFT (hereafter referred to as just DFT) closely resembles quantum DFT, except that the density
functional now applies to spatial distribution of the molecules of the fluid. The first application of DFT as a general methodology to classical systems was introduced by Ebner et. al. [97] for modeling the interfacial properties of a Lennard-Jones fluid.

The underlying basis of all DFTs is that the Helmholtz free energy of an open system can be expressed as a unique functional of the density profiles of the constituent molecules, independent of the external potential. This free energy \( A[\rho(\mathbf{R})] \) is referred to as the intrinsic Helmholtz free energy. The equilibrium density profile of the system can be obtained from this free energy using the energy minimum principle. The partition function of an open system at fixed \( V, T, \) and \( \mu \) in an external field \( (V^{\text{ext}}(\mathbf{R})) \) can be related to the grand potential of the system as,

\[
\Omega = -k_B T \ln \Xi. \quad (3.1)
\]

Legendre transformation of \( \Omega \) yields the intrinsic Helmholtz free energy,

\[
A[\rho(\mathbf{R})] = \Omega[\rho(\mathbf{R})] + \int d\mathbf{R}'\rho(\mathbf{R}') (\mu - V^{\text{ext}}(\mathbf{R}')), \quad (3.2)
\]

or grand potential can be written as

\[
\Omega[\rho(\mathbf{R})] = A[\rho(\mathbf{R})] - \int d\mathbf{R}'\rho(\mathbf{R}') (\mu - V^{\text{ext}}(\mathbf{R}')). \quad (3.3)
\]
Minimization of the grand potential with respect to density yields a variational equation, known as the Euler-Lagrange equation,

$$\frac{\delta A[p(R)]}{\delta \rho(R)} = \mu - V^{\text{ext}}(R).$$  \hspace{1cm} (3.4)

Given an expression for $A[p(R)]$, eq. 3.4 can be solved for the equilibrium density profile. From this density profile, both structural and thermodynamic properties can be calculated following the standard statistical mechanical relations. However a precise expression for intrinsic Helmholtz free energy is still unknown even for a hard sphere fluid. For polyatomic fluids the problem is more complex owing to the contributions of both intramolecular and intermolecular interactions to the free energy functional. Hence the central task of any DFT is to come up with an appropriate approximation for $A[p(R)]$.

A brief review of some of the DFTs developed for polyatomic fluids is presented here. The main focus is on the DFTs based on Wertheim's TPT1 which is pertinent to this research work. However, to begin with, the density functional theory developed by Chandler, McCoy and Singer [98, 99] (CMS-DFT) is discussed since it was the first application of a DFT to polymeric systems. The DFTs based on TPT1 that concern this work are those proposed by Kierlik and Rosinberg [100, 101, 102], Yu and Wu [61], and Tripathi and Chapman [60]. Both the DFTs by Yu and Wu, and Tripathi and Chapman are extensions of the DFT developed by Segura et. al. [62] for associating hard spheres. Hence it is included in the review.
3.2 Chandler, McCoy and Singer

Chandler, McCoy and Singer [98, 99] developed a DFT for polyatomic fluids within the framework of interaction site model (ISM) [37]. In ISM, molecules are modeled as chains of freely jointed spheres which interact with spherically symmetric site-site potentials. These interacting sites coincide with the centers of their respective segments [103]. The free energy for such a system can be expressed as a functional of the site densities, $\rho_i(r)$. A variational principle still exists which states that the free energy has a global minimum for the equilibrium site densities. This free energy functional has two contributions, an ideal part and a non-ideal/excess part. The ideal free energy takes only intramolecular interactions into consideration. This choice for the ideal part of the free energy is not obvious and other choices are possible. For example, McMullen and Freed [104] introduced a density functional formalism in which they assumed no bonding constraints to define their ideal free energy. This ideal free energy was, however, still different to that for a simple monomer fluid due to the fact that the monomers retained their polymer labels. Moreover, calculation of the CMS ideal free energy functional require a single chain simulation. The excess free energy includes all the intermolecular interactions. This excess contribution is calculated from the site-site correlation function of the corresponding uniform fluid, which is estimated by solving the Reference Interaction Site Model (RISM) equations [37] or their extension to polymers (Polymer Reference Interaction Site Model (PRISM) theory [105]). This lead to inconsistencies in the theory due to approximations made
in PRISM, for example, the CMS-DFT does not satisfy the wall contact theorem that relates the bulk pressure of a fluid to its density at contact with the hard wall. Another complication is the ambiguity regarding the closure relations to be used for specific applications.

### 3.3 Kierlik and Rosinberg

Kierlik and Rosinberg [100, 101, 102] were the first to develop a density functional theory for linear chain like molecules based on Wertheim's theory. Although Wertheim's thermodynamic perturbation theory was successfully applied only to bulk homogeneous systems, the derivation in general is applicable to inhomogeneous systems. Starting from a m component mixture of associating fluids with specific number of highly directional attraction sites (components of type 1 and m have only one attraction sites which can only bond to sites on components of type 2 and (m - 1), respectively, while other components of type α have two attraction sites which can only bond to sites on components of type (α - 1) and (α + 1)) in a fixed volume, they derived an expression for free energy from TPT1, in the limit of their complete association.

\[
\beta A[\rho_M] = \int dr^M \rho_M(r^M)[\ln \rho_M(r^M)-1+\omega^*_M(r^M)+\beta V(r^M)]+\beta A^E \rho_M[\rho]-\int \rho(r^M) \ln D_{1,2,\ldots,m}(r^M;[\rho])dr^M
\]

(3.5)

where \(\rho_M(r^M)\) is the multi-point-based molecular density (\(R = \{r_1, r_2, \ldots, r_m\}\) where \(r_i\) is the position of the segment 'i' in the polymer chain), \(\omega^*_M(r^M)\) is the sum of bond
bending and rotational energies, $A_R^{EX}$ is the excess free energy of the reference atomic fluid, $\rho(r)$ is the total segment density at $r$ and $D_1^{1,2,\ldots,m}(r^M)$ is defined as

$$D_1^{1,2,\ldots,m}(r^m) = y_R^{1,2}(r_1^{(1)}, r_1^{(2)})y_R^{2,3}(r_1^{(2)}, r_1^{(3)})\ldots y_R^{m-1,m}(r_1^{(m-1)}, r_1^{(m)}) \tag{3.6}$$

where $y_R^{1,2}(r_1^{(1)}, r_1^{(2)})$ is the cavity correlation function of the inhomogeneous reference fluid and $r_i^{(i)}$ is the position of the segment $i$ on chain 1. $D_1^{1,2,\ldots,m}(r^M)$ takes into consideration the volume exclusion effects of a $m$-mer. The volume exclusion due to a $m$-mer is less than $m$ times the excluded volume of a single atom due to the overlap of excluded volumes of the neighboring atoms. However, approximating it as a product of pair cavity correlation functions treats the excluded volume effect at the pair level only (deficiency in TPT1). $\omega_M^*(r^M)$ takes care of the chain connectivity.

The theory has been applied to study the structure of linear chains of freely joined hard spheres [102] and hard semi-flexible triatomic fluid [106] in slit-like pores. The results are in good agreement with the simulation results. The theory does satisfy the wall contact theorem, but the Gibbs adsorption equation was not verified [102]. However, the multi-point-based density formalism of the theory result in $m^{th}$ order implicit integral equations making the computations extremely demanding.
3.4 Segura, Chapman and Shukla

Segura et. al. [62] developed a density functional theory for associating hard spheres to study their structures against a hard wall (hydrophobic surface). The theory was based on Wertheim's TPT1. The theory was derived for associating fluids with four bonding sites but is general for any number of sites. They developed two versions of the theory.

![Diagram of associating hard spheres](image)

\[ \phi_{AB}(r, \Omega_1, \Omega_2) = \begin{cases} -\epsilon_{AB}, & r_{12} < r_c, \theta_{12} < \theta_c, \theta_{13} < \theta_c, \theta_{24} < \theta_c, \\ 0, & \text{otherwise} \end{cases} \]

**Figure 3.1:** Schematic of the associating hard spheres with four associating sites placed in tetrahedral symmetry on the spherical core; sites A, B, C are outside while site D is inside the plane of the paper. \( \phi_{AB} \) is the association potential between two sites A and B on different associating spheres.

The first version was again based on the fact that Wertheim's theory was derived in general for inhomogeneous systems as noted by Chapman [58] and Kierlik and Rosinberg [59, 100]. The model considers spherical atoms with a hard core and highly
directional attraction sites as shown in figure 3.1. From TPT1, the free energy functional for such a system of associating hard spheres can be written as a perturbation to the reference hard sphere fluid.

\[ A[\rho(r)] = A^{id}[\rho(r)] + A^{EX,hs}[\rho(r)] + A^{EX,assoc}[\rho(r)] \]  

(3.7)

where \( A^{id}[\rho(r)] \) is the ideal gas free energy, \( A^{EX,hs}[\rho(r)] \) is the contribution to the free energy due to the reference fluid of hard spheres and is approximated using the weighted density functional developed by Tarazona [107]. \( A^{EX,assoc}[\rho(r)] \) is the contribution to the free energy due to association and can be written from Chapman et. al. [58].

\[ \beta A^{EX,assoc}[\rho(r)] = \sum_{A \in \Gamma} \int d\rho(r) \left( \ln X_A(r) - \frac{X_A(r)}{2} + \frac{1}{2} \right), \]  

(3.8)

where \( X_A(r) \) is the fraction of atoms not bonded at site A and the sum is over all the sites.

\[ X_A(r_1) = \frac{1}{1 + \sum_{B \in \Gamma} K g_{hs}(\sigma; \rho_{bulk}) f_{AB} \int dr_2 \rho(r) X_B(r_2)}, \]  

(3.9)

where \( K \) is a geometric constant which depends upon the bonding volume, \( g_{hs} \) is the hard sphere correlation function, and \( f_{AB} \) is the association Mayer \( f \)-function (averaged over all configurations of sites A and B),

\[ f_{AB} = \frac{(1 - \cos \theta_C)^2}{4} \left[ \exp \left( \frac{\epsilon_{AB}}{KT} \right) - 1 \right]. \]  

(3.10)
The set of equations represented by eq. 3.9 can be solved for $X_A(r)$ using Picard’s fixed point iteration.

The second method evaluates the free energy functional due to association based on the (bulk) homogeneous association free energy using a weighted density approximation. Since the hard sphere and association interactions are of similar range, the same weighted density is used for both the terms. Hence,

$$A^{EX,assoc}[\rho(r)] = \int d\rho(r) f^{assoc}[\bar{\rho}(r)],$$

(3.11)

where $f^{assoc}[\bar{\rho}(r)]$ is the homogeneous association free energy per unit volume evaluated at the weighted density, $\bar{\rho}(r)$.

$$\beta f^{assoc}[\bar{\rho}(r)] = \sum_{A \in \Gamma} \left( \ln \bar{X}_A(r) - \frac{X_A(r)}{2} + \frac{1}{2} \right),$$

(3.12)

and

$$\bar{X}_A(r_1) = \frac{1}{1 + \sum_{B \in \Gamma} K g_{hs}(\sigma_i; \rho_{bulk}) f_{AB} \bar{\rho}(r_1) \bar{X}_B(r_1)}.$$  

(3.13)

Both the methods were successfully applied to associating hard spheres confined between two hard walls. However, the first method requires the solution of two integral equations and is computationally expensive. Hence, method 2 was used by Segura, Chapman and co-workers in all their later works with associating fluids [108, 109]. This approach has been widely applied to investigate the effect of association on the phase behavior and structure of associating fluids confined between hydrophobic
surfaces.

3.5 Yu and Wu

Yu and Wu [61] extended the idea of using a weighted density approximation for associating fluids from Segura et. al. [62] to freely jointed hard chain fluids. However the density independent weights for calculating the weighted densities are based on the Fundamental Measure Theory (FMT) of Rosenfeld [110].

The free energy functional for chain fluids is expressed as the sum of an ideal gas term $A_{id}[\rho_M(r^M)]$ and an excess term $A_{EX}[\rho_M(r^M)]$ due to intra- and intermolecular interactions.

$$A[\rho_M(r^M)] = A_{id}[\rho_M(r^M)] + A_{EX}[\rho_M(r^M)].$$

Yu and Wu used the same ideal free energy functional as used by Woodward [111]. All monomers in a ideal chain are non-interacting, i.e. the chain is made up of point monomers, where successive monomers in a given chain are held at a fixed separation given by the bond length, $\sigma$, but otherwise are allowed full configurational freedom. The free energy of such a random flight chain based on the molecular density $\rho_M(r^M)$ is given as,

$$\beta A_{id}[\rho_M] = \int dr^M \rho_M(r^M) [\ln \rho_M(r^M) - 1] + \beta \int dr^M \rho_M(r^M)V_b(r^M),$$
where $dV = dr_1 dr_2 \ldots dr_M$ represents a set of differential volume, $V_b(r^M)$ is the bonding potential which represents the chain connectivity.

$$\exp[-\beta V_b(r^M)] = \prod_{i=1}^{M-1} \frac{\delta(|r_{i+1} - r_i| - \sigma_1)}{4\pi \sigma_i^2},$$  \hspace{1cm} (3.16)

where $M$ is the number of segments in the chain. On the contrary, the excess free energy was derived as a functional of the segment densities. It is decomposed as

$$\beta A^{EX}[\rho_M] = \int dr \left( \Phi^{hs}[\{n_\alpha(r)\}] + \Phi^{chain}[\{n_\alpha(r)\}] \right),$$  \hspace{1cm} (3.17)

where $\Phi^{hs}[\{n_\alpha(r)\}]$ and $\Phi^{chain}[\{n_\alpha(r)\}]$ are the reduced free energy densities due to hard sphere repulsion and chain connectivity, respectively, and $\{n_\alpha(r)\}$ is the set of the weighted densities. Both $\{n_\alpha(r)\}$ and $\Phi^{hs}[\{n_\alpha(r)\}]$ are computed from FMT. The chain connectivity term is based on SAFT for a bulk fluid. For a bulk fluid it is given by,

$$\Phi^{chain,b} = \frac{1 - M}{M} \rho_{1b} \ln y^{hs,b}_{11}(\sigma_1)$$  \hspace{1cm} (3.18)

where $\rho_{1b}$ is the bulk segment density and $y^{hs,b}_{11}(\sigma_1)$ is the contact value of the cavity correlation function between segments in the bulk. To extend eq. 3.18 to inhomogeneous systems using FMT (following the same methodology as used by Segura et. al. [62]), $\rho_{1b}$ is replaced by $n_0 \zeta_1$ and $y^{hs,b}_{11}(\sigma_1)$ is replaced by,

$$y^{hs}_{11}(\sigma_1, n_\alpha) = \frac{1}{1 - n_3} + \frac{n_2 \sigma_1 \zeta_1}{4(1 - n_3)^2} + \frac{n_2^2 \sigma_1^2 \zeta_1}{72(1 - n_3)^3},$$  \hspace{1cm} (3.19)

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where \( \zeta_1 = 1 - n_{V21}.n_{V21}/n_{21}^2, \ \zeta = 1 - n_{V2}.n_{V2}/n_2^2, \) and \( n_{\alpha j} \) are the six weighted densities from FMT \((\alpha = 0, 1, 2, 3, V1, V2)\) for component \( j \). Hence the inhomogeneous free energy density due to chain connectivity is given as

\[
\Phi_{\text{chain}}[\{n_\alpha(r)\}] = \frac{1 - M}{M} n_{01}(r) \zeta_1(r) \ln y_{11}^{ht}(\sigma_1, \{n_\alpha(r)\}). \tag{3.20}
\]

One of the assumption that goes in the derivation is that all of the segments in the chain are of the same size. Furthermore, as the final form of the functionals are based on (multi-point-based) molecular densities, the calculations of segment density profiles require solving \( m^{th} \) order implicit integral equations.

The theory was compared with Kierlik and Rosinberg [102] and simulation results for the structure of hard chain fluid in slit-like pores. Even though the theory is in better agreement with simulation data than Kierlik and Rosinberg for the average density profile of the segments in the chain, it underestimates the contact densities. Moreover, Kierlik and Rosinberg were able to get better density distributions for the individual segments in the chain.

In addition to hard chain fluid, Wu and co-workers have applied their theory to mixtures of polymeric fluids [61], block copolymers near selected surfaces [112], and semi-flexible polymers [113].
3.6 Tripathi, Dominik and Chapman

Tripathi and Chapman [60] developed interfacial SAFT (or iSAFT) as an extension of the first version of the density functional theory of Segura et. al. [62] for associating fluids to polyatomic fluids. The excess free energy functional due to the formation of chains is derived along similar lines as SAFT. Considering the polyatomic system as a mixture of associating atomic fluids in the limit of complete association, the free energy functional can be derived from Wertheim's TPT1. The derivation of the theory (for chains of $m$ segments as shown in the figure 3.2) is briefly discussed below.

![Figure 3.2: Schematic of the chain formed from $m$ associating spheres.](image)

The Helmholtz energy of a mixture of associating fluids can be written as

$$A[\rho_\alpha] = A_{id}[\rho_\alpha] + A_{EX,^{het}}[\rho_\alpha] + A_{EX,^{assoc}}[\rho_\alpha] + A_{EX,^{att}}[\rho_\alpha], \quad (3.21)$$

where various contributions to the free energy functional are: $A_{id}$ is the ideal gas free
energy contribution, $A^{EX,hs}$ due to volume exclusion/short range repulsion, $A^{EX,assoc}$ due to association, and $A^{EX,att}$ due to long range attraction. The ideal gas functional is defined as

$$\beta A^{id}[\rho_\alpha] = \int dr_1 \sum_{\alpha=1}^{m} \rho_\alpha^{seg}(r_1)(\ln \rho_\alpha^{seg}(r_1) - 1). \quad (3.22)$$

$A^{EX,hs}$ is calculated from Rosenfeld's FMT [110] for mixtures of hard sphere fluids. $A^{EX,assoc}$ can be written following TPT1 (eq. 3.8) as

$$\beta A^{EX,assoc}[\rho_\alpha] = \int dr_1 \sum_{\alpha=1}^{m} \rho_\alpha^{seg}(r_1) \sum_{A \in \Gamma^{(\alpha)}} \left( \ln X_\alpha^A(r_1) - \frac{X_\alpha^A(r_1)}{2} + \frac{1}{2} \right). \quad (3.23)$$

The first summation is over all the segments $\alpha$, and the second over all the association sites on segment $\alpha$. $X_\alpha^A$ denotes the fraction of segments of type $\alpha$ which are not bonded at their site A. This fraction is given by the law of mass action.

$$X_\alpha^A(r_1) = \frac{1}{1 + \int dr_2 X_\alpha^{B'}(r_2) \Delta^{\alpha\alpha'}(r_1, r_2) \rho_\alpha^{seg}(r_2)}, \quad (3.24)$$

where $\alpha'$ denotes the neighboring segment of $\alpha$, site A on $\alpha$ bonds to site B on $\alpha'$, and

$$\Delta^{\alpha\alpha'}(r_1, r_2) = K F^{\alpha\alpha'}(r_1, r_2) y^{\alpha\alpha'}(r_1, r_2). \quad (3.25)$$

$K$ is a constant geometric factor which depends upon the bonding volume (the sites on the segments are highly directional, they bond only when the sites on the two segments are within specific orientations, see Segura et. al. [62]), $y^{\alpha\alpha'}(r_1, r_2)$ is the cavity
correlation function for an inhomogenous hard sphere reference fluid, and \( F^{\alpha\alpha'}(r_1, r_2) \) is the association Mayer-\( f \) function given as

\[
F^{\alpha\alpha'}(r_1, r_2) = [\exp(\beta \varepsilon_0 - \beta \nu_{\text{bond}}^{\alpha\alpha'}(r_1, r_2)) - 1],
\tag{3.26}
\]

where \( \varepsilon_0 \) is the association strength and \( \nu_{\text{bond}}^{\alpha\alpha'} \) is the bonding potential. In the limit of complete association, \( X_A^{\alpha}(r_1) \to 0 \) and \( \varepsilon \to \infty \), leading to following simplifications,

\[
X_A^{\alpha}(r_1) = \frac{1}{K \exp(\beta \varepsilon_0) \int dr_2 X_B^{\alpha'}(r_2) \rho_{\alpha'}^{\text{seg}}(r_2) y^{\alpha\alpha'}(r_1, r_2) \exp(-\beta \nu_{\text{bond}}^{\alpha\alpha'}(r_1, r_2))}. \tag{3.27}
\]

Two approximations were made to obtain simple analytical expressions for \( X_A^{\alpha} \),

- Each site reaches its vanishing limit at the same rate, i.e. \( X_B^{\alpha'}(r_2) \approx X_A^{\alpha}(r_1) \).

Thereby,

\[
X_A^{\alpha}(r_1)^2 = \frac{1}{K \exp(\beta \varepsilon_0) \int dr_2 \rho_{\alpha'}^{\text{seg}}(r_2) y^{\alpha\alpha'}(r_1, r_2) \exp(-\beta \nu_{\text{bond}}^{\alpha\alpha'}(r_1, r_2))}. \tag{3.28}
\]

- The inhomogeneous cavity correlation function, \( y^{\alpha\alpha'}(r_1, r_2) \) is approximated by its bulk value (at contact) at a weighted density.

Using these approximations the final expression for \( A^{EX,\text{assoc}} \) is given as

\[
\beta A^{EX,\text{assoc}}[\rho_{\alpha}] = \int dr_1 \sum_{a=1}^{m} \rho_{\alpha}^{\text{seg}}(r_1) \sum_{\alpha'} \left( -\frac{1}{2} \ln y^{\alpha\alpha',\text{bulk}}(o^{\alpha\alpha'}, [\rho_{\alpha}^{\text{seg}}(r_1)]) \right)
\]

\[\text{76}\]
\[ \int dr_2 \exp(-\beta v_{\text{bond}}^{\alpha \alpha'}(r_1, r_2))\rho_\alpha^{\text{seg}}(r_2). \]  

(3.29)

The long range attraction is included using the mean field approximation.

\[ A^{EX, \text{att}}[\rho_\alpha] = \frac{1}{2} \sum_{\alpha=1}^{m} \sum_{\beta=1}^{m} \int dr_1 dr_2 u_{\alpha \beta}^{\text{att}}(|r_2 - r_1|) \rho_\alpha^{\text{seg}}(r_1) \rho_\beta^{\text{seg}}(r_2). \]  

(3.30)

These functionals are based on segment densities, hence only first order decoupled differential (Euler-Lagrange) equations have to be solved in order to obtain the density profiles of the segments.

The theory performs very well in comparison with the DFTs developed by Kierlik and Rosinberg [102] and Yu and Wu [61]. The density profiles of the individual segments are in better agreement with simulation results. The theory was successfully applied to model polymer solutions and blends, even blends of branched and linear chains. Dominik et. al. [114] extended the theory to real systems and calculated the surface tension of n-alkanes and polymer melts.

### 3.7 Conclusions

As discussed in the previous section, iSAFT offers a distinct advantage over the other DFTs based on TPT1. Comparisons for model polymer systems show that iSAFT provides a computationally efficient segment-density based approach with an accuracy equivalent to other molecular density or simulation based approaches. Dominik et. al. [114] even calculated the surface tension of n-alkanes, PS and LLDPE.
polymers from iSAFT. The pure component parameters used to calculate the surface
tension of these real components were regressed to their bulk phase behavior. The
study clearly demonstrates that both bulk phase behavior and interfacial properties
can be described within the single framework of iSAFT (with the same set of pa­
rameters for both the systems). The success of the theory motivates us to extend
it to more complex systems, like copolymers and polymer brushes. However, few
shortcomings in iSAFT prevent us from doing so.

![Figure 3.3](image)

**Figure 3.3:** (a) Comparison of the density profiles of a single 50-mer hard chain tethered
to a hard surface (at z = 0) from simulation (symbols) and iSAFT (solid line). (b) Density
profile of a single 50-mer ideal gas chain tethered to a hard surface (at z = 0).

The approximations in iSAFT are most accurate for the average segment density of
homonuclear polymers. If the segments on the polymer are too dissimilar, the theory
becomes less accurate. Even for homonuclear polymers, iSAFT does not constrain
all of the segments to satisfy stoichiometry. That is, although the average segment
density profiles agree well with the simulation results, the density of the individual
segments in a chain averaged over the system are not equal. As an example, consider
the case of a single chain tethered to a hard surface, the segment tethered at the
surface fixes the position of the second segment within the bonding length (without
overlapping the surface or other segments), the second segment fixes the third and
so on. With no solvent present, the chain tries to reduce its configurational entropy
by coiling around. This limits the chain to within a few molecular diameters from
the surface as seen in the simulation results shown in the figures 3.3a for a hard
chain and 3.3b for an ideal chain. An ideal chain is more collapsed onto the surface
than a hard chain due to absence of volume exclusion. iSAFT was tested for hard
chain tethered at a hard surface. Comparisons with simulation results (figure 3.3a)
show that the theory predicts that the chains are too extended. The reason for the
stoichiometry problem and the issue with the tethered chains appears to be related
to the fact that in the present theory each segment only has information about the
segments it is bonded to. Ideally, each segment on the chain should have information
about the chemical potential of every other segment on the chain. In iSAFT, although
the bond connectivity has been accounted for while defining the association Mayer-f
function, the later segments somehow do not know that the first segment is tethered
to the surface, and hence they try to reach out further away from the wall. However,
this information can be propagated along the chain by having the theory enforce
stoichiometry.

The approximation that 'Each site reaches its vanishing limit at the same rate, i.e. $X_B'(r_2) \approx X_A'(r_1)' does not correctly constrain stoichiometry. It is true that in the limit of complete association that both $X_A$ and $X_B$ tends to zero, but probably not at the same rate. Thus the central task is to get an accurate expression for $X_A$. Modified iSAFT density functional theory developed in this research work addresses this problem and is directly applicable to a range of polymer systems with heteronuclear chains.
Chapter 4

Modified iSAFT: a new density functional theory for inhomogenous polymers

iSAFT as developed by Tripathi and Chapman [60, 115] is powerful and computational efficient density functional theory (DFT) for inhomogeneous polymer systems. However, as discussed in the last chapter, the approximations made in iSAFT are in general more applicable to homonuclear polymer chains. This chapter presents a new DFT labeled as modified iSAFT as it shares the same basis as iSAFT and demonstrates its applicability to a range of heteronuclear polymer systems.
4.1 Introduction

The central approximation of any density functional theory is an expression for the intrinsic Helmholtz free energy of the system. However a precise expression for this free energy is still unknown even for a hard sphere fluid. For fluids containing polyatomic molecules the problem is more complex owing to the contributions of both intramolecular and intermolecular interactions to the free energy. The most common molecular model for a polyatomic molecule is a chain of spherical segments which are tangentially bonded to each other. The preliminary step in developing the free energy for such a fluid is to split the free energy into an ideal and an excess part. Existing DFTs for polyatomic molecules vary in the way intramolecular interactions are included into the ideal or the excess part. In principle, both intramolecular and intermolecular contributions can be incorporated in the excess free energy [116]. Moreover some DFTs express the free energy as a functional of the multi-point molecular density $\rho_M(R)$, where $R (= \{r_i\}, i = 1, N)$ denotes the positions of all the segments on a polymer molecule while others express the free energy as a functional of the segment densities, $\{\rho_i(r_i)\}$. The many body nature of the molecular density and the bonding constraints result in $N^{th}$ order implicit integral equations for the density profile, making the computations demanding as opposed to a segment density based functional which leads to a system of $N$ nonlinear equations for the density profile.

Tripathi and Chapman [60, 115] proposed a segment-density based DFT known as interfacial SAFT (or iSAFT). The ideal free energy considers an ideal gas of monomers
and the excess free energy includes both intra- and intermolecular interactions. An advantage of this approach is that the theory predicts the change in the free energy functional on bonding an ideal gas of segments to form an ideal gas of chains, in terms of the segment densities. The excess free energy is also derived in terms of segment densities by treating the polyatomic system as a mixture of associating atomic segments in the limit of complete association (similar to SAFT [46] for homogeneous fluids). This leads to a DFT that offers accuracy comparable to molecular density based theories at a computational expense comparable to those of atomic DFTs. The theory was successfully applied to study polymer melts, solutions and blends confined in slit-like pores. Dominik et. al. [114] extended the theory to real systems and calculated the interfacial properties of n-alkanes and polymers. All these applications were for homonuclear chains (chains having similar segments). Limitations of the Tripathi and Chapman form of DFT are seen most clearly when applied to heteronuclear chains. Since a segment in a chain only knows about its nearest neighbors, information about unlike segments is not shared sufficiently along a chain. For example, in block copolymers, one block has little information about the other block. One consequence is that the theory does not constrain the overall stoichiometry of segments in the system. Overall stoichiometry means that the average densities of all the segments on a molecule in the system are equal. These limitations are present because the stoichiometry was assumed in the derivation of the theory rather than having the theory enforce stoichiometry.
The objective of the current work is to extend iSAFT to satisfy stoichiometry and to demonstrate the applicability of modified iSAFT to heteronuclear chains by applying it to various model systems. The next section presents the theoretical development of modified iSAFT. The theory satisfies the overall stoichiometry, and each segment knows about all the other segments in the chain. Furthermore, the theory requires only the bulk chemical potential of the chain as an input rather than segment bulk chemical potentials in the case of the original iSAFT. However, the theory is computationally more expensive than original iSAFT. The theory has been successfully applied to study complex systems like lipids near a surface, lipid bilayers, thin and ultra-thin copolymer films, and ordering in bulk copolymer melts. The results for these systems and their comparisons with results from molecular simulations are discussed in the subsequent section.

4.2 Model and theory

Consider a fluid mixture of polyatomic molecules where the molecules consist of spherical segments tangentially bonded together to form flexible chains. Each of the segments of the chains can be different. For the sake of simplicity, the derivation is presented for a pure fluid of chain molecules with ‘m’ segments, but the theory is in general applicable to mixtures.

The grand free energy of a chain of ‘m’ segments at fixed $V$, $T$, and $\mu$ in an
external field \( (V_{\text{ext}}(R)) \) can be related to the intrinsic Helmholtz free energy as

\[
\Omega[\{\rho_{\alpha}(r)\}] = A[\{\rho_{\alpha}(r)\}] - \sum_{\alpha=1}^{m} \int dr' \rho_{\alpha}(r')(\mu_{\alpha} - V_{\alpha}^{\text{ext}}(r')) ,
\]

where \( \rho_{\alpha} \) is the density of the \( \alpha \)th segment, \( \mu_{\alpha} \) is its chemical potential, and \( V_{\alpha} \) is the external field acting on that segment. Minimization of the grand potential with respect to density of the segments yield a system of variational equations, known as the Euler-Lagrange equations,

\[
\frac{\delta A[\{\rho_{\alpha}(r)\}]}{\delta \rho_{\alpha}(r)} = \mu_{\alpha} - V_{\alpha}^{\text{ext}}(r) \quad \forall \alpha = 1, m.
\]

Solution of this set of equations gives the equilibrium density profile of the segments. From the equilibrium density profiles, both structural and thermodynamic properties can be calculated following the standard statistical mechanical relations. The intrinsic Helmholtz free energy functional of such a chain of \( 'm' \) segments is obtained along similar lines as iSAFT [60]. Considering the polyatomic system as a mixture of associating spherical segments in the limit of complete association, the free energy functional can be derived from Wertheim’s TPT1 [46, 47, 58, 26, 27, 28, 29, 62]. The model considers spherical segments with hard cores and highly directional attraction sites. For a linear chain of \( m \) segments, consider an \( m \) component stoichiometric mixture of associating spheres. Component 1 has a single association site labeled ‘A’, components 2 till (\( m-1 \)) have two association sites labeled ‘A’ and ‘B’ while component
m has one association site labeled 'B'. Site 'A' on component 'i' can associate only with site 'B' on component 'i+1'. The chain is formed in the limit of complete association. To extend the model to branched chains, the segments at which the branches attach to the backbone will have additional sites to bond with the segments in the branch. The Helmholtz free energy of such a mixture of associating spheres can be written as

\[ A[\{\rho_\alpha\}] = A^{id}[\{\rho_\alpha\}] + A^{EX,hs}[\{\rho_\alpha\}] + A^{EX,assoc}[\{\rho_\alpha\}] + A^{EX,att}[\{\rho_\alpha\}], \quad (4.3) \]

where various contributions to the free energy functional are: \( A^{id} \) is the ideal gas free energy contribution, \( A^{EX,hs} \) due to volume exclusion/short range hard sphere repulsion, \( A^{EX,assoc} \) due to association, and \( A^{EX,att} \) due to long range attraction.

### 4.2.1 Free energies

The ideal gas functional is defined by

\[ \beta A^{id}[\{\rho_\alpha\}] = \int dr_1 \sum_{\alpha=1}^{m} \rho_\alpha^{seg}(r_1)(\ln \rho_\alpha^{seg}(r_1) - 1), \quad (4.4) \]

where \( \beta = 1/kT \), \( k \) is the Boltzmann’s constant, \( T \) is the temperature. Here, the de Broglie wavelength and other temperature dependent terms that do not affect the fluid structure have been ignored. \( A^{EX,hs} \) is calculated from a density functional theory for a mixture of hard spheres. Rosenfeld’s fundamental measure theory [110]
is used here, where

$$
\beta A^{EX, hs}[\rho_\alpha] = \int dr \Phi[n_\alpha(r)].
$$  \tag{4.5}

$$
\Phi[n_\alpha] = -n_0 \ln(1 - n_3) + \frac{n_1 n_2}{1 - n_3} + \frac{n_2^3}{24\pi(1 - n_3)^2} - \frac{n_0 n_2}{1 - n_3} - \frac{n_2(n_0 n_2)}{8\pi(1 - n_3)^2}.
$$  \tag{4.6}

and \( n_\alpha \) are the weighted densities. The long range attraction is included using the mean field approximation.

$$
A^{EX, att}[\rho_\alpha] = \frac{1}{2} \sum_{\alpha=1}^{m} \sum_{\gamma=1}^{m} \int_{|r_2 - r_1| > \sigma_{\alpha\gamma}} dr_1 dr_2 u_{\alpha\gamma}^{att}(|r_2 - r_1|) \rho_\alpha^{seg}(r_1) \rho_\gamma^{seg}(r_2).
$$  \tag{4.7}

\( A^{EX, assoc} \) can be written following TPT1 using the extension (to fluid mixtures with molecules having multiple bonding sites) and general notation of Chapman [58, 62] as,

$$
\beta A^{EX, assoc}[\rho_\alpha] = \int dr_1 \sum_{\alpha=1}^{m} \rho_\alpha^{seg}(r_1) \sum_{A \in \Gamma^{(\alpha)}} \left( \ln X_A^\alpha(r_1) - \frac{X_A^\alpha(r_1)}{2} + \frac{1}{2} \right).
$$  \tag{4.8}

The first summation is over all the segments \( \alpha \), and the second over all the association sites on segment \( \alpha \) where \( \Gamma^{(\alpha)} \) is the set of all the associating sites on segment \( \alpha \). \( X_A^\alpha \) denotes the fraction of segments of type \( \alpha \) which are not bonded at their site \( A \). This
fraction is given by [58, 62],

$$X_A^\alpha(r_1) = \frac{1}{1 + \int dr_2 X_B^\alpha(r_2) \Delta^{\alpha\alpha'}(r_1, r_2) \rho_{\alpha'}^{seg}(r_2)}, \quad (4.9)$$

where \(\alpha'\) denotes the neighboring segment which bonds with segment \(\alpha\); site A on \(\alpha\) bonds to site B on \(\alpha'\). For hard sphere segments that do not overlap,

$$\Delta^{\alpha\alpha'}(r_1, r_2) = K F^{\alpha\alpha'}(r_1, r_2) \gamma^{\alpha\alpha'}(r_1, r_2), \quad (4.10)$$

where \(K\) is a constant geometric factor which accounts for the entropic cost associated with the orientations of the two segments to form the bond. \(F^{\alpha\alpha'}(r_1, r_2)\) is the association Mayer-\(f\) function given as

$$F^{\alpha\alpha'}(r_1, r_2) = [\exp(\beta \varepsilon_0 - \beta \nu_{\text{bond}}^{\alpha\alpha'}(r_1, r_2)) - 1], \quad (4.11)$$

where \(\varepsilon_0\) is the bond energy and \(\nu_{\text{bond}}^{\alpha\alpha'}(r_1, r_2)\) is the bonding potential. In the limit of \(\varepsilon_0 \to \infty\) we have complete association or chain formation. For tangentially bonded segments the bonding potential, \(\nu_{\text{bond}}^{\alpha\alpha'}(r_1, r_2)\) is given by

$$\exp[-\beta \nu_{\text{bond}}^{\alpha\alpha'}(r_1, r_2)] = \frac{\delta(|r_1 - r_2| - \sigma^{\alpha\alpha'})}{4\pi(\sigma^{\alpha\alpha'})^2}, \quad (4.12)$$

and \(\gamma^{\alpha\alpha'}(r_1, r_2)\) is the cavity correlation function for the inhomogeneous hard sphere reference fluid.
4.2.2 Functional derivatives of free energies

In order to solve eqn. 4.2 for the density profile, the functional derivative of the free energy is required. The functional derivative of the free energy can be interpreted as the inhomogeneous chemical potential. The different contributions to the inhomogeneous chemical potential of a segment $\alpha$ are given by

$$\frac{\delta \beta A^{ud}}{\delta \rho_{\alpha}^{seg}(r)} = \ln \rho_{\alpha}^{seg}(r), \quad (4.13)$$

$$\frac{\delta \beta A^{EX,hs}}{\delta \rho_{\alpha}^{seg}(r)} = \int dr_{1} \delta \Phi[n_{\alpha}(r_{1})] \frac{\delta}{\delta \rho_{\alpha}^{seg}(r)}, \quad (4.14)$$

$$\frac{\delta \beta A^{EX,att}}{\delta \rho_{\alpha}^{seg}(r)} = \sum_{\gamma=1}^{m} \int_{|r-r_{1}|>\sigma_{\alpha\gamma}} dr_{1} \beta \mu_{\alpha\gamma}(|r-r_{1}|) \rho_{\gamma}^{seg}(r_{1}), \quad (4.15)$$

$$\frac{\delta \beta A^{EX,assoc}}{\delta \rho_{\alpha}^{seg}(r)} = \sum_{A \in \Gamma^{(\alpha)}} \left[ \ln X_{A}^{\gamma}(r) - \frac{X_{A}^{\gamma}(r)}{2} + \frac{1}{2} \right] + \sum_{\gamma=1}^{m} \int \rho_{\gamma}^{seg}(r_{1}) \sum_{A \in \Gamma^{(\gamma)}} \left[ 1 - \frac{X_{A}^{\gamma}(r_{1})}{2} \right] \frac{\delta \ln X_{A}^{\gamma}(r_{1})}{\delta \rho_{\alpha}^{seg}(r)} dr_{1}, \quad (4.16)$$

where $\Gamma^{(\alpha)}$ is the set of associating sites on segment $\alpha$. In eqn. 4.16, the fraction of segments that are not bonded at an associating site ($X_{A}^{\gamma}(r)$) and the functional derivatives ($\frac{\delta \ln X_{A}^{\gamma}(r_{1})}{\delta \rho_{\alpha}^{seg}(r)}$) are required. Michelsen and Hendriks [117] showed by algebraic manipulation that for homogeneous systems the association chemical potential could be written in a form that does not involve the derivatives of fractions of non-bonded segments. A similar simplification is obtained for inhomogeneous systems by manipulating eqs. 4.9 and 4.16. The inhomogeneous chemical potential due to
association is then given by

\[
\frac{\delta \beta A_{E,x,assoc}}{\delta \rho_{\alpha}^{\text{seg}}(\mathbf{r})} = \sum_{A \in \Gamma(\alpha)} \ln X_{A}^{\alpha}(\mathbf{r}) -
\]

\[
\frac{1}{2} \sum_{\gamma=1}^{m} \sum_{A \in \Gamma^{\gamma}} \int \int_{|\mathbf{r}_1 - \mathbf{r}_2| = \sigma^{\gamma'}} \rho_{\gamma A}^{\text{seg}}(\mathbf{r}_1) \rho_{\gamma' B}^{\text{seg}}(\mathbf{r}_2) X_{A}(\mathbf{r}_1) X_{B}(\mathbf{r}_2) \delta \Delta^{\gamma\gamma'}(\mathbf{r}_1, \mathbf{r}_2) \frac{\delta \rho_{\alpha}^{\text{seg}}(\mathbf{r})}{\rho_{\alpha}^{\text{seg}}(\mathbf{r})} \mathrm{d}\mathbf{r}_1 \mathrm{d}\mathbf{r}_2, \tag{4.17}
\]

where in the second term of the eqn., the first sum is over all segments \( \gamma \) and the second sum is over all the sites \( A \) on segment \( \gamma \), each of which bond to the site \( B \) on its neighboring segment \( \gamma' \). In eqn. 4.17, the value of \( y_{\gamma\gamma'}(\mathbf{r}_1, \mathbf{r}_2) \) is only needed at contact due to the presence of \( \delta(\mathbf{r}_1 - \mathbf{r}_2) - \sigma^{\gamma'} \) in the integral. Since its exact form in an inhomogeneous system is not known in a tractable form, various approximations have been proposed as simplification [101]. Here, \( y_{\gamma\gamma'}(\mathbf{r}_1, \mathbf{r}_2) \) is approximated by

\[
y_{\gamma\gamma'}(\mathbf{r}_1, \mathbf{r}_2) = \left( y_{\gamma\gamma'}^{\gamma'}[\{ \tilde{\rho}_{\alpha}^{\text{seg}}(\mathbf{r}_1) \}] \ast y_{\gamma\gamma'}^{\gamma'}[\{ \tilde{\rho}_{\alpha}^{\text{seg}}(\mathbf{r}_2) \}] \right)^{1/2}, \tag{4.18}
\]

where \( \tilde{\rho}_{\alpha}^{\text{seg}}(\mathbf{r}_1) \) is the weighted density of segment \( \alpha \) at position \( \mathbf{r}_1 \). In the current work a simple weighting is used,

\[
\tilde{\rho}_{\alpha}^{\text{seg}}(\mathbf{r}_1) = \frac{3}{4\pi(\sigma_{\alpha})^3} \int_{|\mathbf{r}_1 - \mathbf{r}_2| < \sigma_{\alpha}} \mathrm{d}\mathbf{r}_2 \rho_{\alpha}^{\text{seg}}(\mathbf{r}_2). \tag{4.19}
\]
Equation 4.18 allows us to approximate

$$\frac{\delta \Delta \gamma'(r_1, r_2)}{\delta \rho_{\alpha \text{seg}}(r)} = \Delta \gamma'(r_1, r_2) \frac{1}{2} \left[ \frac{\delta \ln y_{\gamma' \text{contact}}[\{\tilde{\rho}_{\alpha}^{\text{seg}}(r_1)\}]}{\delta \tilde{\rho}_{\beta}^{\text{seg}}(r)} + \frac{\delta \ln y_{\gamma' \text{contact}}[\{\tilde{\rho}_{\beta}^{\text{seg}}(r_2)\}]}{\delta \tilde{\rho}_{\alpha}^{\text{seg}}(r)} \right].$$

(4.20)

Using eqs. 4.9 and 4.20 in eqn. 4.17 and taking the limit of complete association (i.e. $\varepsilon_0 \rightarrow \infty$ and $X_A^\alpha(r) \rightarrow 0$) gives the inhomogeneous chemical potential due to the formation of chains.

$$\frac{\delta \beta A^{\text{EX, chain}}}{\delta \rho_{\alpha \text{seg}}(r)} = \sum_{A \in \Gamma^{(\alpha)}} \ln X_A^\alpha(r) - \frac{1}{2} \sum_{\gamma=1}^{m} \sum_{\gamma'} \int \rho_{\gamma}^{\text{seg}}(r_1) \frac{\delta \ln y_{\gamma' \text{contact}}[\{\tilde{\rho}_{\alpha}^{\text{seg}}(r_1)\}]}{\delta \tilde{\rho}_{\alpha}^{\text{seg}}(r)} \, dr_1,$$

(4.21)

where $\{\gamma\}$ is the set of all segments bonded to segment $\gamma$. The cavity correlation function is further approximated by its bulk counterpart evaluated at the weighted density. In eqn. 4.21, the first term is essential to enforce stoichiometry. Only with a stoichiometric distribution of segments in the system will all $X_A^\alpha \rightarrow 0$. In this limit, the term contributes, $\frac{1}{2} \varepsilon_0$ for each bonding site. Thus the penalty of not having a stoichiometric distribution of segments is infinite. Since the fraction of unbonded segments, $X_A^\alpha(r)$ depend on the density distribution of the segments, eqs. 4.2 and 4.9 are solved simultaneously.
4.2.3 Equilibrium density profile

Substituting the free energy functional derivatives in Euler-Lagrange eqn. 4.2 for a segment $\alpha$ gives

$$\ln \rho_{\alpha}^{\text{seg}}(r) + \sum_{A \in \Gamma(\alpha)} \ln X_{\alpha}^{A}(r) - \frac{1}{2} \sum_{\gamma=1}^{m} \sum_{\gamma'}^{(\gamma')} \int \rho_{\gamma}^{\text{seg}}(r_1) \frac{\delta \ln y_{\text{contact}}[(\rho_{\alpha}^{\text{seg}}(r_1))]}{\delta \rho_{\beta}^{\text{seg}}(r)} dr_1$$

$$+ \frac{\delta \beta A^{EX,hs}}{\delta \rho_{\alpha}^{\text{seg}}(r)} + \frac{\delta \beta A^{EX,att}}{\delta \rho_{\alpha}^{\text{seg}}(r)} = \beta(\mu_\alpha - V_{\alpha}^{ext}(r)). \quad (4.22)$$

The set of these non-linear equations (for $m$ segments) can be solved with eqn. 4.9 for $X_{\alpha}^{A}$, for the density profile of the segments. However, in eqn. 4.9, $X_{\alpha}^{A}$ for a segment $\alpha$ depends on $X_{\alpha}^{B+1}$ for segment $\alpha + 1$. This coupling of $X_{\alpha}^{A}$ and $X_{\alpha}^{B+1}$ leads to numerical complexities. This interdependence is decoupled for a linear chain (of $m$ segments, see fig. 4.1) by simultaneously solving eqn. 4.22 for the segment densities and eqn. 4.9 for the $X_{A}^{\alpha}$'s. The derivation is shown in the appendix. It should be noted that the approach can be extended to branched chains, as shown in chapter 7.

The final expressions for $X_{A}^{\alpha}$ and $X_{B}^{\alpha}$ are given by
\[
X^{(j)}_A(r_j) = \frac{1}{\exp(\beta \sum_{i=j+1}^{m} \mu_i)} \int \ldots \int dr_{j+1} dr_{j+2} \ldots dr_m \exp \left( \sum_{i=j+1}^{m} [D_i(r_i) - \beta V^{\text{ext}}_i(r_i)] \right) \prod_{i=j}^{m-1} \Delta^{(i,i+1)}(r_i, r_{i+1}) \]  \tag{4.23}

and

\[
X^{(j)}_B(r_j) = \frac{1}{\exp(\beta \sum_{i=1}^{j-1} \mu_i)} \int \ldots \int dr_1 dr_2 \ldots dr_{j-1} \exp \left( \sum_{i=1}^{j-1} [D_i(r_i) - \beta V^{\text{ext}}_i(r_i)] \right) \prod_{i=1}^{j-1} \Delta^{(i,i+1)}(r_i, r_{i+1}) \]  \tag{4.24}

where,

\[
D_\alpha(r) = \frac{1}{2} \sum_{\gamma=1}^{m} \sum_{\gamma'} \int \rho^{\text{seg}}(r_1) \frac{\delta \ln g_{\text{contact}}^{\gamma\gamma'}[\bar{\rho}^{\text{seg}}(r_1)]}{\delta \bar{\rho}^{\text{seg}}(r)} dr_1 - \frac{\delta \beta A^{E_X,hs}}{\delta \rho^{\text{seg}}(r)} - \frac{\delta \beta A^{E_X,att}}{\delta \rho^{\text{seg}}(r)}. \tag{4.25}
\]

The \(X^{(j)}_A\)'s relate the chemical potential of the segment 'j' to the environment experienced by segments connected to 'j' through site 'A'. Such sharing of information along a molecule is essential to modeling the structure of molecules with different segment types such as copolymers. Note that we can drop the \(K \exp(\beta \varepsilon_0)\) in the expressions for \(\Delta(i,j)\)'s since they cancel out with similar terms in the bulk \(\mu_j\)'s. The multiple integrals are evaluated as a recurrence,

\[
I_{1,j}(r) = \int I_{1,j-1}(r') \exp[D_{j-1}(r') - \beta V^{\text{ext}}_{j-1}(r')] \Delta^{(j-1,j)}(r', r) dr', \tag{4.26}
\]

\[
I_{1,1}(r) = 1. \tag{4.27}
\]
and

\begin{align}
I_{2,j}(r) &= \int I_{2,j+1}(r') \exp[D_{j+1}(r') - \beta V^\text{ext}_j(r')] \Delta^{(j+1)}(r, r') dr', \\
I_{2,m}(r) &= 1,
\end{align}

where \( I_{1,j}(r) = \frac{1}{\exp(\beta \sum_{i=1}^{j-1} \mu_i) x^{i,j}_A(r)} \) and \( I_{2,j}(r) = \frac{1}{\exp(\beta \sum_{m=j+1}^m \mu_i) x^{i,j}_A(r)} \). Finally, the Euler-Lagrange eqn. 4.2 can be written as

\begin{align}
\ln \rho_j(r) - D_j(r) - \ln I_{1,j}(r) I_{2,j}(r) &= \beta \mu_M - \beta V^\text{ext}_j(r),
\end{align}

where \( \mu_M = \sum_{j=1}^m \mu_j \) is the bulk chemical potential of the chain. Rearranging eqn. 4.30 gives

\begin{align}
\rho_j(r) &= \exp(\beta \mu_M) \exp[D_j(r) - \beta V^\text{ext}_j(r)] I_{1,j}(r) I_{2,j}(r).
\end{align}

The equilibrium grand free energy is given by

\begin{align}
\beta \Omega[\{\rho_\alpha(r)\}] &= \sum_{\alpha=1}^m \int dr \rho_\alpha(r) \left[ D_\alpha(r) + \frac{n(\Gamma^{(\alpha)})}{2} - 1 \right] + \beta A^{EX,hs} + \beta A^{EX,att},
\end{align}

where \( n(\Gamma^{(\alpha)}) \) is the total number of associating sites on segment \( \alpha \).

Picard-type iteration method is used to solve the set of eqs. 4.31 for the density profile of the segments. For the systems considered in this work, the inhomogeneity is only in one dimension (z). For the density profile, a grid is set up in the z dimension.
with grid size, $\Delta z = 0.1\sigma$. The iteration starts with bulk densities for the density profiles of all the segments. The $D_j$s are then calculated using eqs. 4.25 followed by the calculation for $I_{1,j}$s and $I_{2,j}$s using the recurrence relations. A set of new density profiles is obtained from eqs. 4.31, which are then mixed with the previous results as the new input. These steps are repeated until the converged density profile is obtained. All the numerical integrations were performed using the trapezoidal rule.

4.3 Results and discussion

The density profile of a segment $j$, in a linear chain of $m$ segments is given by

$$\rho_i(r_j) = \exp(\beta u_M) \int \int \int dr_1 dr_j dr_{j+1} \cdots dr_m \exp \left( \sum_{i=1}^{m} [D_i(r_i) - \beta V_{i}^{ext}(r_i)] \right) \prod_{i=1}^{m} \Delta^{i,i+1}(r_i, r_{i+1}).$$

(4.33)

From eqn. 4.33, it follows that

$$\int dr_j \rho_j(r_j) = \int dr_{j-1} \rho_{j-1}(r_{j-1}),$$

(4.34)

which means that modified iSAFT constrains the overall stoichiometry of the chain even for complex heteronuclear systems. As a preliminary test to check the accuracy of modified iSAFT, it was first applied to homonuclear hard chain fluids confined in slit-like pores. The results are in good agreement with molecular simulation and are similar to iSAFT [60]. Hence, they are not repeated in this work.
4.3.1 Ideal chains

In terms of multipoint molecular density \( \rho_M(\mathbf{R}) \), the exact equilibrium density profile of a random flight ideal chain in an external field is given by [111]

\[
\rho_M(\mathbf{R}) = \exp(\beta \mu_M - \beta \sum_{i=1}^{m-1} \nu_{\text{bond}}^{i,i+1}(|\mathbf{r}_{i+1} - \mathbf{r}_i|) - \beta \sum_{i=1}^m V_i^{\text{ext}}(\mathbf{r}_i)).
\]  

(4.35)

The density profile of segment \( j \) is given by

\[
\rho_j(\mathbf{r}) = \int d\mathbf{R} \delta(\mathbf{r} - \mathbf{r}_j) \rho_M(\mathbf{R}),
\]  

(4.36)

or

\[
\rho_j(\mathbf{r}_j) = \exp(\beta \mu_M) \int \ldots \int d\mathbf{r}_1 \ldots d\mathbf{r}_{j-1} d\mathbf{r}_{j+1} \ldots d\mathbf{r}_m \exp[-\beta \sum_{i=1}^m V_i^{\text{ext}}(\mathbf{r}_i)] \exp[-\beta \sum_{i=1}^{m-1} \nu_{\text{bond}}^{i,i+1}(|\mathbf{r}_{i+1} - \mathbf{r}_i|)].
\]  

(4.37)

One of the strengths of modified iSAFT is that it automatically accounts for the direct bond connectivity between the segments in the chain, a constraint that is normally forced through the ideal chain functional in the existing theories. Instead we can readily write down the free energy functional for an ideal chain from modified iSAFT in terms of segment densities. From this functional, the density profile of a
segment \( j \) (in a linear ideal chain of \( m \) segments) is given by

\[
\rho_j(r_j) = \exp(\beta \mu_M) \int \cdots \int dr_1 \cdots dr_{j-1} dr_{j+1} \cdots dr_m \exp\left[-\beta \sum_{i=1}^{m} V^\text{ext}(r_i)\right] \exp\left[-\beta \sum_{i=1}^{m-1} \nu^{i,i+1}(|r_{i+1} - r_i|)\right].
\]  

(4.38)

Comparing this with eqn. 4.37 shows that modified iSAFT gives the exact density profile for a linear ideal chain in an external field.

4.3.2 Lipids

Lipids play an important role in biological systems. They are categorized by a polar head group which is hydrophilic and long hydrocarbon tail groups which are hydrophobic in nature. Due to the difference in these interactions, these spontaneously form bilayers when placed in an aqueous medium. In an aqueous milieu, the polar head groups tend to orient themselves towards the solvent while hydrocarbon tail groups hide themselves from the solvent. This lead to formation of lipid bilayers or micelles, see fig. 4.2a. Biological membranes are a form of lipid bilayer.

Recently, Frischknecht and Frink [118] applied molecular dynamics simulation and the Chandler McCoy Singer (CMS) density functional theory [98, 99] to study lipid bilayers. The lipid model used consisted of a freely jointed chain of tangent spheres with a head group and two tail groups. The head is composed of two segments while each tail has eight smaller segments, as shown in fig. 4.2b. The ratio of head to tail segment diameters is chosen to be \( \sigma_h/\sigma_t = 1.44 \) on the basis of previous theoretical work on lipid models [119] which result in lamellar and bilayer forming lipids. The
Figure 4.2: (a) Self-assembly of lipid molecules. Lipid bilayer on the left and Micelle on the right. The head groups face outside towards the solvent while the long tail groups hide away from the solvent. (b) Schematic of the lipid and solvent molecule. A lipid molecule has a head group with two bigger segments (gray) and two tail groups with eight smaller segments (black) in each. The solvent molecule (white) is of the same size as the tail segments.

The solvent is included in the model as a single segment with $\sigma_s = \sigma_t$. The segment-segment interactions are based on the Lennard-Jones (LJ) potential.

\begin{equation}
    u_{\alpha\beta}(r) = u_{\alpha\beta}^{LJ}(r) - u_{\alpha\beta}^{LJ}(r_c),
\end{equation}

where

\begin{equation}
    u_{\alpha\beta}^{LJ}(r) = 4\epsilon_{\alpha\beta} \left[ \left( \frac{\sigma_{\alpha\beta}}{r} \right)^{12} - \left( \frac{\sigma_{\alpha\beta}}{r} \right)^6 \right],
\end{equation}

and $r_c$ is the cut-off distance. If $r_c = 2^{1/6} \sigma_{\alpha\beta}$ the interaction between segments $\alpha$ and $\beta$ is purely repulsive. The attractive interactions are included by taking a larger cut-off, $r_c = 3.5 \sigma_{\alpha\beta}$. The energy constants for all the segments (head, tail or solvent),
\[ \epsilon_{\alpha\beta}/kT = 1. \]

**Figure 4.3:** Comparison of the density profiles of head segments (gray) and tail segments (black) from modified iSAFT (curves) and molecular simulation (symbols: head segments (■) and tail segments (▪)) for: (a) repulsive chains near a repulsive wall at a bulk density of \( \rho_0 \sigma^3 = 0.711 \), and (b) attractive chains near an attractive wall with a bulk density of \( \rho_0 \sigma^3 = 0.695 \). The simulation results are from Frischknecht and Frink [118].

For comparison, the attractions in modified iSAFT are treated as a perturbation to hard sphere repulsion in the spirit of Weeks-Chandler-Anderson (WCA) perturbation theory [120, 121].

\[ u_{\alpha\beta}(r) = u_{\alpha\beta}^{\text{ref}}(r) + u_{\alpha\beta}^{\text{att}}(r), \tag{4.41} \]

where

\[ u_{\alpha\beta}^{\text{ref}}(r) = \begin{cases} \infty & \text{if } r < \sigma_{\alpha\beta} \\ 0 & \text{if } r \geq \sigma_{\alpha\beta} \end{cases}, \tag{4.42} \]
and

\[
\eta_{\alpha\beta}(r) = \begin{cases} 
  u_{\alpha\beta}^{LJ}(r_{min}) - u_{\alpha\beta}^{LJ}(r_c) & \text{if } \sigma_{\alpha\beta} < r \leq r_{min} \\
  u_{\alpha\beta}^{LJ}(r) - u_{\alpha\beta}^{LJ}(r_c) & \text{if } r_{min} < r < r_c 
\end{cases}
\]  

(4.43)

\( r_{min} = 2^{1/6} \sigma_{\alpha\beta} \) is the position of potential minima. It is to be noted that in modified iSAFT the pure repulsion is treated as hard repulsion (with temperature and density independent hard sphere diameter).

As a rigorous test of modified iSAFT to predict the fluid structure of such a heteronuclear chain, the density profiles of lipid molecules adsorbed at a surface are calculated first. The surface is a flat wall and the surface-segment interaction as a function of the distance from the surface is given by the integrated LJ potential.

\[
V_{\alpha}(z) = \frac{2\pi \epsilon_{\omega\alpha}}{3} \left[ \frac{2}{15} \left( \frac{\sigma_{\omega\alpha}^{12}}{z^6} \right) - C \left( \frac{\sigma_{\omega\alpha}^{6}}{z^3} \right) \right],
\]  

(4.44)

where \( \epsilon_{\omega\alpha} = 1 \) and \( \sigma_{\omega\alpha} = 1.44 \). For \( C = 0 \), the surface-segment interaction is purely repulsive.

Two kinds of surface-lipid systems are studied. In the first case all the segments of the lipid molecule have purely repulsive interactions among themselves and with the surface (case RR). The density profiles of both the head and the tail segments of the lipid for this case are shown in figure 4.3a. The results from modified iSAFT are compared with results from molecular dynamics simulation by Frischknecht and Frink [118]. The figure shows excellent agreement between the theoretical predictions and simulation results.
Figure 4.4: Comparison of the density profiles of head segments (gray), tail segments (black) and solvent molecules (dashed gray) from modified iSAFT (curves) and molecular simulation (symbols: head segments (■), tail segments (●) and solvent molecules (♦)) for a solution of: (a) repulsive chains in a repulsive solvent near a repulsive wall with a bulk density of $\rho_b \sigma^3 = 0.709$ and solvent fraction $x_s = 0.630$, and (b) attractive chains in an attractive solvent near an attractive wall with a bulk density of $\rho_b \sigma^3 = 0.683$ and solvent fraction $x_s = 0.635$. The simulation results are from Frischknecht and Frink [118].

In the second case (case AA) attractions are switched on between the segments in the lipid molecule and also between surface and the segments ($C = 1$). All head-head, head-tail and tail-tail are uniformly attractive. Figure 4.3b compares the results from modified iSAFT with molecular dynamics results for this case. Again the agreement is excellent. Hence, modified iSAFT is able to correctly incorporate the packing effects of different size segments in the lipid molecule.

To test the ability of the theory to incorporate the effect of a solvent, both these cases RR and AA are considered in the presence of a solvent. In RR case, the solvent
is also purely repulsive while in the AA case it is uniformly attractive. The density profiles of the head groups, tail groups and solvent molecules for these cases are shown in figures 4.4a and b, respectively. The results are in good agreement with the simulation results. Since the lipid molecules lose configurational entropy near the surface, they push the solvent molecules near the surface. This is effectively captured by the theory.

![Figure 4.5: Modified iSAFT prediction for the lipid bilayer structure. The state point is $p_0 = 0.68$, $x_s = 0.442$. The density profile of the head segments is shown in black, tail segments in gray and solvent molecule in dashed gray curve.](image)

Finally the theory is applied to study the structure of a lipid bilayer. The attractive interactions between the different segments are included to mimic the energetics of real bilayer forming lipid molecules. Similar segments, head-head, tail-tail and solvent-solvent, uniformly attract each other. In addition, a head segment uniformly attracts the solvent segments, while the interactions between a tail and solvent segment and a head and tail segment, is purely repulsive. For the calculation, the com-
putational domain size was $40\sigma$. Reflective boundary conditions were used on either sides of the domain, with the center of the bilayer at one of the reflecting boundaries. The initial guess for the calculation was step-like density profiles for all three types of segments. Figure 4.5 shows the theory predictions for bilayer formation at a state point, bulk segment density: $\rho_b\sigma^3 = 0.68$ and number fraction of solvent segments: $x_s = 0.442$. The head groups have two peaks forming the ends of the bilayer while the tail groups orient themselves between the head groups. The solvent molecules are present on the outer sides.

4.3.3 Block Copolymers

Block copolymers are polymer chains comprised of two or more chemically distinct polymer chains covalently bonded together. Since the covalent bond prevents the macroscopic separation of the chemically distinct blocks, these copolymers undergo microphase separations leading to heterogeneities in composition at the molecular level. Thin films of block copolymers near preferential surfaces exhibit a wide variety of microscopic structures which are exploited in a number of technological applications like stabilization of nanoparticle dispersions [122, 123], copolymer-based lithography and photonic materials [124].

Modified iSAFT can be applied to study the molecular structure of these heteronuclear chains. The block copolymers studied for this work are modeled as freely jointed chains of tangent spheres, with different blocks having different types of seg-
ments. Although the segments of different types are of the same size ($\sigma$), they have
different long range attractions described by a square-well potential.

$$u_{\alpha\beta}^{\text{attr}}(r) = \begin{cases} -\epsilon_{\alpha\beta} & \text{if } \sigma_{\alpha\beta} \leq r \leq \gamma \sigma_{\alpha\beta} \\ 0 & \text{if } r > \gamma \sigma_{\alpha\beta} \end{cases},$$

(4.45)

where $\gamma \sigma_{\alpha\beta}$ is the width of the potential, which is fixed at $\gamma = 1.2$. If $\epsilon_{\alpha\beta}$ is positive, segments $\alpha$ and $\beta$ attract each other whereas if $\epsilon_{\alpha\beta}$ is negative, they repel each other. The surface is a flat wall and the surface-segment interaction is also given by the
square-well potential,

$$V_{\alpha}(z) = \begin{cases} -\epsilon_{\alpha W} & \text{if } 0 < z < \sigma_{\alpha} \\ 0 & \text{otherwise} \end{cases},$$

(4.46)

where $z$ is the perpendicular distance from the surface. Again, if $\epsilon_{\alpha W}$ is positive, the surface attracts segment $\alpha$ whereas if $\epsilon_{\alpha W}$ is negative, the surface repels segment $\alpha$.

Figure 4.6a shows the density profiles of segments of type A and B of a symmetric
diblock copolymer “AAAABBBB” confined in a slit-like pore of width, $H = 10\sigma$. Like
segments, “A-A” and “B-B” attract each other with $\epsilon_{AA}/kT = 1.0$ and $\epsilon_{BB}/kT = 0.5$,
while “A-B” repel each other with $\epsilon_{AB}/kT = -0.5$. The two surfaces preferentially
attract “A” with $\epsilon_{\omega A}/kT = 1.0$ and repel “B” with $\epsilon_{\omega B}/kT = -1.0$. The density
profiles obtained from the theory are compared with the simulation results from Cao
and Wu [112]. They are in good quantitative agreement. As expected, the density of
Figure 4.6: Comparison of the density profiles of A segments (black) and B segments (gray) from modified iSAFT (curves) and molecular simulation (symbols: A segments (●) and B segments (■)) for the copolymer (a) AAAABBBA, and (b) ABBBBA, in a selective slit pore. The reduced energy parameter is defined as $\epsilon^* = \beta \epsilon$. The reduced energies are given by $\epsilon_{wA}^* = 1.0$, $\epsilon_{wB}^* = -1.0$, $\epsilon_{AA}^* = 1.0$, $\epsilon_{BB}^* = 0.5$ and $\epsilon_{AB}^* = -0.5$ and the average packing fraction of the copolymer in the pore is $\eta = 0.1$. The simulation results are from Cao and Wu [112].

"A" segments is higher near the surface. There is a discontinuity at $z/\sigma = 1$ due to the termination of the wall potential. Beyond $z/\sigma = 4$, the densities reach a uniform value. Differences between the theory and simulation results are due in part to the inconsistencies in the reported simulation results of Cao and Wu [112]. The authors report that the densities are scaled with the average densities in the simulation cell, but the average of the scaled density is not 1.0 and the raw densities are no longer available [125]. Therefore, the true state point of the simulation is unclear.

Figure 4.6b compares the density profiles from theory and simulation for segments of type "A" and "B" of a block copolymer "ABBBBA" confined in a slit-like pore.
of width, \( H = 10\sigma \). The segment-segment and the segment-surface interactions were the same as in the previous case (figure 4.6a). The theoretical results are in good quantitative agreement with the results from simulation from Cao and Wu [112]. The density of segment “A” is higher than the density of segment “B” near the surface and both reach a uniform value away from the surface. Again, uncertainty in the true state point of the simulations prevents a rigorous test of the theory [125].

Figure 4.7: (a) Comparison of the density profiles of A segments (black) and B segments (gray) from modified iSAFT and (curves) and molecular simulation (symbols: A segments (•) and B segments (•)) for the copolymer BBBAAABBBB in a selective slit pore. The reduced energies are given by \( \varepsilon_{wA}^* = 5.0, \varepsilon_{wB}^* = -5.0, \varepsilon_{AA}^* = 1.0, \varepsilon_{BB}^* = 0.5 \) and \( \varepsilon_{AB}^* = -0.5 \) and the average packing fraction of the copolymer in the pore is \( \eta = 0.1 \). The simulation results are from Cao and Wu [112]. (b) Modified iSAFT prediction for the microstructure of symmetric diblock copolymer of 50 segments (25A25B) in a selective slit pore. The density profile of A segment is shown in black and B segment in gray. The reduced energies are given by \( \varepsilon_{wA}^* = 1.0, \varepsilon_{wB}^* = -1.0, \varepsilon_{AA}^* = 1.0, \varepsilon_{BB}^* = 0.5 \) and \( \varepsilon_{AB}^* = -0.5 \) and the average packing fraction of the copolymer in the pore is \( \eta = 0.1 \).

The next system considered is a triblock copolymer “BBBAAABBBB” confined in a pore of width, \( H = 10\sigma \). In this case the walls are strongly selective, \( \varepsilon_{wA}/kT = 5 \) and
\( \epsilon_{wB}/kT = -5 \), while the segment-segment interactions are the same as in figures 4.6a and b. The theoretical density profiles for both the segment types closely agree with the results from molecular simulation as shown in figure 4.7a. The structure is mainly governed by the two surfaces. The density of “A” segment is very high near the surface and there are essentially no “B” segments near the surface.

Now consider the case of a long symmetric diblock copolymer with 50 segments (25A25B) confined in the same pore with weakly selective walls. The segment-segment and segment-surface interactions are same as in figures 4.6a and b. The density profiles of both “A” and “B” obtained from the theory are shown in figure 4.7b. The results are similar to the results obtained by Cao and Wu [112] using their density functional theory. The long copolymer has to fit into the smaller confined space by adjusting its configurations. Hence lamellae of “A” and “B” are formed which are parallel to the two surfaces. In this case, two lamellae of “A” and “B” are formed. One of the lamellae of “A” is in the middle while two half lamellae of “A” are near the two surfaces. The two lamellae of “B” lie between the “A” lamellae. The period of the lamellae and thereby number of lamellae depend upon their equilibrium lamellar period, \( L_0 \) in the bulk system. Even in the absence of two surfaces these diblock copolymers self assemble into parallel lamella with the equilibrium period \( L_0 \) depending upon the interactions between the two distinct polymer blocks. A detailed study of the effect of confinement on this equilibrium period and thereby the microstructure of these diblock copolymers is the subject of chapter 5 of this
4.4 Conclusions

A new density functional theory for inhomogeneous polymeric fluids has been proposed. The theory is based on Wertheim's first order thermodynamic perturbation theory for associating fluids and is derived along similar lines as iSAFT [60]. The theory is generally applicable to mixtures of heteronuclear chains, e.g. lipids, copolymers, grafted polymers, polymer/colloid and polymer/nanoparticle systems. The theory only requires the segment interaction potential and the bulk chemical potential of the chain as input. For lipid melts near surfaces, the theory shows excellent agreement with the simulation results. For lipid solutions, solvent molecule is modeled as a single spherical segment. Comparisons of the results from the theory with results from molecular simulations demonstrate that this simple model efficiently accounts for the effect of the solvent on the microstructure of lipids near the surface.

The theory is further applied to study the structure of a lipid bilayer. For copolymers, the microstructures of thin films of block copolymers were studied using the theory. The theory successfully captures the effect of copolymer chain architecture, and segment-segment and surface-segment interactions on the microstructure of these systems and the results are in excellent agreement with the simulation results.

Appendix: Derivation of $X_A^j$ and $X_B^j$ for a linear chain of ‘m’ segments
The Euler-Lagrange equation for a segment $\beta$ is given by

$$
\ln \rho_\beta^{seg}(r) + \sum_{A \in \Gamma^{(\beta)}} \ln X_A^\beta(r) - \frac{1}{2} \sum_{\gamma=1}^m \sum_{\gamma'} \int \rho_\gamma^{seg}(r_1) \frac{\delta \ln \gamma'}{\delta \rho_\gamma^{seg}(r)} \text{d}r_1
$$

$$
+ \frac{\delta \beta A_{EX,hs}}{\delta \rho_\beta^{seg}(r)} + \frac{\delta \beta A_{ATT}}{\delta \rho_\beta^{seg}(r)} = \beta (\mu_\beta - V_\beta^{ext}(r)). \tag{4.47}
$$

Eqn. 4.47 can be further written as

$$
\ln \rho_\beta^{seg}(r) + \sum_{A \in \Gamma^{(\beta)}} \ln X_A^\beta(r) = D_\beta(r) + \beta (\mu_\beta - V_\beta^{ext}(r)), \tag{4.48}
$$

where $D_\beta(r)$ is given by

$$
D_\beta(r) = \frac{1}{2} \sum_{\gamma=1}^m \sum_{\gamma'} \int \rho_\gamma^{seg}(r_1) \frac{\delta \ln \gamma'}{\delta \rho_\gamma^{seg}(r)} \text{d}r_1 - \frac{\delta \beta A_{EX,hs}}{\delta \rho_\beta^{seg}(r)} - \frac{\delta \beta A_{ATT}}{\delta \rho_\beta^{seg}(r)}. \tag{4.49}
$$

Physically, $\ln \rho_\beta^{seg}(r) + \sum_{A \in \Gamma^{(\beta)}} \ln X_A^\beta(r) = \ln \rho_{0,\beta}^{seg}(r)$, where $\rho_{0,\beta}^{seg}(r)$ is the density of monomers [58],

$$
\rho_{0,\beta}^{seg}(r) = \rho_\beta^{seg}(r) \prod_{A \in \Gamma^{(\beta)}} X_A^\beta(r), \tag{4.50}
$$

since bonding at a site on a segment is assumed independent of bonding at the other sites on the same segment. For the first segment,

$$
\ln \rho_1(r_1) + \ln X_A^{(1)}(r_1) = D_1(r_1) + \beta (\mu_1 - V_1^{ext}(r_1)), \tag{4.51}
$$

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or

\[ \rho_1(r_1)X_A^{(1)}(r_1) = \exp[D_1(r_1) - \beta V_1^{\text{ext}}(r_1)] \exp(\beta \mu_1). \]  

(4.52)

Now using this result in eqn. 4.9 for \( X_B^{(2)} \) (neglecting the 1 in the denominator in comparison to the second term which contains the bonding energy and \( \varepsilon_0 \to \infty \)) can be rewritten as

\[ X_B^{(2)}(r_2) = \frac{1}{\exp(\beta \mu_1) \int dr_1 \exp[D_1(r_1) - \beta V_1^{\text{ext}}(r_1)]\Delta^{(1,2)}(r_1, r_2)}. \]  

(4.53)

Substituting for \( X_B^{(2)}(r_2) \) in the Euler-Lagrange equation for the second segment leads to an expression for \( \rho_2(r_2)X_A^{(2)}(r_2) \), from which an expression for \( X_B^{(3)}(r_3) \) similar to eqn. 4.53 can be obtained. Repeating this procedure through the last segment in the chain, lead to accurate expressions for \( X_A \) and \( X_B \) for all the segments in the chain.

\[ X_A^{(j)}(r_j) = \frac{1}{\exp(\beta(\mu_{j+1} + \mu_{j+2} + \ldots + \mu_m)) \int \ldots \int dr_{j+1}dr_{j+2}\ldots dr_m \exp[D_{j+1}(r_{j+1}) - \beta V_{j+1}^{\text{ext}}(r_{j+1})} \]

\[ +D_{j+2}(r_{j+2}) - \beta V_{j+2}^{\text{ext}}(r_{j+2}) + \ldots + D_m(r_m) - \beta V_m^{\text{ext}}(r_m)]\Delta^{(j+1,1)}(r_j, r_{j+1})\Delta^{(m-1,m)}(r_{m-1}, r_m), \]  

(4.54)

and

\[ X_B^{(j)}(r_j) = \frac{1}{\exp(\beta(\mu_1 + \mu_2 + \ldots + \mu_{j-1})) \int \ldots \int dr_1dr_2\ldots dr_{j-1} \exp[D_1(r_1) - \beta V_1^{\text{ext}}(r_1)} \]

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+D_2(r_2) - \beta V_2^{ext}(r_2) + \cdots + D_{j-1}(r_{j-1}) - \beta V_{j-1}^{ext}(r_{j-1})] \Delta^{(1,2)}(r_1, r_2) \Delta^{(2,3)}(r_2, r_3) \cdots \Delta^{(j-1,j)}(r_{j-1}, r_j) \frac{\partial^4}{\partial r_1 \partial r_2 \partial r_3 \partial r_4} \frac{\partial^4}{\partial r_1 \partial r_2 \partial r_3 \partial r_4} + \cdots \cdot \Delta^{(j-1,j)}(r_{j-1}, r_j) \frac{\partial^4}{\partial r_1 \partial r_2 \partial r_3 \partial r_4} \frac{\partial^4}{\partial r_1 \partial r_2 \partial r_3 \partial r_4} (4.55)
Chapter 5

Modified iSAFT: Application to symmetric diblock copolymers

5.1 Introduction

Recent research in the field of diblock copolymer-thin films have been spurred by their potential applications in the development of the next generation of sub micron scale electronic and optical devices [126] and lithographic templates for semiconductors [127]. An important area of research in this field has been the symmetric (AB) diblock copolymers. These are block copolymers formed by (covalently) bonding two immiscible (A and B) homopolymers such that the volume fractions of the homopolymers in a copolymer molecule are identical. The covalent bond restricts the macroscopic separation of these chemically dissimilar homopolymer blocks which leads to the formation of A-rich and B-rich lamellae at length scales comparable to
the molecular dimensions, that is, around 50 to 1000 Å [49]. A variety of lamellar micro-domains with different motifs, chemistries, sizes and periodicity can be created by tuning in the molecular parameters (molecular weight, species, film thickness and external potentials). All the aforementioned applications of the diblock copolymers harness this spontaneous self-assembly. Furthermore, these applications will be facilitated by the recent developments in block copolymer synthesis, such as atom transfer radical polymerization [128], to widen the spectrum of available copolymer materials or decrease their cost of manufacture.

Experimental studies on confined thin films of symmetric diblock copolymers [129, 130, 131, 132, 133, 134] have provided many insights into the general features of the lamellar morphologies. However, the detailed results are, of course, confined to the specific systems that were examined. Furthermore, few of the experimentally observed lamellar morphologies are found to be kinetically favored rather than the thermodynamically stable one [135]. Hence, the concurrent development of the theoretical models to determine the detailed microstructure of these inhomogeneous polymer systems is important. Shull [136] developed a unified mean field theory applicable to bulk diblock copolymer melts, melts near a single surface and confined thin films. The theory is applicable in both weak segregation and strong segregation limits (WSL and SSL). Turner [137] considered symmetric diblock copolymer-thin films confined between two parallel flat surfaces, such that both the surfaces have preferential affinity towards one of the blocks. The free energy calculations in the SSL showed that
the lamella are parallel to the two surfaces. There can be integer ‘n’ (symmetric) or half-integer ‘$n+\frac{1}{2}$’ (anti-symmetric) number of lamella depending upon the separation between the surfaces. Walton et. al. [138] extended this phenomenological free energy model for strong segregation to account for the vertical/perpendicular morphology where the lamella are oriented normal to the two surfaces. They found that below a certain critical film thickness (or number of lamella), the lamellar morphology could be either parallel symmetric or perpendicular. Above this critical number, only parallel symmetric morphology is stable. Parallel anti-symmetric morphology is never favored when the two surfaces are identical and meta-stable when the perpendicular morphology is anticipated. However, when the two surfaces are dissimilar, parallel anti-symmetric morphology can be realized for a limited number of lamella. Owing to their previous successes with other inhomogeneous polymer systems, self-consistent field theory (SCFT) has also been applied to study the lamellar morphologies in thin films of symmetric diblock copolymers. Pickett and Balazs [139] did two dimensional numerical SCFT calculations (on a spatial lattice) for diblock copolymers confined by neutral and preferential (selective affinity towards one of the blocks) surfaces. For neutral surfaces, the morphology is always perpendicular. However, for preferential surfaces the morphologies can be either perpendicular or parallel depending upon the film thickness. Matsen [135] used continuous space SCFT to account for the mixed lamellar morphologies (perpendicular morphology at one and parallel at the other surface) reported in experimental [131] and Monte Carlo simulation [140] results, in case
of preferential confining surfaces. However, these morphologies were found to be relatively unstable to perpendicular morphologies. Hence, although these morphologies are kinetically favored, they are thermodynamically unstable for symmetric diblock copolymers. Similar conclusions are drawn from other SCFT studies by Tang [127] and Geisinger et. al. [141, 142].

Density functional theories (DFTs) also have recently been applied to study inhomogeneous polymer systems. As mentioned earlier, these theories retain the monomer or statistical segment length-level information rather than the coarse-grained representation of the polymer. Both the long-ranged structural quantities which depend on the chain connectivity as well as the short-ranged quantities which depend upon the local packing are well described by the DFTs [143, 144]. On the contrary, mean field and SCF theories neglect the fluctuations in the local composition from an average value. DFTs include the compressibility effects important for liquid state theories which are missed by mean field and SCF theories. The natural formalism of the DFTs is the grand canonical ensemble where the fluctuations in the number of polymer chains in the system keep the chemical potential constant. Thus the system is compressible and phase transitions can include fluctuations in density of the system. In case of confined copolymer films the compressibility, local density fluctuations and the packing effects are important especially near to the confining surfaces and the interfaces of the two blocks, as demonstrated by Geisinger et. al. [141, 142] through comparisons between Monte Carlo simulations and SCF calculations. Molec-
ular simulations of these systems are computationally expensive and are limited to short chain molecules with simple interactions. Furthermore, DFTs can take advantage of the symmetry of the system, to further reduce the computational time. For example, studying the (parallel/perpendicular) lamellar morphologies of symmetric diblock copolymers using DFT/SCF theories is an one dimensional problem or mixed morphologies is a two-dimensional problem. Thus, DFTs provide an approach that incorporates molecular-level detail but is simple enough that the calculation time is modest and physical insight is retained even in complex situations. A thorough review of classical DFT is given by Evans [56] and recently by Wu and Li [145].

Frischknecht et. al. [50] were the first to study symmetric diblock copolymers confined between two parallel smooth surfaces in detail with DFT. They applied Chandler-McCoy-Singer (CMS) DFT to investigate the lamellar morphologies of diblock copolymers with different incompatibilities between their blocks and at different surface interaction strengths. However, the applicability of CMS-DFT, which is based on the polymer reference interaction site model (PRISM) theory [105] for the bulk polymer fluids, is complicated by the ambiguities regarding the closure relations to be used for specific applications. Cao and Wu [112, 146] have also applied their DFT [61] to study the microstructure of block copolymers near planar surfaces and in slit-like pores. Ye et. al. [147] also applied their DFT [148, 149] to study the adsorption of block copolymers at selective walls. Like the DFT by Cao and Wu, their theory also applies the weighted density functional approximation to the bulk equation of state.
for hard chains developed by Hu et. al. [150] and the ideal free energy is based on molecular density, as derived by Woodward. The use of molecular density introduces an apparent complexity, as it is a 3N-dimension function and thus the numerical effort to solve the resulting equations will scale exponentially with N.

On the contrary, modified iSAFT is more rigorous segment-based DFT as demonstrated in previous chapter. Modified iSAFT was applied to study the microstructure of block copolymers near selective (planar) surfaces. The density profiles obtained were in excellent agreement with the simulation results. In this work, modified iSAFT is applied to study the effect of confinement on the lamellar morphologies of symmetric diblock copolymers.

The outline of this chapter is as follows. In section 2, the copolymer model system and theoretical formulations is described. The lamellar morphologies of the symmetric diblock copolymer thin films depend upon the lamellar period of these copolymers in their bulk ordered melts (in the absence of the confining surfaces). Hence, modified iSAFT is first applied to calculate the lamellar periods of the bulk copolymer melts (in SSL). Next, these copolymer melts are confined between two parallel flat surfaces, to form ultra-thin films. Both the surfaces preferentially attract one block and repel the other block of the copolymer. The lamellar morphologies are investigated by calculating the density profiles of the two blocks and the free energy of the copolymer. The results and their discussions are presented in section 3. Section 4 summarizes the conclusions from the current work.
5.2 Model system and theory

The symmetric diblock copolymer molecule is modeled as a freely jointed chain of tangentially bonded spheres (segments) of two types. One type of segment forms the ‘A’ block and the other type forms the ‘B’ block. Each block has N segments. Although both type of segments have the same segment size, \( \sigma \), they have different long range attractions. These attractions are modeled as a perturbation to the 6-12 Lennard-Jones (LJ) potential in the spirit of Weeks-Chandler-Anderson (WCA) perturbation theory [120, 121].

\[
u_{\alpha \beta}^{\text{att}}(r) = \begin{cases} u_{\alpha \beta}^{LJ}(r_{\text{min}}) - u_{\alpha \beta}^{LJ}(r_c) & \text{if } \sigma_{\alpha \beta} < r \leq r_{\text{min}} \\ u_{\alpha \beta}^{LJ}(r) - u_{\alpha \beta}^{LJ}(r_c) & \text{if } r_{\text{min}} < r < r_c \end{cases}
\]

where \( r_{\text{min}} = 2^{1/6} \sigma_{\alpha \beta} \) is the position of potential minima, \( r_c = 3.5 \sigma_{\alpha \beta} \) is the potential cut-off distance and

\[
u_{\alpha \beta}^{LJ}(r) = 4 \epsilon_{\alpha \beta} \left[ \left( \frac{\sigma_{\alpha \beta}}{r} \right)^{12} - \left( \frac{\sigma_{\alpha \beta}}{r} \right)^6 \right].
\]

The energy parameters, \( \epsilon_{AA} = \epsilon_{BB} = \epsilon \) and \( \epsilon_{AB} = 0 \). Hence in the model, \( \epsilon \) quantifies the incompatibility between the two blocks of the diblock copolymer. Traditionally, this incompatibility has been characterized by the Flory-Huggins interaction parameter, \( \chi \). As discussed by Frischknecht et. al. [50], for a symmetric diblock copolymer, \( \chi \) can be related to the incompatibility parameter \( \epsilon \) for the continuous potential model.
as

\[
\chi = -\frac{\rho}{2kT} \int dr [u_{AA}^{\text{att}}(r) + u_{BB}^{\text{att}}(r) - 2u_{AB}^{\text{att}}(r)],
\]

(5.3)

where \( k \) is the Boltzmann constant and \( T \) is the temperature. The repulsions between these segments are treated as hard sphere repulsion with temperature and density independent hard sphere diameter (\( \sigma \)).

For copolymer ultrathin films, the copolymer is confined between two smooth planar surfaces separated by \( H \). The surfaces are located at \( z = 0 \) and \( z = H \), where \( z \) is the direction normal to the surfaces. The total external field on a segment '\( \alpha \)' of the copolymer due to these surfaces is given as

\[
V_{\alpha}^{\text{ext}}(z) = V_{w\alpha}(z) + V_{w\alpha}(H - z),
\]

(5.4)

where the first contribution is from the surface at \( z = 0 \) and the second from the surface at \( z = H \). The surface-segment interactions are modeled by a 9-3 LJ potential.

\[
V_{w\alpha}(z) = \begin{cases} 
\infty & \text{if } z \leq \frac{\sigma_{w\alpha}}{2} \\
V_{w\alpha}^{\text{LJ}}(z_{\text{min}}) - V_{w\alpha}^{\text{LJ}}(z_{c}) & \text{if } \frac{\sigma_{w\alpha}}{2} < z \leq z_{\text{min}} , \\
V_{w\alpha}^{\text{LJ}}(z) - V_{w\alpha}^{\text{LJ}}(z_{c}) & \text{if } z_{\text{min}} < z < z_{c}
\end{cases}
\]

(5.5)

where \( z_{\text{min}} = (2/5)^{1/6}\sigma_{w\alpha} \) is the position of potential minima, \( z_{c} = 3\sigma_{w\alpha} \) is the
potential cut-off distance and

\[ V_{\text{wA}}^{LJ}(z) = \frac{4\pi\epsilon_{\text{wA}}}{9} \left( \frac{\sigma_{\text{wA}}}{\sigma_w} \right)^3 \left[ \frac{1}{5} \left( \frac{\sigma_{\text{wA}}}{z} \right)^9 - \frac{3}{2} \left( \frac{\sigma_{\text{wA}}}{z} \right)^3 \right]. \]  

(5.6)

All the interaction diameters are the same, \( \sigma_{\text{wA}} = \sigma_w = \sigma \). Furthermore, the surfaces are symmetric, that is both the surfaces preferentially attract the segments in the A block with \( \epsilon_{wA} = \epsilon_w \) and repel the segments in the B block with \( \epsilon_{wB} = 0 \).

The general formulation of modified iSAFT as a DFT was presented in the previous chapter. As mentioned, the basis of a DFT is the energy minimum principle or mathematically,

\[ \frac{\delta \Omega[\{\rho_{\alpha,A}(r)\}, \{\rho_{\alpha,B}(r)\}]}{\delta \rho_{\alpha}(r)} \bigg|_{\{\rho_{\alpha,A}\}, \{\rho_{\alpha,B}\}\text{ equilibrium}} = 0 \quad \forall \alpha = 1, m, \]  

(5.7)

where \( \Omega \) is the grand free energy of the open system at fixed chemical potential (\( \mu \)), volume (\( V \)), and temperature (\( T \)), \( \rho_{\alpha,A} \) is the density of a segment \( \alpha \) of type A, \( \{\rho_{\alpha,A}\} \) is the set of densities of all the segments in the A block of the copolymer, and \( m (= 2N) \) is the total number of segments in the copolymer chain. Since a segment-based DFT like modified iSAFT treats every segment individually, let \( \{\rho_\alpha\} \) denote the set of densities of all the segments of the copolymer that are enumerated from 1 to \( m \), 1 being the first segment of the copolymer and \( m \) being the last one. It is to be noted that 1 to \( N \) are the segments in the A block and \((N+1)\) to \( m \) are the segments in the B block of the copolymer. The set of eqs. 5.7 can be reformulated in terms of the
Helmholtz free energy functional \( (A[\{\rho_\alpha\}] ) \) as

\[
\frac{\delta A[\{\rho_\alpha\}]}{\delta \rho_\alpha(r)} = \mu_\alpha - V^\text{ext}_\alpha(r) \quad \forall \alpha = 1, m,
\] (5.8)

where \( \mu_\alpha \) is chemical potential of the segment \( \alpha \), and \( V^\text{ext}_\alpha \) is the external field acting onto it. Solution of the set of these (Euler-Lagrange) equations gives the equilibrium density profile of the segments. To derive the Helmholtz free energy, the copolymer chain molecule is considered as the limit of complete association of a mixture of associating atomic molecules (or associating segments), with off-centered association sites. The Helmholtz free energy functional of such a mixture of associating segments can be written as

\[
A[\{\rho_\alpha\}] = A^{\text{id}}[\{\rho_\alpha\}] + A^{\text{EX,hs}}[\{\rho_\alpha\}] + A^{\text{EX,chain}}[\{\rho_\alpha\}] + A^{\text{EX,att}}[\{\rho_\alpha\}],
\] (5.9)

where \( A^{\text{id}} \) is the ideal free energy of the segments, \( A^{\text{EX,hs}} \) is the excess free energy due to the excluded volume of the segments (hard sphere repulsions), \( A^{\text{EX,chain}} \) is the excess free energy due to chain formation in the limit of complete association of the segments, and \( A^{\text{EX,att}} \) is the excess free energy due to the long range attractions between the segments.

The individual free energies and their functional derivatives were derived in chapter 4. Here, the final equilibrium density profile of the segments and grand free energy
of the copolymer molecule are presented.

\[ \rho_\alpha(r) = \exp(\beta \mu_M) \exp[D_\alpha(r) - \beta V^{ext}_\alpha(r)] I_{1,\alpha}(r) I_{2,\alpha}(r), \quad (5.10) \]

where \( \mu_M = \sum_{i=1}^{m} \mu_i \) is the bulk chemical potential of the copolymer chain, and \( I_{1,\alpha} \) and \( I_{2,\alpha} \) are multiple integrals solved using the following recurrence,

\[ I_{1,\alpha}(r) = \int I_{1,\alpha-1}(r') \exp[D_{\alpha-1}(r') - \beta V^{ext}_{\alpha-1}(r')] \Delta^{(\alpha-1,\alpha)}(r', r) dr', \quad (5.11) \]
\[ I_{1,1}(r) = 1. \quad (5.12) \]

and

\[ I_{2,\alpha}(r) = \int I_{2,\alpha+1}(r') \exp[D_{\alpha+1}(r') - \beta V^{ext}_{\alpha+1}(r')] \Delta^{(\alpha,\alpha+1)}(r, r') dr', \quad (5.13) \]
\[ I_{2,1}(r) = 1. \quad (5.14) \]

The equilibrium grand free energy is given by

\[ \beta \Omega[\{\rho_\alpha\}] = \sum_{\alpha=1}^{m} \int dr \rho_\alpha(r) \left[ D_\alpha(r) + \frac{n_\alpha(r)}{2} - 1 \right] + \beta A^{EX,hs} + \beta A^{EX,att}, \quad (5.15) \]

where \( n_\alpha(r) \) is the total number of association sites on segment \( \alpha \).

To calculate the segment density profiles numerically, the computational domain is divided into equally spaced grid points along the dimension normal to the surface. A grid spacing of 0.1\( \sigma \) is used for all our calculations. The density profiles are solved
using Picard's iteration method. For few cases with smaller computational domains, the iterations start with a step density profile (for segments in A and B blocks) as the initial guess. However for most of the cases the initial guess is generated by adding/removing extra grid points to/from a previously converged solution. At every iteration step a new estimate to the density profiles is calculated using eq. 5.10 which is then mixed with the old density profiles as the new guess for the next iteration. All the integrations are calculated using the trapezoidal rule. For free energy calculations, the bulk homogeneous disordered phase is taken to be the reference. Hence all the free energies, $\Omega$ are relative to this state.

5.3 Results and discussion

All the systems considered in this work have a melt like total segment density of $\rho \sigma^3 = 0.85$. The values of $\epsilon$ and $N$ are such that the systems are in the strong segregation limit (SSL) or $\chi(2N) \gg 10$ [49]. Bulk (symmetric) diblock copolymer melts in the SSL are considered first, where the copolymer self assemble into lamellar structure. Then these copolymers melts are confined between two planar surfaces to form ultra thin films. The surfaces preferentially attract one of the blocks of the copolymer. In confinement, the copolymer blocks adjust their lamella to fit into the confining space and account for the selective adsorption of the blocks at the surfaces. Due to this we observe various lamellar phases depending upon the thickness of the film.
5.3.1 Bulk diblock copolymer melts

The calculation of the lamellar density profiles of the diblock copolymer melt is a one dimensional (1-D) problem. Hence the modified iSAFT equations for the segment density profiles are solved in 1-D with periodic boundary conditions at the two ends of the computational domain. For $N = 8$ and $\epsilon/kT = 0.289$, the density profiles of the two blocks are shown in figure 5.1a. The width of the computational domain is fixed to $6\sigma$. The total segment density of the copolymer is also shown in the figure. The density profile of the individual blocks is sinusoidal. The total segment density is constant except at the interface of the two blocks. There is depletion in the total
segment density at the interface, due to the A-B repulsion. Such depletion is also observed in the Monte Carlo simulations of the diblocks [151, 140]. As can be observed from the figure, fixing the width (L) of the computational domain fixes the lamellar period, which may not be the bulk equilibrium period of the copolymer. Hence calculations are done for different widths of the computational domain. Figure 5.1b shows the density profile of one of the blocks at different widths. The (grand) free energy per volume for each of these cases is calculated and plotted against the width of the computational domain as shown in figure 5.2. The width for which free energy is at minimum, is the bulk equilibrium lamellar period ($D_b$) and the free energy at $D_b$ is the equilibrium free energy ($\Omega_b$) of the copolymer. From the figure $D_b = 10.2\sigma$ and $\Omega_b/VkT = -0.2244$. This equilibrium free energy is the balance of the free energies due to the formation of the interfaces between the lamella of the two blocks and stretching of the copolymer chains to form the lamellar structure. At smaller lamellar period, higher number of interfaces increases the free energy. And at higher lamellar period, the chains are highly stretched leading to increase in the free energy. The density profile for $D_b = 10.2\sigma$ is shown fig. 5.1b. Lamella that are highly stretched past their equilibrium period show depletion in the density at their centers, as shown in fig. 5.1b for $L = 15\sigma$.

Figure 5.3a shows the equilibrium lamellar density profiles for diblock copolymers with different incompatibilities between the two blocks ($N = 8$). The bulk equilibrium period, $D_b = 8.8\sigma, 9.2\sigma, 9.6\sigma,$ and $9.9\sigma$ for $\epsilon/kT = 0.17, 0.2, 0.231,$ and $0.25,$
Figure 5.2: Grand free energy of the copolymer per unit volume as a function of the width of the computational domain. For the diblock copolymer, $N = 8$ and $\epsilon/kT = 0.289$.

respectively. For relatively smaller incompatibility between the two blocks, the equilibrium density profiles are approximately sinusoidal. However, as the incompatibility increases, the profiles become more like step functions. Again, the equilibrium periods for these copolymers were calculated from their respective free energy curves shown in fig. 5.3b. As the incompatibility increases, the equilibrium lamellar period increases and the equilibrium free energy decreases. The highly incompatible blocks try to minimize their contacts by decreasing the number of interfaces between them, thereby increasing the equilibrium lamellar period.

The effect of increasing the number of segments in each block is shown in fig. 5.4 ($\epsilon/kT = 0.289$). Increase in the number of segments leads to increase in the equilibrium lamellar period and decrease in the equilibrium free energy. This is due
Figure 5.3: (a) Equilibrium segment density profiles of the A block of the diblock copolymer for $\epsilon/kT = 0.17$ (solid gray curve, $D_b = 8.8\sigma$), 0.2 (dashed gray curve, $D_b = 9.2\sigma$), 0.231 (solid black curve, $D_b = 9.6\sigma$), 0.25 (dashed black curve, $D_b = 9.9\sigma$), and 0.289 (dot-dashed gray curve, $D_b = 10.2\sigma$), and (b) grand free energy of the copolymer per unit volume as a function of the width of the computational domain for $\epsilon/kT = 0.17$ (dot-dashed black curve), 0.2 (dashed gray curve), 0.231 (solid gray curve), 0.25 (dashed black curve), and 0.289 (solid black curve). Number of segments in each of the blocks of the diblock copolymer are 8.

to the fact that longer chains can stretch more in order to decrease the number of contacts/interfaces between the incompatible blocks. The bulk equilibrium period, $D_b = 7.2\sigma$, 8.4$\sigma$, 9.1$\sigma$, 11.0$\sigma$, and 11.6$\sigma$ for $N = 5$, 6, 7, 9, and 10, respectively. The experimental measurements of bulk lamellar spacing as a function of the copolymer chain length at fixed $\chi$ have shown a power law dependence, $D_b \propto N^7$. Modified iSAFT calculations predict a value of 0.689 for $\gamma$ from the slope of $\ln(D_b)$ vs $\ln(N)$, which is in agreement with the experimental data [152, 153, 154], strong segregation theories (SST) [155, 156], SCFT [136, 157, 158] and Chandler, McCoy, and Singer
CMS) density functional theory [144]. Figure 5.4a shows the equilibrium density profiles of these diblock copolymers. For smaller N, the profiles are approximately sinusoidal and for larger N, they become almost step-like.

![Figure 5.4: (a) Equilibrium segment density profiles of the A block of the copolymer for N = 5 (solid black curve, $D_a = 7.2\sigma$), 6 (dashed black curve, $D_a = 8.4\sigma$), 7 (dot-dashed black curve, $D_a = 9.1\sigma$), 8 (solid gray curve, $D_a = 10.2\sigma$), 9 (dashed gray curve, $D_a = 11.0\sigma$), and 10 (dot-dashed gray curve, $D_a = 11.6\sigma$), and (b) grand free energy of the copolymer per unit volume as a function of the width of the computational domain for N = 5 (solid gray curve), 6 (dashed gray curve), 7 (dot-dashed gray curve), 8 (solid black curve), 9 (dashed black curve), and 10(dot-dashed black curve). $\epsilon/kT = 0.289$ for all the cases.]

5.3.2 Confined diblock copolymer ultra-thin films

The lamellar structure of the (symmetric AB diblock) copolymer is significantly affected when they are confined between two planar surfaces separated by H, where H is of the order of the bulk equilibrium lamellar period of the copolymer. The
lamella are constrained to adjust within the confining space. The free energy of these copolymer systems is a balance of free energies due to the formation of interfaces between the lamella of the two blocks, stretching of the copolymer chains to form the lamellar structure and interactions of the blocks with the confining surfaces.

Symmetric surfaces are considered, where both the surfaces preferentially attract the segments in the A block of the copolymer and repel the segments in the B block. The interplay of the three free energies can lead to a number of lamellar structures between the two surfaces. Symmetric lamellar structures are the ones where both the surfaces are covered with the energetically favorable A block. There are integer ‘n’ number of lamella or even number of A - B interfaces. In anti-symmetric lamellar structures, one of the surfaces is covered with energetically favorable A block and the other with the energetically unfavorable B block. There are half-integer ‘n + \frac{1}{2}’ number of lamella or odd number of A - B interfaces. These parallel lamellar structures are designated as L_{2n}^\parallel where \nu is the number of interfaces. Hence, L_{2n}^\parallel denotes the symmetric lamellar phase with n lamella and L_{2n+1}^\parallel denotes the anti-symmetric lamellar phase with n + \frac{1}{2} lamella. It has been found that when both the surfaces have weak/no preference for either of the blocks the lamellas are aligned perpendicular to the two surfaces [138, 135, 151], L_{n}^\perp phase. In this case the copolymer can attain its bulk equilibrium lamellar period D_b.

Consider a symmetric diblock copolymer, N = 8 and \epsilon/kT = 0.289 confined between two planar surfaces with \epsilon_w/kT = 0.1. Figure 5.5 shows the symmetric L_{2n}^\parallel.
Figure 5.5: Symmetric segment density profiles of the A block (solid black curve) and B block (dashed black curve) of the copolymer for (a) \( H = 9\sigma \), (b) \( H = 10.6\sigma \), (c) \( H = 13\sigma \), and (d) \( H = 15\sigma \). For the diblock copolymer, \( N = 8 \) and \( \epsilon/kT = 0.289 \). For surfaces, \( \epsilon_w/kT = 0.1 \).

lamellar structures at different surface separations. At \( H = 9\sigma \), 10.6\( \sigma \) and 13\( \sigma \), we observe one lamellae of both A and B. A “lamellae” is split into two half-lamellae, one at each surface and B “lamellae” lies in the middle. The density profile of A
“lamellae” at the two surfaces is oscillatory due to pronounced packing effects in agreement with the simulation results [141]. There are two A - B interfaces, hence these are designated as $L_2^{||}$ phases. The actual film thickness of the copolymer is $(H - \sigma)$, as the segments cannot penetrate the surfaces. Therefore, at $H = 9\sigma$, the lamella are compressed and at $H = 13\sigma$ the lamella are stretched compared to their bulk equilibrium period, $D_b = 10.2\sigma$. At $H = 15\sigma$, we observe the $L_4^{||}$ phase. Again, two half-lamellae of A are at the two surfaces. The lamellar period is less than $D_b$ or the lamella are compressed. The excess surface free energy $\Omega^s$ of the copolymer at a separation $H$ is calculated as the difference of the free energy $\Omega$ of the copolymer in the confinement (at separation $H$) and the free energy $\Omega_b$ of the bulk ordered copolymer in the absence of confining surfaces.

$$\Omega^s(H) = \frac{\Omega}{A} - \frac{\Omega_b (H - \sigma)}{A D_b}$$

where $A$ is area of the surfaces.

Figure 5.6 shows the excess surface free energy as a function of the effective film thickness of the copolymer, $H_{eff}$.

$$H_{eff} = \frac{H - \sigma + \delta}{D_b}$$

where $\delta$ accounts for the offset in the lamellar period from $D_b$. Intuitively, the excess surface free energy should be at minimum when the lamella in the copolymer film are
Figure 5.6: Excess surface free energy of the copolymer as a function of the effective film thickness, for symmetric phases of the copolymer. For the diblock copolymer, \( N = 8 \) and \( \epsilon/kT = 0.289 \). For surfaces, \( \epsilon_w/kT = 0.1 \).

able to attain their bulk equilibrium period, \( D_b \). However, there is a slight offset from the actual value of \( D_b \) due to packing near the wall. This offset is accounted by \( \delta \).

Thus the excess surface free energy is at minimum at integer values of \( H_{eff} \) when the film lamellar period is in accord with the bulk equilibrium period. The values of the excess free energy are the same at all the integer values of \( H_{eff} \). In any \( L^\parallel_{2n} \) phase, the free energy is higher for \( H_{eff} < n \) when the lamella are compressed and \( H_{eff} > n \) when the lamella are stretched than their preferred lamellar period. For \( H_{eff} > n \), as the lamella are highly stretched the copolymer undergoes the transition from \( L^\parallel_{2n} \) to \( L^\parallel_{2(n+1)} \) phase to decrease the excess surface free energy.

We can also observe the anti-symmetric \( L^\parallel_{2n+1} \) lamellar structures of the diblock copolymer. Figure 5.7 shows the anti-symmetric segment density profiles of the two
blocks of the copolymer at different film thickness. At $H = 14\sigma$ or film thickness of $13\sigma$, there are $1\frac{1}{2}$ lamella of both A and B where half lamellae of A and B are at each of the two surfaces. The lamellar period is smaller than the preferred lamellar period.
and the lamella are compressed. For $1 \frac{1}{2}$ lamella at $H = 16.4\sigma$, the lamellar period is higher and the lamella are stretched. At higher film thickness of $19.4\sigma$, $2\frac{1}{2}$ lamella of both A and B are observed. One of the advantages of modified iSAFT is that these different lamellar phases can be calculated at any film thickness. The lamellar phase with the lowest excess surface free energy, $\Omega^*$ is the equilibrium structure at that film thickness. The excess free energy curve as a function of the effective film thickness for the anti-symmetric phases is calculated and overlaid onto the free energy curve for the symmetric phases. The equilibrium free energy curve for the given symmetric diblock copolymer ($N = 8$ and $\epsilon/kT = 0.289$) confined between the two planar surfaces ($\epsilon_w/kT = 0.1$) is shown in fig. 5.8a. Till $H_{eff} < 4\frac{1}{2}$, the symmetric $L_{2n}^{||}$ lamellar phases are stable around integer ($n$) values of $H_{eff}$ and anti-symmetric $L_{2n+1}^{||}$ lamellar phases are stable around half-integer ($n + \frac{1}{2}$) values of $H_{eff}$. The sole reason for observing the stable anti-symmetric lamellar phases even though the energetically unfavorable B block is at one of the surfaces is that the lamellar period is closer to the (preferred) bulk equilibrium period. The range of film thickness for which these anti-symmetric phases are stable becomes smaller for higher film thicknesses. And when $H_{eff}$ gets larger than $4\frac{1}{2}$, only symmetric phases are stable. For symmetric lamellar phases at higher film thickness, the lamella are not highly stretched or compressed as the lamellar period are closer to the (preferred) bulk equilibrium lamellar period as shown in figure 5.8b. Note that in this figure, a reduced lamellar period $D_{eff}$ of the
copolymers film is defined as
\[
D_{\text{eff}} = \frac{H_{\text{eff}}}{N}
\]
(5.18)

where \(N\) is the number of lamella. Hence, only the symmetric lamellar phases with energetically favorable A block at both the surfaces are stable at higher film thickness.

\[\text{Figure 5.8: (a) Excess surface free energy of the copolymer as a function of the effective film thickness. (b) Reduced lamellar period (for symmetric phases) of the copolymer as a function of the effective film thickness. For the diblock copolymer, } N = 8 \text{ and } \epsilon/kT = 0.289. \text{ For surfaces, } \epsilon_w/kT = 0.1.\]

In other words, the balance between having the lamellar period close to the (preferred) bulk equilibrium period and unfavorable interactions of the B block of the copolymer at one of the surfaces, determines the stability of the anti-symmetric lamellar phases. To test this, the preference of the both the surfaces towards the A block is increased by increasing \(\epsilon_w/kT\) to 0.3. Figure 5.9 shows the symmetric \(L^{\parallel}_{2n}\) lamellar
structures at different surface separations. At $H = 9\sigma$, $10.6\sigma$ and $13\sigma$, $L_2$ phases are observed and at $H = 15\sigma$, the $L_1$ phase is observed. At $H = 9\sigma$ and $15\sigma$ the lamella are compressed and at $H = 13\sigma$ the lamella are stretched than their bulk equilibrium period, $D_0$. Figure 5.10 shows the excess surface free energy of the symmetric lamellar phases as a function of the effective film thickness of the copolymer, $H_{eff}$. The free energy is minimum at the integer values of $H_{eff}$. This minimum free energy is lower than the earlier case where the two surfaces have comparatively weaker preference for the A block of the copolymer, $\epsilon_w/kT = 0.1$.

Figure 5.11 shows the anti-symmetric segment density profiles of the two blocks of the copolymer at different film thickness. At both $H = 14\sigma$ and $16.4\sigma$, the $L_3$ phases are observed. However, the lamella are compressed for $H = 14\sigma$ and stretched for $H = 16.4\sigma$. The excess surface free energy of this $L_3$ phase is calculated and compared with the free energies for the symmetric phases in fig. 5.12. Even the minimum free energy of this phase (at $H_{eff} = 1\frac{1}{2}$) is higher than the free energy for the $L_4$ phase. Hence only the symmetric phases are stable. This is due to the high energy penalty of having the B block at one of the surfaces in case of anti-symmetric phases. To quantify this, the free energy penalty of having the B block rather than the A block near the surface is calculated (at $H_{eff} = 1$) as

$$f_w = \int_0^h \rho_A(z)(V_B^{ext}(z) - V_A^{ext}(z))dz,$$

where $h$ is width of the half-lamellae of A next to the surface. For $\epsilon_w/kT = 0.3$, $\frac{\delta F_{wA}}{A} = 0.6392$. This should be equal to the difference in the minimum excess surface free energy of the anti-symmetric and symmetric phases. From the calculations,
Figure 5.9: Symmetric segment density profiles of the A block (solid black curve) and B block (dashed black curve) of the copolymer for (a) $H = 9\sigma$, (b) $H = 10.6\sigma$, (c) $H = 13\sigma$, and (d) $H = 15\sigma$. For the diblock copolymer, $N = 8$ and $\epsilon/kT = 0.289$. For surfaces, $\epsilon_w/kT = 0.3$.

\[
\Omega_{\text{min,anti-symmetric}}^s - \Omega_{\text{min,symmetric}}^s = 0.6205.
\]

For the earlier case with $\epsilon_w/kT = 0.1$, $\frac{\delta f_w A}{\sigma^3} = 0.2101$ and $\Omega_{\text{min,anti-symmetric}}^s - \Omega_{\text{min,symmetric}}^s = 0.2048$. Hence, calculating just the free energies of symmetric phases
and $f_w$ can tell us if the anti-symmetric phases will be stable or not. This is useful to calculate the minimum affinity ($\epsilon_w$) of the surface towards the A block over which only the symmetric phases are stable.

### 5.4 Conclusions

Modified iSAFT has been applied to study the lamellar microstructures of the symmetric diblock copolymers, in the strong segregation limit. For bulk copolymer melts, the equilibrium lamellar period, $D_b$ increases with the increase in the incompatibility of the two blocks of the copolymer. The increase in the number of segments of the diblock copolymer also increases $D_b$, which follows a power law dependence on
number of segments. These diblock copolymers are then confined between two parallel surfaces, where the surfaces selectively prefer one of the blocks of the copolymer, to form ultra-thin copolymer films. These films show two types of parallel lamellar phases. In symmetric lamellar phases, the preferred block is present at the two surfaces and in anti-symmetric lamellar phases one of the surfaces is covered with the energetically unfavorable block. For comparatively weaker surface preference, the symmetric lamellar phases are stable near integer values of the effective film thickness \( H_{\text{eff}} \), when the lamellar period is in accord with \( D_b \). The anti-symmetric lamellar phases are stable only at smaller film thickness near half-integer values of \( H_{\text{eff}} \). However, only symmetric lamellar phases are found to be stable when the sur-

**Figure 5.11:** Anti-symmetric segment density profiles of the A block (solid black curve) and B block (dashed black curve) of the copolymer for (a) \( H = 14\sigma \), and (b) \( H = 16.4\sigma \). For the diblock copolymer, \( N = 8 \) and \( \epsilon/kT = 0.289 \). For surfaces, \( \epsilon_w/kT = 0.3 \).
Figure 5.12: Excess surface free energy of the copolymer as a function of the effective film thickness. For the diblock copolymer, \( N = 8 \) and \( \epsilon/kT = 0.289 \). For surfaces, \( \epsilon_w/kT = 0.3 \).

faces strongly prefer one of the blocks. A method has been suggested to find out if the anti-symmetric phases are stable or not only by calculating the free energy and segment density profiles of the symmetric phases.

The detailed segment density profiles of both the phases are qualitatively similar to the profiles obtained by MC simulations and support the discrepancies with the previous SCF theories. The packing structure is observed near the surfaces, as reported in these simulations. The fluctuations in the total segment density of the diblock at the interfaces of the two blocks are also observed. These packing effects and fluctuations can affect the relative stabilities of the symmetric and anti-symmetric lamellar phases.

Recently, there have been a number of studies on the block copolymer in the
cylindrical pores [159, 160, 161, 162] and cylindrical morphologies of block copolymer [163, 164, 165, 166, 167, 168, 169]. The general formalism of modified iSAFT will allow to apply it to these asymmetric and multi-block copolymers in cylindrical morphologies. With modified iSAFT we will be even able to account for the difference in the segment sizes of the blocks of these copolymers. Including the compressibility and the packing effects will better resolve the detailed structure near the confining surfaces.
Chapter 6

Modified iSAFT: Application to grafted polymer chains

Tethered/grafted polymer chains are polymer molecules with one of their ends attached to a solid surface. The chain end can be chemically bonded to the solid substrate or it can be a chemical group that strongly adsorbs on the solid surface. Grafted polymer chains have several industrial applications in colloid stabilization, adhesives, lubricants, modification of surface hydrophobicity, microfluidic devices and biophysics. This chapter discusses the application of modified iSAFT to two most important aspects of grafted polymers, their structures and the force of interaction between two grafted (planar) surfaces in the absence or presence of free polymer solvent.
6.1 Introduction

Organic and inorganic fillers have been extensively used to produce polymer composites. Recently, the interest has shifted to cases where one of the dimensions of these fillers is of the order of a nanometer [170]. Addition of the nano fillers can significantly improve the mechanical, thermal, electrical and optical properties as compared to the pure polymer or the conventional micro- or macro-composites [171]. In addition, since the weight fraction of these additives is low, these nanocomposites are generally lighter than the conventional composites. Examples include the 'Nano sandwiches' in nature such as bones, shells, and wood [172], polypropylene reinforced by particulate fibers and polymer/clay nanocomposites [173] like clay montmorillonite fillers in nylon-6 [174]. One of the challenges in the synthesis of polymer/clay nanocomposites is dispersing the broad clay sheets in the polymer matrix [175]. This depends upon the polymer-mediated interactions between the dispersed particles. The van der Waals interactions between the particles are usually attractive leading to aggregation/flocculation of these particles and diminishing the properties of the nanocomposite. One way of stabilizing the dispersion is to end-graft polymers onto the particle surfaces. Steric hindrance due to the grafted polymer chains (or polymer brushes [176, 52, 51]) prevent the surfaces from coming close together, however, their preferred separation depends upon the effective interaction of the brushes in the free polymer matrix. In polymer/clay nanocomposites, depending upon this separation, the mixture will form an intercalated or exfoliated composite, or a phase separated
system [177]. In an intercalated composite, the clay sheets are separated at a fixed separation such that few free polymer chains can penetrate between the sheets. While in an exfoliated composite, the clay sheets are effectively separated from each other and well dispersed in the free polymer matrix.

Traditionally, colloidal dispersions are stabilized by grafting polymer chains on the surface of colloidal particles [178, 179, 180]. In case of colloids in solution, if the repulsive barrier due to the steric hindrance of the grafted polymer chains compensates the attractive minimum due to the van der Waals interactions between the colloid particles, then the particles do not aggregate. However, the situation is more complex for polymer-colloid mixtures. Depending on the quality of the solvent, grafting density, and the degree of polymerization of the grafted and free polymers, the inter-colloid interactions can become attractive destabilizing the colloidal dispersion. [181, 182, 183, 152].

Similar scenario occurs in polymeric alloys where the constituent homopolymers are compatibilized by diblock copolymers [184, 185]. The copolymer molecules act as amphiphiles forming thin monolayers between the immiscible homopolymer domains, preventing them from macrophase separation. Hence, block copolymers help produce a stable blend in which the homopolymer domains do not coarsen [186, 187, 188]. The stability of the blend depends upon the effective interactions between the copolymer monolayers in the presence of the homopolymers [189, 190]. It has been found that when the homopolymer molecules are large relative to the copolymer molecules,
there can be an attraction between the monolayers bringing the monolayers close together [191, 192, 193]. As the monolayers approach each other, they force out the two homopolymers, which then macrophase separate.

As mentioned, in all these applications the effective force of interaction between two grafted monolayers determines stabilization or non-stabilization. If the size of the grafting surfaces is significantly larger than the height of the grafted monolayers, they can be treated as planar. A number of theoretical models have been developed to study the interaction between these flat grafted monolayers in the presence of free polymer. It is well known that interaction is purely repulsive for smaller free polymer chain lengths (relative to the grafted polymer). However, attraction can occur for large free polymer chain lengths. These theoretical models explore the origin of the attractive forces between the sterically hindered (flat) grafted monolayers in a solution of long polymer chains. Earlier models either ignored the penetration of the free polymer in the monolayer [194] or assumed complete penetration [195]. Vincent et. al. [182] accounted for the entropically constrained interpenetration of the free polymer in the grafted monolayers. However, they do not take into account the compression of two monolayers as they approach each other.

Using statistical mechanics, the Gaussian chain model [53] for long polymer chains can be solved using the self-consistent field theory (SCFT) introduced by Edwards [54]. In this approach, the molecular interactions are treated by a mean field which has to be evaluated numerically. However, for polymer brushes an analytical expression can
be obtained assuming that the chains are strongly stretched [196, 197, 198, 199, 200, 201, 183, 202]. Zhulina et. al. [183] used this analytical SCFT or strong stretching theory (SST) to study the interactions between grafted colloid particles. In SST, the grafted polymer chains assume their most probable conformations, i.e. fluctuations around this conformation are not taken into account. However, these fluctuations are important for the brush structure, especially at low grafting densities or shorter chains. Hence, several research groups have applied numerical SCFT to calculate the effective interaction between two flat grafted monolayers in the presence of free polymer. van Lent et. al. [203] and Wijmans et. al. [204] applied the lattice version of SCFT developed by Scheutjens and Fleer [205]. van Lent et. al. showed that the effective interaction between the grafted monolayers not only depends on the depletion of the free polymer in the monolayers, which was usually regarded as the origin of attraction, but also on the conformational changes of the two monolayers as they approach each other. They only considered cases where the relative degree of polymerization of free and grafted polymer chains ($\alpha = N_f/N_g$) is greater or equal to one. Wijmans et. al. did more systematic study for different chain lengths and grafting densities. Their main conclusions are: (1) for a given grafting density ($\rho_g$ : defined as the number of chains tethered to unit area of the surface), attraction occurs only when $\alpha$ is greater than a critical value otherwise the interaction is purely repulsive; and (2) the critical value of $\alpha$ decreases with increase in $\rho_g$. However, the critical values of $\alpha$ or the domains of repulsion/attraction were not specifically calculated for different
grafting densities, and bulk free polymer concentrations. More detailed study on this issue was done by Ferreira et. al. [206]. Using continuous SCFT, they found that the boundary between the repulsive and attractive domains follows the scaling relation, 
\[ \rho_g \sqrt{N_g} \propto \alpha^{-2} \]
for both densely and sparsely grafted monolayers. It has to be noted that in all these theoretical studies, the grafted polymers are chemically identical to the surrounding free polymers, except for their degree of polymerization. Hence, this problem of entropic interactions between two grafted monolayers in a matrix of parent homopolymer is theoretically and numerically equivalent to the case for the wetting behavior of homopolymer on a chemically identical grafted monolayer [207, 206, 208].

When a homopolymer comes in contact with a chemical identical grafted monolayer at high grafting densities, a positive surface tension arises due to the entropic constraints and the homopolymer dewets the brush. The phenomena is known as autophobicity [209, 210, 211, 212, 213, 214, 215, 216, 217, 218, 219, 220, 221, 222, 223, 224]. Autophobicity indirectly spurs the effective attraction between two grafted monolayers in the homopolymer matrix as the system would rather prefer to replace the two brush-homopolymer interfaces by a single brush-homopolymer interface [206]. Matsen and Gardiner [208] used this analogy to show that the repulsion/attraction boundary satisfies the scaling relation, 
\[ \rho_g \sqrt{N_g} \propto \alpha^{-0.7} \]
using a numerically more accurate Fourier-space algorithm for SCFT than the real-space algorithm used by Ferreira et. al.

Another statistical mechanics based approach that has been applied to polymer
brushes are the density functional theories (DFTs). McCoy, Ye and Curro applied the Chandler, McCoy and Singer density functional theory (CMS-DFT) to study the structure of athermal [225] and attractive [226] grafted polymer chains in the presence of implicit or explicit solvent. The authors also discuss the approximations in the SCFTs which are not present in a typical DFT. However, the applicability of CMS-DFT, which is based on the polymer reference interaction site model (PRISM) theory [105] for the bulk polymer fluids, is complicated by ambiguities regarding the closure relations to be used for specific applications [226].

In this work, modified iSAFT density functional theory is used to study the effective interaction between (flat) grafted monolayers in the presence of free polymer. Including compressibility, the scaling relation for the boundary between the repulsive and attractive domains is expected to be different from the previous theoretical studies using SCFT. In particular, the interest is in cases where the segment sizes of the polymer in the monolayers and the free polymer are not identical, which are not easily accessible to SCFT. These cases have previously not been addressed by other theoretical models as well. This work will show that a simple scaling relation accounts for the effect of the difference in the segment sizes of the grafted and free polymers on the boundary between the repulsive and attractive domains.

The structure of the grafted monolayers plays an important role in determining the force of interactions between them. Depending upon the number of polymer chains attached to the surface (grafting density) and the quality of the solvent,
these chains can either stretch away from the surface or collapse onto it. In fact, the structure of these grafted polymer chains is responsible for the novel behavior in their applications. Hence, a number of theoretical and experimental works have focussed only on the structure of these grafted monolayers. The theoretical works include the scaling theories developed by Alexander [51] and de Gennes [52], SCFTs [180, 199, 227] and computer simulations using both molecular dynamics (MD) [228, 229, 230, 231] and Monte Carlo (MC) [232, 233, 234, 235]. Experimentally, the surface forces apparatus [236, 237], small-angle neutron scattering [238] and neutron reflectivity [239, 240, 241] have been very important in determining the structure of the polymer brushes. These approaches have been discussed in several reviews in the literature. [242, 243, 244, 245]. Hence, determining the structure of grafted monolayers in the absence/presence of the free polymer solvent using modified iSAFT, is the first part of this work.

The outline of this chapter is as follows. The extension of modified iSAFT to grafted polymer chains is presented in section 2. Section 3 presents the results and discussions. As mentioned, first, the structure of the tethered monolayers in the absence/presence of an explicit free polymer solvent is investigated. The results are compared with the MD simulation results from Grest and Murat [230, 231]. The theory shows excellent agreement with these simulation results. Second, the force of interaction when two of these monolayers are brought close to each other in the presence of free polymer, is calculated. The effective interaction between the grafted
monolayers in the presence of free polymer strongly depends upon the conformational
changes of the monolayers as they approach each other. Hence, modified iSAFT is
also applied to study how their structures and the force of interaction changes as they
approach and interpenetrate each other in the absence of free polymer. Next, the free
polymer is added around the monolayers and the effect of free polymer concentration,
grafting density, and ratio of the segment sizes of the grafted and free polymers on
the force of interaction, is investigated.

6.2 Extension of modified iSAFT to grafted polymer chains

The general formulation of modified iSAFT for a fluid of free polymer chains of
'm' segments was presented in detail in chapter 4. The equilibrium density profile
\((\{\rho_\alpha(r_\alpha)\})\) of the segments of the chain in the presence of an external field
\((\{V^{\text{ext}}_\alpha(r_\alpha)\})\)
is given by

\[
\rho_\alpha(r) = \exp(\beta \mu_M) \exp[D_\alpha(r) - \beta V^{\text{ext}}_\alpha(r)] I_{1,\alpha}(r) I_{2,\alpha}(r),
\]

(6.1)

where \(\mu_M(= \sum_{i=1}^{m} \mu_i)\) is the bulk chemical potential of the polymer chain.

\[
D_\alpha(r) = \sum_{\gamma=1}^{m} \sum_{\gamma'} \int \rho^{\text{seg}}(r_1) \frac{\delta \ln y^{\text{contact}}[\{\rho_\alpha(r_1)\}]}{\delta \rho^{\text{seg}}_\alpha(r)} dr_1 \frac{\delta \beta A^{EX,hs}[\{\rho_\alpha\}]}{\delta \rho^{\text{seg}}_\alpha(r)} \frac{\delta \beta A^{EX,att}[\{\rho_\alpha\}]}{\delta \rho^{\text{seg}}_\alpha(r)},
\]

(6.2)
where, \( y_{\text{contact}}'[\{\bar{\rho}_{i}(r_{1})\}] \) is the cavity correlation function of hard sphere fluid at contact approximated to its bulk value at the weighted density, \( \bar{\rho}_{i}^{\text{seg}}(r_{1}) = \frac{3}{4\pi(\sigma_{i})^{3}} \int_{|r_{1}-r_{2}|<\sigma_{i}} dr_{2}\bar{\rho}_{i}^{\text{seg}}(r_{2}) \), \( A^{\text{EX,hs}} \) is the excess free energy due to the excluded volume of the segments (hard sphere repulsions), and \( A^{\text{EX,att}} \) is the excess free energy due to the long range attractions between the segments. \( I_{1,\alpha} \) and \( I_{2,\alpha} \) are multiple integrals solved using the following recurrence,

\[
I_{1,\alpha}(r) = \int I_{1,\alpha-1}(r') \exp[D_{\alpha-1}(r') - \beta V_{\alpha-1}^{\text{ext}}(r')]\Delta^{(\alpha-1,\alpha)}(r', r) dr', \tag{6.3}
\]

\[
I_{1,1}(r) = 1, \tag{6.4}
\]

and

\[
I_{2,\alpha}(r) = \int I_{2,\alpha+1}(r') \exp[D_{\alpha+1}(r') - \beta V_{\alpha+1}^{\text{ext}}(r')]\Delta^{(\alpha,\alpha+1)}(r, r') dr', \tag{6.5}
\]

\[
I_{2,\alpha}(r) = 1, \tag{6.6}
\]

where,

\[
\Delta^{\alpha\alpha'}(r_{1}, r_{2}) = K \exp(\beta \varepsilon_{0}) \frac{\delta(|r_{1} - r_{2}| - \sigma_{\alpha\alpha'})}{4\pi(\sigma_{\alpha\alpha'})^{2}} - 1]y^{\alpha\alpha'}(r_{1}, r_{2}). \tag{6.7}
\]

\( K \) is a constant geometric factor that depends upon the associating volume, and \( \varepsilon_{0} \) is the association energy. In the limit of complete association, \( \varepsilon_{0} \to \infty \). Note that we can drop the \( K \exp(\beta \varepsilon_{0}) \) term in the expressions for \( \Delta(i, j) \)'s since they cancel out the same terms in the bulk chemical potential.

In the case of grafted polymer chains, one of the end segments is physically/chemically
tethered to the wall. If we consider a flat wall and that the chains are uniformly distributed over the surface of the wall, then the problem reduces to a one dimensional problem with the relevant dimension along the normal to the wall. The external field exerted by the wall on the tethered segment ‘1’ is

\[
V_{1}^{\text{ext}}(z) = \begin{cases} 
  v & \text{if } z = 0 \\
  \infty & \text{otherwise}
\end{cases}
\]  

(6.8)

And for the other segments

\[
V_{i}^{\text{ext}}(z) = \begin{cases} 
  \infty & \text{if } z < \frac{\sigma_{j}}{2} \\
  0 & \text{otherwise}
\end{cases}
\]  

(6.9)

Then the density of segment ‘1’ is

\[
\rho_{1}(0) = \exp(\beta \mu_{M}) \exp[D_{1}(0) - \beta v]I_{1,1}(0)I_{2,1}(0),
\]  

(6.10)

and for the other segments

\[
\rho_{j}(z) = \exp(\beta \mu_{M}) \exp[D_{1}(0) - \beta v] \exp[D_{j}(z)]I_{1,j}(z)I_{2,j}(z), \text{ for } z > \frac{\sigma_{j}}{2},
\]  

(6.11)

where,

\[
I_{1,1}(z) = 1,
\]  

(6.12)
\[ I_{1,2}(z) = \Delta^{(1,2)}(0, z), \text{ for } z > \frac{\sigma_2}{2}, \quad (6.13) \]

\[ I_{1,j}(z) = \int I_{1,j-1}(z') \exp[D_{j-1}(z')] \Delta^{(j-1,j)}(z', z) dz', \text{ for } z > \frac{\sigma_j}{2}, \quad (6.14) \]

and

\[ I_{2,m}(z) = 1, \quad (6.15) \]

\[ I_{2,j}(z) = \int I_{2,j+1}(z') \exp[D_{j+1}(z')] \Delta^{(j,j+1)}(z, z') dz', \text{ for } z > \frac{\sigma_j}{2}, \quad (6.16) \]

\[ I_{2,1}(0) = \int I_{2,2}(z') \exp[D_2(z')] \Delta^{(1,2)}(0, z') dz', \text{ for } z' > \frac{\sigma}{2}. \quad (6.17) \]

The term \( \exp(\beta \mu_m - \beta v) \) is calculated from the grafting density (\( \rho_g \), or the number of chains tethered per unit area of the surface) of the chain as

\[ \int dz \rho_1(z) = \exp(\beta \mu_m) \exp[D_1(0) - \beta v] I_{1,1}(0) I_{2,1}(0) = \rho_g, \quad (6.18) \]

or

\[ \exp(\beta \mu_m - \beta v) = \frac{\rho_g}{\exp(D_1(0)) I_{1,1}(0) I_{2,1}(0)}. \quad (6.19) \]

Substituting this in eq. 6.11 gives the density profile of all the segments in the chain.

For tethered segment,

\[ \rho_1(z) = \rho_g \delta(z), \quad (6.20) \]
and for other segments,

$$\rho_j(z) = \frac{\rho_0}{I_{1,1}(0)I_{2,1}(0)} \exp[D_j(z)]I_{1,j}(z)I_{2,j}(z), \text{ for } z > \frac{\sigma_j}{2}. \quad (6.21)$$

Clearly, this derivation is only for the polymer chains grafted to the wall at \( z = 0 \). For the case of two grafted monolayers, similar results can be obtained for the polymer chains grafted to the wall at \( z = H \), where \( H \) is the separation between the two surfaces. The force of interaction between the two grafted surfaces (in the absence/presence of free polymer) at separation \( H \), is given by [246]

$$f(H) = \frac{1}{A} \left( -\frac{1}{A} \frac{\delta \Omega}{\delta H} \bigg|_{H} - \frac{1}{A} \frac{\delta \Omega}{\delta H} \bigg|_{H \to \infty} \right), \quad (6.22)$$

where \( \Omega \) is the equilibrium grand free energy, \( A \) is the surface area of the two surfaces, and \( H \to \infty \) implies the limit when the separation between the two surfaces is large enough that the monolayers do not interact with each other. If \( f \) is positive, the surfaces repel each other and if \( f \) is negative, they attract. In the current work, the two hard surfaces are grafted with same polymer chains at the same grafting density. Hence, the density profiles of the two grafted monolayers are symmetric. For such a symmetric system, the functional derivative of the grand free energy can be simplified as [246]

$$\frac{1}{A} \frac{\delta \Omega}{\delta H} = \sum_\alpha \int \rho_\alpha(z) \frac{dV_{\alpha,ext}^s(z)}{dz} dz, \quad (6.23)$$

where \( V_{\alpha,ext}^s \) is the external field on segment \( \alpha \) due to a single surface at \( z = 0 \). For
hard walls, this reduces to the sum of the contact densities of the grafted and free polymer chains at the surface at $z = 0$ (see appendix for derivation).

Hence, the structure of the grafted polymer chains (and the free polymer) has to be calculated first before calculating the force of interaction between them. To calculate the segment density profiles numerically, the computational domain is divided into equally spaced grid points along the dimension normal to the surface ($z$). The density profiles are solved using Picard's iteration method. All the integrations are calculated using the trapezoidal rule.

### 6.3 Results and discussion

#### 6.3.1 Structure of polymer brush in the absence of free polymer solvent

Modified iSAFT is used to calculate the structure of grafted monolayer (or polymer brushes) in the absence of free polymer solvent. To test the accuracy of modified iSAFT, the results are compared with the simulation results of Grest and Murat [230]. In these simulations, no solvent molecules were explicitly present. Instead, intermolecular attractions are incorporated to mimic the effect of the quality of solvent implicitly. The inter-molecular attractions are modeled by the Lennard-Jones (LJ) potential.

$$u_{ij}(r) = u_{ij}^{LJ}(r) - u_{ij}^{LJ}(r_c), \quad (6.24)$$
where,

\[ u_{LJ}^{ij}(r) = 4\epsilon_{ij} \left[ \left( \frac{\sigma_{ij}}{r} \right)^{12} - \left( \frac{\sigma_{ij}}{r} \right)^{6} \right] \]  \hspace{1cm} (6.25)

\( r_c \) is the potential cut-off, \( \sigma_{ij} = (\sigma_i + \sigma_j)/2 \) and \( \epsilon_{ij} = \sqrt{\epsilon_i \epsilon_j} \). If \( r_c = 2^{1/6}\sigma_{ij} \) then the potential is purely repulsive. To include attraction the range of LJ interaction (or potential cut-off) is extended to \( r_c = 2.5\sigma_{ij} \). In modified iSAFT, the long range attractions are added as a perturbation to the hard repulsion (reference fluid). For the LJ potential, the attractions are treated in the spirit of Weeks-Chandler-Anderson (WCA) perturbation theory [120, 121].

\[ u_{ij}(r) = u_{ij}^{ref}(r) + u_{ij}^{att}(r), \]  \hspace{1cm} (6.26)

where

\[ u_{ij}^{ref}(r) = \begin{cases} \infty & \text{if } r < \sigma_{ij} \\ 0 & \text{otherwise} \end{cases} \]  \hspace{1cm} (6.27)

and

\[ u_{ij}^{att}(r) = \begin{cases} 0 & r \leq \sigma_{ij} \\ u_{ij}^{LJ}(r_{\min}) - u_{ij}^{LJ}(r_c) & \sigma_{ij} < r < r_{\min} \\ u_{ij}^{LJ}(r) - u_{ij}^{LJ}(r_c) & r_{\min} \leq r < r_c \end{cases} \]  \hspace{1cm} (6.28)

\( r_{\min} = 2^{1/6}\sigma_{ij} \) is the position of the (LJ) potential minima.

We first studied the structure of hard (athermal) chains tethered to a flat hard surface. This corresponds to the case where chains are present in an implicit good solvent. The chains are assumed to be uniformly distributed on the surface. Hence
Figure 6.1: (a) Segment density profile of hard chains tethered to a hard wall for $N_g = 50$ and $\rho_g \sigma^2 = 0.1$. $N_g$ is the number of segments in the chain and $\rho_g$ is the grafting density, which is the number of chains grafted per unit area of the wall. (b) Segment density profiles of hard chains tethered to a hard wall for $N_g = 100$ and $\rho_g \sigma^2 = 0.03$ ( ■ ), 0.07 ( ▲ ) and 0.1 ( ● ). Symbols are the simulation results from Grest and Murat [230] and curves are the predictions from modified iSAFT.

the dimension along which there is inhomogeneity in the chain structure is normal to the surface ($z$). Figures 6.1a and b show the density profile of polymer brushes at different grafting densities. At lower grafting densities the profiles are parabolic, and in good qualitative agreement with previous SCFT results [227]. However, at high grafting densities the profiles become flatter than a parabola. The quantitative comparison is made with the results from molecular dynamics (MD) simulations by Grest and Murat [230]. As can be seen from figures 6.1a and b, the predictions from modified iSAFT are in good quantitative agreement with the simulation results.

Figure 6.2a shows the density profile of these polymer brushes (having different chain lengths) as a function of the distance from the grafting surface scaled by the
Figure 6.2: (a) Segment density profiles vs \( z/N_g \) of hard chains tethered to a hard wall for \( N_g = 50 \) (solid curve), 100 (dot dashed curve), 150 (dashed curve) and \( \rho_g \sigma^2 = 0.1 \). The predictions are from modified iSAFT. (b) Brush height \( h \) (■) and average brush height \( <z> \) (○) vs \( N_g \rho_g^{1/3} \) for hard chains tethered to a hard wall for \( N_g = 50, 100 \) and 150 at different grafting densities. The dashed curves are linear fits to the data.

Chain length \( (z/N_g) \) at a fixed \( \rho_g \), where \( \rho_g \) is the grafting density and \( N_g \) is the number of segments in the chain. The profiles overlap each other except near the end of the brush where the profiles show a gradual exponential decay (instead of a parabolic decay). The shape of the density profiles in figures 6.1a, 6.1b, and 6.2a are similar to the SCFT prediction [227] for the density profile at good solvent condition as \( \rho(z) = C_1 \rho_g^{2/3} - C_2 (z/N_g)^2 \), where \( C_1 \) and \( C_2 \) are constants independent of \( \rho_g \) and \( N_g \). Furthermore, this density profile predict a scaling relationship for the average brush height \( <z> \) as \( <z> \sim N_g \rho_g^{1/3} \) in accordance with the scaling theories of
Alexander [51] and de Gennes [52], where $< z >$ can be defined as

$$< z > = \frac{\int z \rho(z) dz}{\int \rho(z) dz}.$$  \hspace{1cm} (6.29)

$< z >$ is calculated for a number of polymer brushes at various $N_g$ and $\rho_g$. Figure 6.2b shows that modified iSAFT follows the scaling relation for $< z >$. The maximum distance to which the brushes extend away from the wall is defined as the brush height $h$. Figure 6.2b also shows that $h$ follows the same scaling relation. Numerically, $h$ is calculated as the normal distance from the wall after which the total segment density of the tethered chains, $\rho \sigma^3 < 10^{-6}$.

![Figure 6.3](image_url)

**Figure 6.3:** (a) Segment density profiles of attractive chains tethered to a hard wall for $N_g = 200$ and $\rho_g \sigma^3 = 0.1$ at $\epsilon/kT = 0$ ( ), $T^* = 4$ ( ), $T^* = 3$ ( ) and $T^* = 2$ ( ). Symbols are the simulation results from Grest and Murat [230] and curves are the predictions from modified iSAFT. (b) Average brush height, $< z >$ vs $N_g^{1/3}$ for attractive chains tethered to a hard wall at $T^* = 4$ (good solvent), for $N_g = 50, 100$ and 200 at different grafting densities. Symbols are the prediction from modified iSAFT and the dashed curve is linear fit to this data.
Next, the attraction are added between the segments of the polymer brush to study the effects of decreasing the quality of the (implicit) solvent. The quality of the solvent is varied by changing the reduced temperature \( (T^* = kT/\varepsilon) \). Reduced theta temperature, \( T_\theta^* = 3.0 \), as shown by Grest and Murat [230]. They calculated this value of the theta temperature by simulating dilute free chains and calculating their mean square radius of gyration, \( < R_g^2 > \). For a single chain, \( < R_g^2 > \sim N_g^\nu \) where \( \nu = 1/2 \) for a theta solvent, 0.59 for a good solvent and 1/3 for a poor solvent. Thus the calculations for \( T^* > T_\theta \) corresponds to a good solvent condition, and \( T^*(< T_\theta) \) corresponds to a poor solvent condition.

Figure 6.3a shows the density profile of polymer brushes in different solvent con-
ditions. In a good solvent the brush is extended and follows a parabolic profile. However, as the solvent quality decreases the brush height decreases and the profiles become flatter than a parabola and almost step-like.

SCFT predicts that the scaling variable for average brush height changes with the solvent quality [227]. For good solvent, $<z> \sim N_g \rho_g^{1/3}$; for theta solvent, $<z> \sim N_g \rho_g^{1/2}$; and for poor solvent, $<z> \sim N_g \rho_g$. Figures 6.3b, 6.4a and 6.4b show that modified iSAFT agrees with these scaling relations. It should be noted that for all the cases studied here, $N_g$ and $\rho_g$ are chosen such that chains strongly overlap; i.e. $\rho_g \gg \rho_g^*$, where $\rho_g^*$ is the overlap threshold. $\rho_g^*$ scales as $\sim N_g^{-a}$, where $a = 6/5$ for good solvent, 1 for a theta solvent and 2/3 for a poor solvent.

6.3.2 Structure of polymer brushes in the presence of an explicit solvent

Molecular Dynamics simulation for polymer brushes in the presence of free polymer have been done by Grest [231]. The calculations were done for free polymers with a small number of segments ($N_f = 2, 5$ and 10). Both the tethered and the free chains were purely repulsive. To study the effect of explicit solvent on the structure of the polymer brush, the overall density of the monomers in the system was fixed at $\rho \sigma^3 = 0.85$.

The structure of both the polymer brush and the free polymer are calculated using modified iSAFT. The number of segments in the tethered chain are fixed to $N_g = 100$
Figure 6.5: (a) Segment density profiles of hard chains tethered to a hard wall for $N_g = 100$ and $\rho_g \sigma^2 = 0.1$ in the presence of implicit solvent (●) and explicit solvent with $N_f = 2$ (▲), $N_f = 5$ (■) and $N_f = 10$ (▼). Symbols are the simulation results from Grest [231] and curves are the predictions from modified iSAFT. (b) Segment density profiles of polymer brushes ($N_g = 100$ and $\rho_g \sigma^2 = 0.1$) and the free polymer solvent ($N_f = 10$, $\rho_f \sigma^3 = 0.682$) from modified iSAFT.

and the grafting density is fixed to $\rho_g \sigma^2 = 0.1$. The calculations are done for three different cases, $N_f = 2$, 5 and 10. The density of free polymer for all the three cases is $\rho_f \sigma^3 = 0.682$, based on the overall monomer density in the system. Figure 6.5a compares the density profiles of the polymer brush for these three cases with that in the presence of an implicit solvent ($N_f = 0$). As can be seen from the figure, the presence of an explicit solvent (free polymer) significantly affects the structure of the brush. Since the chains are purely repulsive, the origin of the effect is solely due to the entropic interactions. Due to volume exclusion, the explicit solvent molecules compress the brush causing it to partially collapse compared to the case of implicit solvent. This compression increases with the increase in the number of segments in
the solvent and the brush height decreases further. As the solvent density is large, the solvent chains penetrate into the brush, as seen in figure 6.5b. However, near the wall the brush monomers dominate, where there is a strong layering due to the presence of the hard surface.

6.3.3 Interaction between two grafted monolayers in the absence of free polymer

Now, consider two grafted monolayers in the absence of free polymer. The structure and thermodynamic properties of the monolayers depend on the number of segments ($N_g$) in the grafted chains and their grafting density ($\rho_g$). As the segments of the chains are purely repulsive, the chains are implicitly in good solvent condition. Figure 6.6 shows the segment density profiles of the two monolayers ($N_g = 101, \rho_g \sigma^2 = 0.03$) at different separations, $H = 70 \sigma$ and $H = 50 \sigma$. Since the brush height of both of them is about $38 \sigma$, their free ends are in contact at $H = 70 \sigma$. At smaller separations, they interpenetrate and compress each other, as shown in the figure for $H = 50 \sigma$. Figure 6.7a compares the total segment density profiles of both the grafted monolayers calculated from modified iSAFT with the simulation results of Murat and Grest [247], at different separations. In this figure, the normal distance $z$ is scaled by the separation $H$ between the grafted surfaces. Modified iSAFT is in good agreement with the simulations results. At $H = 30 \sigma$, the monolayers are highly compressed. The total segment density increases everywhere between the two
surfaces and becomes almost uniform except in the vicinity of the surfaces where the chains are depleted.

Figure 6.6: Segment density profiles of the two grafted monolayers ($N_g = 101, \rho_g \sigma^2 = 0.03$) at separations, (a) $H = 70 \sigma$ and (b) $H = 50 \sigma$.

Figure 6.7b shows the interaction force between the two monolayers ($N_g = 101, \rho_g \sigma^2 = 0.03$) as a function of the separation between them. At large separations, the individual monolayers are unperturbed as they do not know about each other and the interaction force is zero. The monolayers start interacting when the separation between them is about twice the brush height of the individual unperturbed monolayers. We can denote the height of a single unperturbed monolayer as $H_0$ and define a compression ratio $q$ as $H/2H_0$. For chains in an implicit good solvent, $H_0 \sim N_g \rho_g^{1/3}$. As the monolayers approach each other, the interaction force is purely repulsive as $f > 0$ for all $q < 1$. Figure 6.8 shows the interaction force between two monolay-
Figure 6.7: (a) Comparison of the total segment density profiles of the two grafted monolayers ($N_g = 101$, $\rho_g \sigma^2 = 0.03$) at different separations from modified iSAFT with the simulation results from Murat and Grest [247]. The symbols denote the simulations results for $H = 50 \sigma$ (▲) and $H = 30 \sigma$ (■). The curves are the theoretical results. (b) Interaction force between the two grafted monolayers as a function of the separation between them.

ers as a function of the compression ratio for different grafting densities and chain lengths. At fixed $\rho_g$, the force curves for different chain lengths almost overlap each other. This suggests that the interaction force scales with $\rho_g$. The scaling theory of Alexander [51] states that for the good solvent conditions, the interaction force should scale as $f \sim \rho_g^{3/2} F(H/2H_0)$. Figure 6.9 plots the interaction force scaled by $\rho_g^{3/2}$ as a function of the compression ratio for different interacting monolayers with different polymer chain lengths and grafting densities. As can be seen from the figure, modified iSAFT is in agreement with the scaling relation.
6.3.4 Interaction between two grafted monolayers in the presence of free polymer

The presence of free polymer around the grafted monolayers significantly affect their structure and the interactions between them. For large separations between them, they do not interact and behave as two independent monolayers immersed in the free polymer solution. These monolayers and the free polymer interpenetrate each other and the monolayers are compressed. The degree of interpenetration depends upon the chain lengths of the grafted \((N_g)\) and free \((N_f)\) polymers, grafting density \(\rho_g\) and the bulk free polymer density \(\rho_f\) for \(\sigma_g = \sigma_f = \sigma\), where \(\sigma_g\) and \(\sigma_f\) are the segments sizes of the grafted and free polymer chains, respectively. As all the polymer
chains are athermal, they are implicitly in good solvent condition. Figure 6.10a shows the segment density profiles of the grafted and free polymers for $N_g = 101$, $\rho_g \sigma^2 = 0.1$, $N_f = 100$, and $\rho_f \sigma_f^2 = 0.25$ when the grafted monolayers have no interaction. The free polymer decreases the unperturbed brush height from $H_0 = 55 \sigma$ in the absence of free polymer to about $44 \sigma$ in the presence of it. Each monolayer interpenetrates the free polymer to a certain extent after which the free polymer reaches its bulk density. The monolayers start interacting as the separation is reduced. In addition to the penetrating the free polymer the monolayers themselves interpenetrate each other. In doing so, they expel the free polymer between them and the density of the free polymer decreases, as shown in figs. 6.10b and c. Eventually, at low enough separation almost all the free polymer leaves the gap between the monolayers. Figure 6.11a shows the interaction force between the two grafted monolayers as they approach each other.

Figure 6.9: Interaction force between the two grafted monolayers in the absence of free polymer scaled by $\rho_g^{3/2}$ as a function of the compression ratio for $N_g = 51$ and $\rho_g \sigma^2 = 0.1$ (◇), $N_g = 101$ and $\rho_g \sigma^2 = 0.1$ (■), $N_g = 151$ and $\rho_g \sigma^2 = 0.1$ (●), $N_g = 101$ and $\rho_g \sigma^2 = 0.03$ (▲), $N_g = 101$ and $\rho_g \sigma^2 = 0.01$ (▼)
Force is zero at large separations, it becomes attractive at intermediate separations before turning repulsive at lower separations. The attraction roughly begins when the free ends of the two grafted monolayers come in contact with each other. The mutual overlap of these free ends of the monolayers is entropically more favorable than the overlap of the two monolayers with the free polymer, hence the monolayers attract each other and push the free polymer out. At lower separations when almost all the free polymer has been expelled, the monolayers overlap extensively and compress each other which leads to repulsion.

Figure 6.11b shows the effect of changing the bulk free polymer density on the interaction force between the grafted monolayers at fixed grafting density and chain lengths of the grafted and free polymers. The unperturbed brush height (when the two grafted monolayers are far apart) decreases as the bulk free polymer density increases. The attractive region also decreases with the increase in the bulk free polymer density such that it completely disappears for $\rho_f \sigma^3 = 0.75$. For this case, the interaction force is purely repulsive. At such high bulk free polymer density, the grafted monolayers are already highly compressed and therefore they sterically hinder themselves from approaching towards each other.

Similar behavior for the interaction force is observed on changing the chain length of the free polymer while keeping its bulk density fixed, as shown in fig. 6.12. The interaction force is purely repulsive for smaller chain length while at larger free polymer chain lengths, the force is attractive at intermediate separations and repulsive at lower
Figure 6.10: Segment density profiles of the two grafted monolayers \((N_g = 101, \rho_g \sigma_g^2 = 0.1)\) and the free polymer \((N_f = 100, \rho_f \sigma_f^3 = 0.25)\) at separations, (a) \(H = 90 \sigma\), (b) \(H = 80 \sigma\), (c) \(H = 70 \sigma\), and (d) \(H = 65 \sigma\). \(\sigma_g = \sigma_f = \sigma\).

There is a higher entropic advantage for the free ends of the two monolayers to mutually overlap each other rather than the two monolayers overlapping with the longer free polymer chains. Hence, the attractive minimum increases with
Figure 6.11: (a) Interaction force between the two grafted monolayers in the presence of free polymer as a function of the separation between them for \( N_g = 101, N_f = 100, \rho_g \sigma_g^2 = 0.1, \) and \( \rho_f \sigma_f^2 = 0.25. \)  \( \sigma_g = \sigma_f = \sigma. \)  (b) Interaction force between the two grafted monolayers in the presence of free polymer as a function of the separation between them for different bulk free polymer densities: \( \rho_f \sigma_f^2 = 0.25 \) (dot-dashed curve), \( \rho_f \sigma_f^2 = 0.4 \) (dashed curve), \( \rho_f \sigma_f^2 = 0.6 \) (dotted curve), and \( \rho_f \sigma_f^2 = 0.75 \) (solid curve). Other parameters are fixed at \( N_g = 101, N_f = 100, \rho_g \sigma_g^2 = 0.1, \) and \( \sigma_g = \sigma_f = \sigma. \)

the increase in the free polymer chain length. Furthermore, the attractive minimum occurs only when the free polymer exceeds a certain minimum chain length.

Figure 6.13a shows that for a fixed grafting density and bulk free polymer density, it is the ratio of the chain lengths of the free and grafted polymers, \( \alpha = N_f/N_g, \) that determines whether the force is purely repulsive or has a attractive minimum. In this figure, the grafting densities are scaled by \( 1/\sqrt{N_g}. \) The figure shows that locus of the critical values of \( \alpha \) (i.e. the boundary between the purely repulsive and attractive domains) calculated using modified iSAFT agrees with the scaling relation obtained from previous theoretical studies using SST [209] and numerical SCFT [206, 208]:

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Figure 6.12: Interaction force between the two grafted monolayers in the presence of free polymer as a function of the separation between them for different free polymer chain lengths: \( N_f = 50 \) (dot-dashed curve), \( N_f = 100 \) (dashed curve), and \( N_f = 150 \) (solid curve). Other parameters are fixed at \( N_g = 101, \rho_g \sigma_g^2 = 0.1, \rho_f \sigma_f^2 = 0.6 \), and \( \sigma_g = \sigma_f = \sigma \).

\[
\rho_g \sqrt{N_g} \propto \alpha^{-\lambda}, \quad \text{where } \lambda \text{ is the scaling exponent. From modified iSAFT, } \lambda = 2.
\]

As discussed earlier that for a fixed \( \rho_g, \) and \( \alpha, \) the force is purely repulsive at higher bulk free polymer densities and attractive at lower densities (see fig. 6.11b). Hence, the critical values of \( \alpha \) increases with the increase in the bulk free polymer density, as shown in fig. 6.13b. Again, the locus of these values for different bulk free polymer densities follows the scaling relation: \( \rho_g \sqrt{N_g} \propto \alpha^{-2}. \)

Next we investigate the effect of changing the relative sizes of the segments in the free and grafted polymers, \( \beta = \sigma_f / \sigma_g \), on the interaction force between the grafted monolayers. Figure 6.14a shows the boundaries between purely repulsive and attractive domains for different values of \( \beta, \) at fixed bulk free polymer density. The boundaries shift towards the attractive domain or in other words the critical density.
Figure 6.13: (a) Locus of the critical values of $\alpha = N_f/N_g$ at which the interaction force between the grafted monolayers becomes attractive for fixed bulk free polymer density, $\rho_f \sigma_f^3 = 0.6$. The chain lengths of the grafted polymers are $N_g = 101$ (■) and $N_g = 151$ (●). $\sigma_g = \sigma_f = \sigma$. (b) Locus of the critical value of $\alpha$ at which the interaction force between the grafted monolayers becomes attractive for different bulk free polymer densities: $\rho_f \sigma_f^3 = 0.6$ (■), and $\rho_f \sigma_f^3 = 0.75$ (●). $N_g = 101$ and $\sigma_g = \sigma_f = \sigma$.

value of $\alpha$ increases as the relative segment size of the grafted polymers increases. This is due to the fact that the steric hindrance is higher for grafted monolayers with bigger segments. Another interesting feature is that even for $\sigma_g \neq \sigma_f$, the repulsion/attraction boundaries follows the same scaling relation, $\rho_g \sqrt{N_g} \propto \alpha^{-2}$.

The steric hinderance between the two monolayers depends upon the volume of the segments of grafted polymers, hence these different boundaries for different segment sizes of the grafted polymer (relative to the size of free polymer segments) may scale by $\beta^3$. In fact, this is the case as shown in figure 6.14b. The figure shows that for cases where the relative segment sizes of the grafted and free polymers are different,
Figure 6.14: (a) Locus of the critical value of $\alpha$ at which the interaction force between the grafted monolayers becomes attractive for different relative segment sizes of the grafted and free polymers: $\sigma_g = \sigma_f(\square)$, $\sigma_g = 1.1\sigma_f(\bullet)$, and $\sigma_g = 1.2\sigma_f(\triangle)$. The bulk free polymer density, $\rho_f\sigma_f^3 = 0.6$ and $N_g = 101$. $\sigma_f = \sigma$. (b) Scaling relation for the locus of the critical value of $\alpha$ for different relative segment sizes of the grafted and free polymer: $N_g = 101, \sigma_g = \sigma_f(\square)$; $N_g = 101, \sigma_g = 1.1\sigma_f(\bullet)$; $N_g = 101, \sigma_g = 1.2\sigma_f(\triangle)$; and $N_g = 151, \sigma_g = \sigma_f(\bigcirc)$. $\sigma_f = \sigma$. The bulk free polymer density, $\rho_f\sigma_f^3 = 0.6$. $\sigma_f = \sigma$.

the critical value of $\alpha$ where the interaction force between the two monolayers turns from purely repulsive to attractive follows the scaling relation, $\rho_g \sqrt{N_g} \beta^3 \propto \alpha^{-2}$.

6.4 Conclusions

Modified iSAFT density functional theory has been extended to study the structure of polymer brushes in the absence/presence of free polymer solvent. In the absence of the solvent or for 'dry brush', the structure is governed by the grafting density and the segment-segment interactions of the polymer chain. The theory is in good quantitative agreement with the MD simulation results in literature and follows
the scaling relations of Alexander [51] and de Gennes [52]. The presence of a solvent in the case of 'wet brush', compresses the brush due to entropic effects. The increase in the number of segments in the free polymer solvent at the same monomer density decreases the brush height. Again the theoretical results are in good quantitative agreement with the simulation results.

The force of interaction between the two grafted monolayers in the absence/presence of free polymer is also investigated. In case of no free polymer, the interaction force is always repulsive due to the steric hindrance of the monolayers. The detailed segment density profiles of the two monolayers show that as the monolayers approach, they compress each other. The interaction force for different grafting densities and chain lengths of the grafted polymer follows the scaling relation, \( f \sim \rho_g^{3/2} F(H/2H_0) \), previously proposed by Alexander [51] and confirmed using molecular dynamics simulations by Murat and Grest [247] and Chandler McCoy Singer (CMS) DFT by McCoy and Curro [248]. However, the interpretation of the arguments to the function, \( F(H/H_0) \), is different in the two studies. McCoy and Curro defined an average layer thickness of the grafted monolayers, \( L \) as \( 2 \frac{\int s(x) dx}{\int \rho(x) dx} \). From their DFT results, they developed an empirical expression for \( L/2H_0 \) as a function of \( H/2H_0 \) and showed that \( f \sim \rho_g^{3/2} F(L/2H_0) \). On the contrary, simulation results from Murat and Grest show that \( f \sim \rho_g^{3/2} F(H/2H_0) \) which is in agreement with our results using modified iSAFT.

The situation is more complicated when free polymer is present between the two
grafted monolayers, where the interactions can have an attractive minimum depending upon the grafting density, relative chain lengths ($\alpha$) and segment sizes ($\beta$) of the free and grafted polymers, and bulk free polymer density. First we considered cases where the segment sizes of the free and grafted polymers are the same or $\beta = 1$. For a given grafting and bulk free polymer density, the interaction force has an attractive minimum if $\alpha$ is greater than a critical value. This critical value of $\alpha$ increases with the increase in the bulk free polymer density at a given grafting density, and decreases with the increase in the grafting density at fixed bulk free polymer density. Furthermore, the locus of these critical values of $\alpha$ follows a scaling relation, $\rho_g \sqrt{N_g} \propto \alpha^{-2}$, where the constant of proportionality is different at different bulk free polymer densities.

In all these cases the segments of the grafted and free polymers are purely repulsive and their sizes are the same, hence both of them are chemically identical. The problem of repulsion/attraction between the two grafted monolayers in the presence of chemically identical free polymer is theoretically and numerically equivalent to the case of wetting/dewetting of a free polymer on a chemically identical grafted monolayer [207, 206, 208]. This equivalence breaks down when the free and grafted polymers are not chemically identical. One such case have been considered, where the segment sizes of the free and grafted polymers are not the same, or $\beta \neq 1$. At fixed grafting and bulk free polymer densities, increase in the (relative) segment size of the grafted polymers increases the critical value of $\alpha$. However, the locus of the
critical values of $\alpha$ still follow the scaling relation, $\rho_g \sqrt{N_g} \propto \alpha^{-2}$ with different proportionality constant. We have shown that this proportionality constant depends on $\beta^3$, and that the critical values of $\alpha$ or the boundary between the purely repulsive and attractive domains for different $\beta$ scale as, $\rho_g \sqrt{N_g \beta^3} \propto \alpha^{-2}$.

**Appendix: Derivation of the force of interaction between the two polymer grafted hard walls**

The grand free energy is given as

$$\Omega[\rho(r)] = A[\rho(r)] - \sum_{\alpha} \int \rho_{\alpha}(r) u_{\alpha}(r) dr,$$

(6.30)

where $u_{\alpha}(r) = \mu_{\alpha} - V_{\alpha}^{ext}(r)$, and $\alpha = \{1, ..., N_g^1, 1, ..., N_g^2, 1, ..., N_f\}$. Here the first set in $\alpha$ or $\{1, ..., N_g^1\}$ corresponds to the segments in the chains grafted to the surface at $z = 0$, the second set $\{1, ..., N_g^2\}$ corresponds to the segments in the chains grafted to the surface at $z = H$, and the third set $\{1, ..., N_f\}$ corresponds to the segments in the free polymer chains. In this work, $N_g^1 = N_g^2 = N_g$.

In a density functional formalism,

$$\frac{\delta \Omega}{\delta \rho_{\alpha}(r)} = 0,$$

(6.31)

and

$$\frac{\delta \Omega}{\delta u_{\alpha}(r)} = -\rho_{\alpha}(r).$$

(6.32)

Force of interaction between the surfaces is given by the functional derivative of
the grand free energy, $\frac{\delta \Omega}{\delta H}$.

$$\frac{\delta \Omega}{\delta H} = \sum_{\alpha} \int \frac{\delta \Omega}{\delta \rho_\alpha (r)} \frac{\partial \rho_\alpha (r)}{\partial H} dr + \sum_{\alpha} \int \frac{\delta \Omega}{\delta u_\alpha (r)} \frac{\partial u_\alpha (r)}{\partial H} dr,$$  \hspace{1cm} (6.33)

or

$$\frac{\delta \Omega}{\delta H} = \sum_{\alpha} \int \rho_\alpha (r) \frac{dV^{\text{ext}}_\alpha (r)}{dH} dr.$$  \hspace{1cm} (6.34)

In one dimension

$$\frac{\delta \Omega}{\delta H} = A \sum_{\alpha} \int \rho_\alpha (z) \frac{dV^{\text{ext}}_\alpha (z)}{dH} dz,$$  \hspace{1cm} (6.35)

where

$$V^{\text{ext}}_\alpha (z) = V^{\text{ext},s_1}_\alpha (z) + V^{\text{ext},s_2}_\alpha (H - z).$$  \hspace{1cm} (6.36)

$V^{\text{ext},s_1}_\alpha$ is the external potential on segment $\alpha$ due to the surface at $z = 0$ and $V^{\text{ext},s_2}_\alpha$ due to the other surface at $z = H$. If both these surfaces are similar, i.e. $V^{\text{ext},s_1}_\alpha (z) = V^{\text{ext},s_2}_\alpha (H - z)$ and density profiles of the grafted chains at the two surfaces are symmetric, then this functional derivative can be expressed as [246]

$$\frac{\delta \Omega}{\delta H} = A \sum_{\alpha} \int \rho_\alpha (z) \frac{dV^{\text{ext},s_1}_\alpha (z)}{dz} dz.$$  \hspace{1cm} (6.37)

For the polymer chains grafted at the surface at $z = 0$, the external potential acting on the segments are: for the tethered segment,

$$\exp(-\beta V^{\text{ext},s_1}_1 (z)) = \exp(-\beta \nu \delta (z))$$  \hspace{1cm} (6.38)
or

\[
\frac{d\beta V_{1}^{\text{ext,sl}}(z)}{dz} = -\frac{1}{\exp(-\beta V_{1}^{\text{ext,sl}}(z))} \frac{d\exp(-\beta V_{1}^{\text{ext,sl}}(z))}{dz} = -\frac{\delta'(z)}{\delta(z)}, \quad (6.39)
\]

and for the other segments,

\[
\exp(-\beta V_{j}^{\text{ext,sl}}(z)) = H(z - \frac{\sigma_j}{2}), \quad (6.40)
\]

where \(H(z)\) is the Heaviside step function. Or,

\[
\frac{d\beta V_{j}^{\text{ext,sl}}(z)}{dz} = -\frac{1}{\exp(-\beta V_{j}^{\text{ext,sl}}(z))} \frac{d\exp(-\beta V_{j}^{\text{ext,sl}}(z))}{dz} = -\frac{\delta(z - \frac{\sigma_j}{2})}{H(z - \frac{\sigma_j}{2})}. \quad (6.41)
\]

For all the segments of the chains grafted to the surface at \(z = H\) and the free polymer, the external potential due to the surface at \(z = 0\) is

\[
\exp(-\beta V_{j}^{\text{ext,sl}}(z)) = H(z - \frac{\sigma_j}{2}), \quad (6.42)
\]

and eq. 6.41 applies.

Hence,

\[
\frac{1}{A} \frac{\delta \beta \Omega}{\delta H} = - \int \rho_{g} \delta(z) \frac{\delta'(z)}{\delta(z)} \, dz - \sum_{j=2}^{N_{2}} \int \rho_{j}(z) \frac{\delta(z - \frac{\sigma_j}{2})}{H(z - \frac{\sigma_j}{2})} \, dz
\]

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\[-\sum_{j=1}^{N^2} \int \rho_j(z) \frac{\delta(z - \frac{\sigma_j}{2})}{H(z - \frac{\sigma_j}{2})} dz - \sum_{j=1}^{N_f} \int \rho_j(z) \frac{\delta(z - \frac{\sigma_j}{2})}{H(z - \frac{\sigma_j}{2})} dz \]

\[= -\sum_{j=2}^{N^2} \rho_j(\frac{\sigma_j}{2}) - \sum_{j=1}^{N^2} \rho_j(\frac{\sigma_j}{2}) - \sum_{j=1}^{N_f} \rho_j(\frac{\sigma_j}{2}). \quad (6.43)\]

And the force of interaction between the grafted surfaces is

\[
\frac{f(H)}{A} = \left[ -\sum_{j=2}^{N^2} \rho_j(\frac{\sigma_j}{2}) - \sum_{j=1}^{N^2} \rho_j(\frac{\sigma_j}{2}) - \sum_{j=1}^{N_f} \rho_j(\frac{\sigma_j}{2}) \right]_{H} - \\
\left[ -\sum_{j=2}^{N^2} \rho_j(\frac{\sigma_j}{2}) - \sum_{j=1}^{N^2} \rho_j(\frac{\sigma_j}{2}) - \sum_{j=1}^{N_f} \rho_j(\frac{\sigma_j}{2}) \right]_{H \to \infty} \quad (6.44)\]

where, \(H \to \infty\) implies the limit when the separation between the two surfaces is large enough that they do not interact with each other.
Chapter 7

Modified iSAFT: Extension to inhomogenous branched polymers

7.1 Introduction

Polymers confined between solid surfaces to form thin films are a classical example of inhomogeneous polymer systems. Understanding the microstructure of these polymer films is of fundamental importance for many technological processes such as lubrication, adhesion, coatings, paints, printing inks, chromatography, membrane separations, and preparation of nanocomposites [249, 250] and biomedical applications such as surface modification of medical implants like artificial heart valves, and joint prostheses [251, 252]. Knowledge of the structure is also critically important to understanding the dynamics of these confined polymers, which is relevant to the mechanical properties of thin films, such as in nanocomposites [253].
The structure of confined polymer chains are quite different from the chains in the bulk. The translational freedom and number of available conformations of the chains decreases in the confined space, which induces an entropic penalty on the polymer chains due to the confinement [254, 255]. On the other hand, there is an energetic advantage if the polymer-surface interactions are favorable for adsorption. At dense polymer concentrations, another entropic effect known as the packing effect comes into play. In these systems, packing some of the molecules near the surface increases the available free volume in rest of the fluid thereby increasing the entropy of the fluid. As evident, polymer chain architecture plays an important role in determining these entropic and enthalpic effects. For different architectures such as linear and branched, we expect different behavior near the confining surfaces. In a branched polymer chain, there are one or more small multi-functional units called the branch points, which are directly linked to more than two long chains. A variety of branched chain architectures are possible depending on the number and position of the branch points. In star polymer, a polymer chain has only one branch point, from which many branches of the chain (or the arms) originate. Branched polymers with two or more branch points are called comb polymers, when a backbone and the branches can be distinguished. If there are numerous branch points that are densely spaced along the backbone, the highly branched polymer is called molecular bottle brush. Recently more complex architectures such as dendrimers or cascade polymers have been synthesized that combine a central branch point with a regular repetitive
branching pattern [256, 257, 258]. Even though these branched architectures require
greater study, preliminary results do suggest that their interfacial behavior differs
significantly from that of linear polymers of the same chemistry, and this may of­
fer distinct advantages in applications [253]. For example, the homopolymer combs
provide higher surface coverage and thinner films than the comparable linear poly­
mers [259]. This can be exploited in establishing the design criteria for fabricating
polymer films with prescribed properties, such as surface coverage, layer thickness,
hesion, and wettability. The greater availability of chain-end-functional groups also
permits the stronger adhesion of interactions between a functionalized dendrimer and
a surface than the corresponding linear polymer. Other property differences, such as
lack of entanglements in dendrimers, decreased crystallinity, and a compact 3D shape,
can be exploited to give materials with superior performance at the solid-liquid in­
terface [260, 261].

These branched polymers are often encountered in rubbers, thermoplastic and
thermosetting resins, and organic and inorganic gels which have numerous appli­
cations as sealants, coatings, and inert or interactive supports in traditional (au­
tomotive, textile, and construction industries) and biomedical (contact lenses, and
drug delivery systems) fields. For these reasons, the theoretical modeling of confined
branched polymers is important. The models reported in the literature are specific
to certain architectures. In practice, more complex chain architectures with different
blocks (branches or the backbone) having different compatibilities, surface affinities
and segment sizes may be needed to provide the necessary flexibility in fine-tuning the structure of the thin polymer films. Therefore the objective of the current work is to develop a general model, which can simulate these complex heteronuclear chain architectures. However, the approach is still limited to flexible chains architectures with no loops or cycles.

In previous chapters, modified iSAFT was successfully applied to study the structure of confined heteronuclear polymers such as diblock copolymers. However, in these previous works, the formulation is derived only for linear heteronuclear chains. In this work, the theory is extended in general such that it is applicable to complex branched heteronuclear chain architectures. The derivation is presented in section 2. To test the theory, modified iSAFT is applied to confined star-like branched polymers, since they are nice stepping-stone model objects for studying systems where the topology/architecture of the molecule plays an important role [262, 263]. The results from modified iSAFT and comparisons with the simulation results of Yethiraj and Hall [264, 265] are discussed in section 3. The final section summarizes the important features of the theory and the systems studied, with few concluding remarks.

7.2 Model and theory

The branched polymer molecule is modeled as a flexible chain of tangentially bonded spherical segments. Each of the segments of the chain can be different (to account for the heterogeneity in the chain structure). For the sake of simplicity,
the derivation is presented for a pure fluid of branched chain molecules having m backbone segments and two branches at backbone segments 'j' and 'k', as shown in fig. 7.1a. The branch at 'j' has $m_j$ segments enumerated as $b_j1, b_j2, ..., b_j m_j$. This notation is used to distinguish the branch segments from the backbone segments. The generalization to chains with multiple branches will follow.

Figure 7.1: (a) Model of a branched chain molecule. The backbone has 'm' segments and the two branches at backbone segment 'j' and 'k' are 'b_j' and 'b_k', respectively. b_j has $m_j$ segments while b_k has $m_k$ segments. The total number of segments in the chain, N = m + $m_j + m_k$. (b) Schematic of the formation of a branched polymer chain of N segments from N associating spheres. For a middle segment $\alpha$, site 'A' associates with site 'B' on the segment $\alpha' = \alpha + 1$ and site 'B' associates with site 'A' on the segment $\alpha' = \alpha - 1$. The branch points on the backbone 'j' and 'k' have additional associating site 'C' which associates with the branch segments, 'b_j $m_j$' and 'b_k $m_k$', respectively. End segments 1, m, 'b_j 1' and 'b_k 1' have only one associating site, 'A' or 'B'.

The grand free energy (Ω) of the chain fluid at fixed volume (V), temperature (T), and chemical potential ($\mu$) in the presence of an external field ($V^{ext}(R)$) is related to
the intrinsic Helmholtz free energy ($A$) as

$$\Omega[\{\rho_\alpha(r)\}] = A[\{\rho_\alpha(r)\}] - \sum_{\alpha=1}^{N} \int dr' \rho_\alpha(r') (\mu_\alpha - V^{\text{ext}}_\alpha(r')). \quad (7.1)$$

where $N = m + m_j + m_k$ is the total number of segments in the chain molecule, $\rho_\alpha$ is the density of the $\alpha$th segment, $\mu_\alpha$ is its chemical potential, and $V^{\text{ext}}_\alpha$ is the external field acting on that segment. Minimization of the grand free energy with respect to density of the segments yield a system of variational equations, known as the Euler-Lagrange equations,

$$\frac{\delta A[\{\rho_\alpha(r)\}]}{\delta \rho_\alpha(r)} = \mu_\alpha - V^{\text{ext}}_\alpha(r) \quad \forall \alpha = 1, N. \quad (7.2)$$

Solution of this set of equations gives the equilibrium density profile of the segments. From the equilibrium density profiles, other structural and thermodynamic properties can be calculated following the standard statistical mechanical relations. However, this requires an analytical expression for the intrinsic Helmholtz free energy functional. This is obtained along the similar lines as statistical associating fluid theory (SAFT) \[46, 47, 58\] for homogeneous chain fluids, as shown in detail in chapter 4. Considering the polyatomic system as a mixture of associating spherical segments in the limit of complete association, the free energy functional can be derived from Wertheim's first order thermodynamic perturbation theory (TPT1) \[46, 47, 58, 26, 27, 28, 29, 62\]. Consider a stoichiometric mixture of
associating segments enumerated as 1, 2, ..., m, bj1, bj2, ..., bj,mj, bk1, bk2, ..., bk,mk.

These associating segments have hard cores and highly directional associating sites. In the limit of complete association, these association sites bond to form chains. To obtain our branched chain model, an associating segment can only associate with its neighboring segments in the chain, as shown in fig. 7.1b. The Helmholtz free energy functional of such a mixture of associating segments can be written using a perturbation expansion as

$$ A[\{\rho_\alpha\}] = A^{id}[\{\rho_\alpha\}] + A^{EX, hs}[\{\rho_\alpha\}] + A^{EX, chain}[\{\rho_\alpha\}] + A^{EX, att}[\{\rho_\alpha\}], \quad (7.3) $$

where $A^{id}$ is the ideal gas free energy contribution, and rest are the excess contributions: $A^{EX, hs}$ due to volume exclusion/repulsive interactions, $A^{EX, chain}$ due to association between the segments to form chains, and $A^{EX, att}$ due to long range attractions.

The free energies and their functional derivatives were derived in detail in chapter 4. In brevity, the functional derivatives of the free energies or the different contributions to inhomogeneous chemical potentials of the segment ‘$\alpha$’ are given by

$$ \frac{\delta \beta A^{id}[\{\rho_\alpha\}]}{\delta \rho_\alpha(r)} = \ln \rho_\alpha(r), \quad (7.4) $$

$$ \frac{\delta \beta A^{EX, hs}[\{\rho_\alpha\}]}{\delta \rho_\alpha(r)} = \int d\mathbf{r}_1 \frac{\delta \Phi[\{n_\alpha(\mathbf{r}_1)\}]}{\delta \rho_\alpha(r)}, \quad (7.5) $$
\[
\frac{\delta \beta A_{EX,assoc}^{\alpha\{\rho_{\alpha}\}}}{\delta \rho_{\alpha}(r)} = \sum_{A \in \Gamma^{(\alpha)}} \ln X^{\alpha}_{A}(r) - \frac{1}{2} \sum_{\gamma=1}^{N} \sum_{\gamma'} \int \rho^{\gamma}_{\gamma'}(r_1) \frac{\delta \ln y_{contact}^{\gamma\gamma'}(\{\rho^{\gamma}_{\gamma'}(r_1)\})}{\delta \rho_{\alpha}(r)} \, dr_1,
\]

(7.6)

\[
\frac{\delta \beta A_{EX,att}^{\alpha\{\rho_{\alpha}\}}}{\delta \rho_{\alpha}(r)} = \sum_{\gamma=1}^{N} \int_{|r-r_1|>\sigma_{\alpha\gamma}} dr_1 \beta u^{att}_{\alpha\gamma}(|r-r_1|) \rho_{\gamma}(r_1),
\]

(7.7)

where, the terms have their usual meanings as in chapter 4. There are two differences here. For repulsive interactions (or volume exclusion), the White Bear version of Rosenfeld’s fundamental measure theory (FMT) [110], derived by Roth et. al. [266] and independently by Yu and Wu [267], is used. And for the chain functional, different weighted densities are used. Following the weighted density functional approach developed by Yu and Wu [61] to define the excess free energy functional due to chain formation, \(\rho^{\gamma}_{\gamma'}\) is defined in terms of the Rosenfeld’s weighted densities as

\[
\rho^{\gamma}_{\gamma'}(r) = n_{0,\gamma}(r)\xi_{\gamma}(r),
\]

(7.8)

where \(\xi_{\gamma} = 1 - n_{v2,\gamma}n_{v2,\gamma}/n_{2,\gamma}^2\), and Rosenfeld’s weighted densities are substituted for \(\rho^{\gamma}_{\gamma'}\) such that

\[
y_{contact}^{\gamma\gamma'}(\{\rho^{\gamma}_{\gamma'}(r_1)\}) = \frac{1}{1-n_3} + \left(\frac{\sigma_{\gamma}\sigma'_{\gamma}}{\sigma_{\gamma} + \sigma'_{\gamma}}\right) \frac{n_2\xi}{2(1-n_3)^2} + \left(\frac{\sigma_{\gamma}\sigma'_{\gamma}}{\sigma_{\gamma} + \sigma'_{\gamma}}\right)^2 \frac{n_2^2\xi}{18(1-n_3)^3},
\]

(7.9)

where \(\xi = 1 - n_{v2}n_{v2}/n_2^2\). \(X_{\lambda}'s\) are given by [58, 62]

\[
X^{\alpha}_{A}(r_1) = \frac{1}{1 + \int dr_2 X^{\alpha'}_{B}(r_2) \Delta^{\alpha\alpha'}(r_1, r_2) \rho_{\alpha'}(r_2)},
\]

(7.10)
Substituting these inhomogeneous chemical potentials or the functional derivatives of the free energy in Euler-Lagrange eqn. 7.2 for the segment $\alpha$ gives

$$\ln \rho_\alpha(r) + \sum_{A \in \Gamma(\alpha)} \ln X^\alpha_A(r) = D_\alpha(r) + \beta \mu_\alpha, \quad (7.11)$$

where $D_\alpha(r)$ is given by

$$D_\alpha(r) = \frac{1}{2} \sum_{\gamma=1}^{N} \sum_{\gamma'} \int \rho^\gamma_\gamma(r_1) \frac{\delta \ln y^\gamma_\gamma}{\delta \rho_\alpha(r)} dr_1 - \frac{\delta \beta A^EX_{hs}}{\delta \rho_\alpha(r)} - \beta V^\alpha_{ext}(r). \quad (7.12)$$

The set of these non-linear eqs. 7.11 (for all the segments) can be solved with eqn. 7.10 for $X^\alpha_A$, for the density profile of the segments. However, in eqn. 7.10, $X^\alpha_A$ for a segment $\alpha$ depends on $X^\alpha_{A+1}$. This coupling of $X^\alpha_A$ and $X^\alpha_{A+1}$ leads to numerical complexities. This interdependence is decoupled for the branched chain molecule by simultaneously solving eqn. 7.11 for the segment densities and eqn. 7.10 for the $X^\alpha_A$'s.

The procedure is similar to that followed for the linear chains in chapter 4. For the first segment

$$\rho_1(r_1) X^1_A(r_1) = \exp[D_1(r_1)] \exp(\beta \mu_1). \quad (7.13)$$

Substituting this result in eqn. 7.10 for $X^2_B$ (neglecting the 1 in the denominator in comparison to the second term which contains the bonding energy and $\varepsilon_0 \rightarrow \infty$) gives

$$X^2_B(r_2) = \frac{1}{\exp(\beta \mu_1) \int dr_1 \exp[D_1(r_1)] \Delta^{(1,2)}(r_1, r_2)}. \quad (7.14)$$
Substituting for $X^2_B$ in the Euler-Lagrange equation for the second segment leads to an expression for $p_2(r)X^2_A(r)$, from which an expression for $X^3_B$ similar to eqn. 7.14 can be obtained. Repeating this procedure through the $j^{th}$ backbone segment in the chain gives

$$
\frac{1}{X^j_B(r_j)} = \exp(\beta \sum_{i=1}^{j-1} \mu_i) \int \ldots \int dr_1 dr_2 \ldots dr_{j-1} \exp[\sum_{i=1}^{j-1} D_i(r_i)] \prod_{i=1}^{j-1} \Delta^{(i,i+1)}(r_i, r_{i+1})
$$

$$
= \exp(\beta \sum_{i=1}^{j-1} \mu_i)I_{1,j}(r_j), \quad (7.15)
$$

where $I_{1,j}$ is a recursive function, $I_{1,1}(r) = 1$ and $I_{1,j}(r) = \int dr'I_{i,j-1}(r') \exp[D_{j-1}(r')]\Delta^{(j-1,j)}(r, r')$. For brevity, this procedure is labeled as proc. A, since it is used numerous times in the derivation.

Similarly, applying proc. A for the linear branch 'b$_j$' from the branch segment 'b$_j$ 1' till the backbone segment 'j' gives

$$
\frac{1}{X^j_C(r_j)} = \exp(\beta \sum_{i=b_j1}^{b_j m_j} \mu_i) \int \ldots \int dr_{b_j1} dr_{b_j2} \ldots dr_{b_j m_j} \exp[\sum_{i=b_j1}^{b_j m_j} D_i(r_i)] \prod_{i=b_j1}^{b_j m_j-1} \Delta^{(i,i+1)}(r_i, r_{i+1})
$$

$$
\Delta^{b_j m_j}(r_j, r_{b_j m_j}) = \exp(\beta \sum_{i=b_j1}^{b_j m_j} \mu_i)Br_j(r_j), \quad (7.16)
$$

where $Br_j$ denotes the branch factor for the branch 'b$_j$' at (backbone) segment 'j'. Clearly, $Br_j(r) = \int dr'I_{1,b_j m_j}(r') \exp[D_{b_j m_j}(r')]\Delta^{b_j m_j}(r, r')$, where $I_{1,b_j}^{br}$ is the $I_1$ function for the segment 'b$_j$ $\alpha$' in the branch 'b$_j$'. The branch factors for all the
backbone segments, other than the segments 'j' and 'k', are defined equal to unity. The recursive function \( I_1 \) for the backbone segments are redefined as, \( I_{1,i}(r) = 1 \) and \( I_{1,j}(r) = \int dr'I_i,j-1(r') \exp[D_{j-1}(r')]Br_{j-1}(r')\Delta^{(j-1,j)}(r,r') \). Reasons for defining the branch factors for backbone segments which do not have a branch and the \( I_1 \) function this way, help to generalize the derivation to chains with multiple branches.

Now substituting for \( X^d_j \) (from eqn. 7.15) and \( X^c_j \) (from eqn. 7.16) in the Euler-Lagrange equation for backbone segment 'j' gives,

\[
\rho_j(r_j)X^d_A(r_j) = \exp(\beta \sum_{i=1}^{j} \mu_i) \exp(\beta \sum_{i=b_j}^{m_j} \mu_i) Br_j(r_j) \exp[D_j(r_j)] I_{1,j}(r_j).
\] (7.17)

Hence, for a backbone segment '\( \alpha \)' after segment 'j',

\[
\frac{1}{X^d_B(r_{\alpha})} = \exp(\beta \sum_{i=1}^{\alpha-1} \mu_i) I_{1,\alpha}(r_{\alpha}).
\] (7.18)

where, \( \sum_{i=1}^{\alpha-1} \) is the sum over all the backbone as well as the branch segments from (backbone) segment '1' to (backbone) segment '\( \alpha - 1 \)'. Physically, this is depicted in fig. 7.2a. This specifies the bonding sites 'B' on all the backbone segments of the chain. Evidently, \( X^d_B \)'s relate the chemical potential of the segment '\( \alpha \)' to the environment experienced by segments connected to '\( \alpha \)' through the bonding site 'B'. Such sharing of information along a molecule is essential to modeling the structure of (heteronuclear) chain molecules with different segment types such as copolymers. This also holds true for the other bonding sites on the segments. Note that we can
drop the $K \exp(\beta e_0)$ in the expressions for $\Delta(i, j)$'s since they cancel out with similar terms in the bulk $\mu_j$'s.

Figure 7.2: Illustration of the calculations of the $I_1$ and $I_2$ functions of the segments of the branched chain. $I_{1,0}$ defines the fraction of segments of type 'o' not bonded sites at their sites 'B' or $X_0^\alpha$ while $I_{2,0}$ defines $X_0^\alpha$. (a) $I_1$ function for the backbone segments with the initiator to the function, $I_{1,1} = 1$, (b) $I_2$ function for the backbone segments with the initiator to the function, $I_{2,1} = 1$, (c) $I_2$ function for the branch 'bj' segments where the initiator to the function, $I_{2,bj,1}^{brj}$ depends upon $I_{1,1}$ and $I_{2,1}$, and (d) $I_1$ function for the branch 'bj' segments with the initiator to the function, $I_{1,1}^{brj} = 1$.

Starting from the last backbone segment 'm', proc. A is repeated to obtain the
fraction of unbonded sites 'A' on the backbone segments as

\[ \frac{1}{X_A^\alpha(r_\alpha)} = \exp(\beta \sum_{i=\alpha+1}^{m} \mu_i) I_{2,\alpha}(r_\alpha), \tag{7.19} \]

where, \( I_2 \) is the complimentary recursive function, \( I_{2,m}(r) = 1 \) and

\[ I_{2,j}(r) = \int dr' I_{2,j+1}(r') \exp[D_{j+1}(r')] Br_{j+1}(r') \Delta^{(j+1)}(r, r'). \]

This is physically depicted in fig. 7.2b. Finally, substituting the expressions for \( X_A^\alpha \) from eqn. 7.19 and \( X_B^\alpha \) from eqn. 7.18 (and \( X_C^\alpha \) from eqn. 7.16 for backbone segments with branches) in the Euler-Lagrange equation for the backbone segment \( \alpha \) gives the density profile of the segment.

\[ \rho_\alpha(r) = \exp(\beta \mu_M) \exp[D_\alpha(r)] Br_\alpha(r) I_{1,\alpha}(r) I_{2,\alpha}(r), \tag{7.20} \]

where \( \mu_M(= \sum_{i=1}^{m} \mu_i) \) is the bulk chemical potential of the chain molecule.

Next, the density profiles of the segments in the branch 'by' are derived. Substituting for \( X_A^j \) from eqn. 7.19 and \( X_B^j \) from eqn. 7.18 in the Euler-Lagrange equation for the backbone segment 'j' gives

\[ \rho_j(r) X_C^j(r) = \exp(\beta \sum_{i=1}^{j-1} \mu_i) \exp(\sum_{i=j+1}^{m} \beta \mu_i) \exp[D_j(r)] Br_j(r) I_{1,j}(r) I_{2,j}(r). \tag{7.21} \]

Using this equation and applying proc. A from segment 'j' onwards to the branch
The expression for the bonding site 'A' on the segment is obtained:

$$\frac{1}{X_A^{b_j/\alpha}(r)} = \exp(\beta \sum_{i=1}^{j-1} \mu_i) \exp(\beta \mu_j) \exp(\beta \sum_{i=j+1}^m \mu_i) \exp(\beta \sum_{i=b_j(\alpha+1)}^{b_jm_j} \mu_i) I_{2,b_j/\alpha}^{brj}(r), \quad (7.22)$$

where, $I_{2,b_j/\alpha}^{brj}$ is the $I_2$ function for the branch segment 'b_j/\alpha':

$$I_{2,b_j/\alpha}^{brj}(r) = \int dr' \exp[D_{b_j}(r')] I_{1,j}(r') I_{2,j}(r') \Delta_{j,b_j/m_j}(r,r'), \quad (7.23)$$

and

$$I_{2,b_j/\alpha}^{brj}(r) = \int dr' I_{2,b_j(\alpha+1)}^{brj}(r') \exp[D_{b_j(\alpha+1)}(r')] \Delta_{b_j(\alpha+1),b_j(\alpha+1)}(r,r'). \quad (7.24)$$

This is depicted in fig. 7.2c. Similarly applying proc. A from the first branch segment 'b_j 1' to the branch segment 'b_j/\alpha' gives

$$\frac{1}{X_B^{b_j/\alpha}(r)} = \exp(\beta \sum_{i=b_j}^{b_j(\alpha-1)} \mu_i) I_{1,b_j/\alpha}^{brj}(r). \quad (7.25)$$

As discussed before, $I_{1,b_j/\alpha}^{brj}$ is the $I_1$ function for the branch segment 'b_j/\alpha' with $I_{1,b_j/\alpha}^{brj}(r) = 1$, as depicted in fig. 7.2d. Finally, substituting $X_A^{b_j/\alpha}$ from eqn. 7.22 and $X_B^{b_j/\alpha}$ from eqn. 7.25 in the Euler-Lagrange equation for the branch segment 'b_j/\alpha' gives its density profile,

$$\rho_{b_j/\alpha}(r) = \exp(\beta \mu_M) \exp[D_{b_j/\alpha}(r)] I_{1,b_j/\alpha}^{brj}(r) I_{2,b_j/\alpha}^{brj}(r). \quad (7.26)$$
Similar expressions can be derived for the segments in the branch \(b_k\).

This derivation can be generalized to chains with multiple branches. The derivation can also be extended to cases where the backbone segments have multiple branches. In that case,

\[
B_{\alpha}(r) = \prod_{i=1}^{n} B_{\alpha,i}(r)
\]  

(7.27)

where the product is over all the ‘n’ branches on the backbone segment ‘\(\alpha\)’ and \(B_{\alpha,i}\) is the branch factor from the branch ‘i’ of (backbone) segment ‘\(\alpha\)’. \(I_1\) and \(I_2\) functions for the backbone segments and the \(I_1\) for the individual branches remains same as defined earlier. Only the initiator to the \(I_2\) function for branch segments changes to account for the presence of multiple branches.

\[
J_{2,b_{\alpha,i}}^{br_{\alpha,i}}(r) = \int dr' \exp[D_{\alpha}(r')] \prod_{k=1,k\neq i}^{n} B_{\alpha,k}(r')I_{1,\alpha}(r')I_{2,\alpha}(r')\Delta^{(\alpha,b_{\alpha,i})}(r,r'),
\]  

(7.28)

where \(br_{\alpha,i}\) denotes the branch ‘i’ at backbone segment \(\alpha\) with ‘n’ branches.

We can also extend this derivation to cases where the branch segment themselves have branches. In that case, we have to define the branch factors for all the segments on the chain such that the branch factor is unity if the segment has no branches. The functions \(I_1\) and \(I_2\) have to be defined for each of the linear branches and their parent backbone segments. Using these functions the segment density profiles of the chain molecule can be obtained.

Once the segment density profiles are obtained, the equilibrium grand free energy
can be calculated in terms of the segment densities as

\[
\beta \Omega[\{\rho_a(r)\}] = \sum_{a=1}^{N} \int dr' \rho_a(r') \left[ D_a(r') \right] + \beta V^\text{ext}_a(r') + \frac{n(i^{(a)})}{2} - 1] + \beta A^{EX,hs} + \beta A^{EX,att}, \tag{7.29}
\]

where \(n(i^{(a)})\) is the total number of associating sites on segment \(a\). Other thermodynamic properties of the confined branched polymer fluid such as interfacial tension can be obtained from the equilibrium grand free energy.

### 7.2.1 Application to star like branched polymers

Star polymers include a classical example of branched polymers where the backbone segment has multiple branches. As shown in the figure 7.3a, we consider the articulation segment ‘c’ as the lone backbone segment. All the branches or ‘f’ arms of the star polymer are similar (with ‘m’ number of segments in each of them), hence the branch factor from each of the arms is the same. Hence,

\[
Br_c(r) = \prod_{i=1}^{f} Br_{c,i}(r) = [Ar(r)]^f \tag{7.30}
\]

where, \(Ar\) is the branch factor from each of the arms, \(Ar(r) = \int dr' \exp[D_m(r')] I^{arm}_{1,m}(r') \Delta^{(c,m)}(r, r')\), ‘m’ being the last segment in the arm directly bonded to the articulation segment.

Hence, the density profile of the articulation segment is given as

\[
\rho_c(r) = \exp(\beta \mu_M) \exp[D_c(r)] [Ar(r)]^f. \tag{7.31}
\]
For the arm segments, initiator to the $I_2$ function is

$$I_{2,m}^{\text{arm}}(r) = \int dr' \exp[D_c(r')] [A(r')]^{f-1} \Delta^{(c,m)}(r, r'). \quad (7.32)$$

And,

$$I_{2,\alpha}^{\text{arm}}(r) = \int dr' \exp[D_{\alpha+1}(r')]I_{2,\alpha+1}^{\text{arm}}(r') \Delta^{(\alpha,\alpha+1)}(r, r'). \quad (7.33)$$

The $I_1$ function for the arm segments is

$$I_{1,1}^{\text{arm}}(r) = 1,$$

$$I_{1,\alpha}^{\text{arm}}(r) = \int dr' \exp[D_{\alpha-1}(r')]I_{1,\alpha-1}^{\text{arm}}(r') \Delta^{(\alpha-1,\alpha)}(r, r'). \quad (7.34)$$

Finally, the density profile of the arm segment ‘$\alpha$’ in terms of $I_1$ and $I_2$ functions is given as

$$\rho_{\alpha}(r) = \exp(\beta \mu_M) \exp[D_{\alpha}(r)]I_{1,\alpha}^{\text{arm}}(r)I_{2,\alpha}^{\text{arm}}(r). \quad (7.35)$$

This is physically depicted in fig. 7.2b.

Picard-type iteration method is applied to solve the set of eqs. 7.31 and 7.35 for the density profile of the articulation and the arm segments of the star polymer. For the systems considered in this work, the inhomogeneity is only in one dimension ($z$). All the numerical integrations are done using the trapezoidal rule.
7.3 Results and discussion

Modified iSAFT is applied to study the partitioning of the star polymer fluid between two confining surfaces. All the segments of the chains are athermal or the model only includes the entropic effects of polymer confinement and neglects the enthalpic effects. The two confining surfaces are impenetrable flat hard walls, hence the inhomogeneity is only in one dimension \( z \). Figure 7.4a shows the total segment density \( \rho(z) \) profiles of 3-arm star polymer fluid \( (m = 5) \) confined between two surfaces separated by \( H = 10 \sigma \), at different average packing fractions \( \eta_{avg} \) of the fluid in the confined space. The profiles are symmetric about the middle of the
confinement, hence the figure only shows the profiles near one of the confining surfaces. As for linear polymer chains, the star polymer chains also do not prefer to be near the surface since they lose their configurational entropy. Hence, the chains are depleted near the surface at lower packing fraction, $\eta_{avg} = 0.1$. After the depletion layer, the segment density profile becomes flat and reaches its bulk value ($\rho_{bulk}$) in the confinement. In the figure, the segment densities are normalized by their bulk values. When the number of chains in the confinement increases, for example at $\eta_{avg} = 0.3$ in the figure, the chains push each other and pack against the surface. This packing effect leads to enhancement of the polymer chains near the surface. The overall segment density profile is oscillatory in the vicinity of the surface, with 'σ' being the period of the oscillations. These oscillations die around $z = 3 \sigma$ and the profile becomes flat at its bulk value. The segment density profile at the intermediate packing fraction of 0.2 clearly shows the competition between the packing and configurational entropic effects. The figure also compares the results obtained from modified iSAFT with the simulation results of Yethiraj and Hall [264] and the results from the DFT approach followed by Malijevsky et. al. [268]. The results from modified iSAFT are in excellent agreement with the simulation results. At higher packing fractions of 0.2 and 0.3, the contact densities predicted from modified iSAFT are in better agreement with the simulation data than the DFT approach by Malijevsky et. al.

Even for the athermal linear polymer fluids, the segment density profiles are governed by the competition between the packing and configurational entropic effects.
Figure 7.4: (a) Total segment density profiles of the confined 3-arm star (m = 5) polymer fluid at $\eta_{avg} = 0.1$ ($\circ$), 0.2 ($\square$), and 0.3 ($\triangle$) from modified iSAFT (solid curves), DFT approach of Malijevsky et. al. [268] (dashed curves), and molecular simulations [264] (symbols). (b) Comparison of the total segment density profiles of the confined 21-segment linear (dashed curve) and 4-arm star (solid curve) polymer fluids at $\eta_{avg} = 0.3$. Symbols are the molecular simulation results for the star polymer fluid from Yethiraj and Hall [265].

Figure 7.4b compares the total segment density profiles of the 21-segment linear and 4-arm star (m = 5) polymer fluids confined between the two flat hard surfaces separated by $H = 10\sigma$, at the same packing fraction. The segment densities are normalized by their average values in the confinement. The profiles are similar for both star and linear polymer fluids with slight difference in their contact densities. The contact density is related to the pressure of the fluid at density equal to its bulk density in the confined space, $\beta P(\rho_{bulk}) = N\rho(0)$. Hence, the compressibility factor ($Z = \beta P/\rho_{bulk}$) of bulk star and linear polymer fluids with same number of segments in the chain are only slightly different at a given fluid density. This suggests that
Figure 7.5: (a) Comparison of the average end- (■) and mid-segments (▲) density profiles of the confined 21-segment linear (dashed curves) and 4-arm star (solid curves) polymer fluids at \( \eta_{\text{avg}} = 0.3 \). The black curves represent the end-segments while the gray curves represent the mid-segments density profiles. Symbols are the molecular simulation results for the star polymer fluid from Yethiraj and Hall [265]. (b) Comparison of the articulation segment (solid curve) and average arm segments (dashed curve) density profiles of the confined 4-arm star (m = 5) polymer fluid.

The volumetric properties of the bulk athermal polymers are not very sensitive to the details of molecular topology. The figure also compares the segment density profile of the star polymer obtained from modified iSAFT with the molecular simulation results from Yethiraj and Hall [265]. As shown in the figure, modified iSAFT is in excellent agreement with the simulation data.

Although the total segment density profile of the confined star and linear polymer fluids are similar, the distribution of the individual segments are quite different. For example, fig. 7.5a compares the average density profiles of the end- and the mid-segments of the star and linear polymers. Here, the mid-segments of the star polymer
Figure 7.6: Comparison of the total segment density profiles of the confined (a) 4-segment linear (dashed curves) and 3-arm star (solid curves) polymer fluids at $\eta_{\text{avg}} = 0.1$ (gray curves), and 0.3 (black curves), (b) 25-segment linear (dot-dashed curves), 4-arm star (dashed curves), and 3-arm star (solid curves) polymer fluids at $\eta_{\text{avg}} = 0.1$ (gray curves), and 0.3 (black curves). In fig. (b), the profiles of the 3-arm and 4-arm star polymer fluids almost overlap each other.

comprises the articulation segment and the segment in each arm directly bonded to it.

To test modified iSAFT, the results for star polymer are compared with the simulation results from Yethiraj and Hall [265]. The theoretical results are in agreement with the simulation results demonstrating the predictive capabilities of modified iSAFT. The conformations of both star and linear polymer chains have to constrained for the mid-segments of the chains to be near to the surface, hence the density of mid-segments near the surface is lower than that of the end-segments. However, the constraint is even severe in the case of the star polymer. Thus the average density of the mid-segments of the star polymer near the surface is considerably lower than
that of the linear polymer. The density of the mid-segments (for both linear and star polymer) at distances of 1 - 2σ are higher than that in the bulk. Hence, although the packing effects pushes the all the segments of the chains towards the surface, the conformational restrictions on the mid-segments prevent them from approaching it.

Figure 7.5b shows the average segment density profile of the articulation segment and the arm segments of the same 4-arm star polymer fluid (m = 5 at \( \eta_{\text{avg}} = 0.3 \) and \( H = 10 \sigma \)). Again, severe conformational constraint on the articulation segment of the chains leads to its depletion near the surface.

To further study the effects of molecular topology on confined (athermal) polymers, two cases are analyzed. The first case compares the segment density profiles of smaller 4-segment linear and 3-arm star (m = 1) polymer fluids while the second case compares the density profiles of larger 25-segment linear, 3-arm star (m = 8), and 4-arm star (m = 6) polymer fluids confined between two hard walls separated by \( H = 10 \sigma \) at average fluid packing fractions of 0.1 and 0.3. Figure 7.6a shows the total segment density profiles for 4-segment linear and 3-arm star polymers. The profiles are similar at both the packing fractions. This is the case even for star polymers with different number of arms as shown in fig. 7.6b for 25-segment linear, 3-arm star and 4-arm star polymers. Infact, the profiles for the 3-arm star and 4-arm star polymers almost overlap each other. Hence, the total segment density profiles of confined athermal polymers are not very sensitive to the molecular topology. However, the profiles of the individual segments depend upon the molecular topology as shown in fig. 7.7.
Figure 7.7: Comparison of the average end- (black curves) and mid-segments (gray curves) density profiles of confined (a) 4-segment linear (dashed curves) and 3-arm star (solid curves) polymer fluids at $\eta_{avg} = 0.1$, (b) 4-segment linear (dashed curves) and 3-arm star (solid curves) polymer fluids at $\eta_{avg} = 0.3$, (c) 25-segment linear (dot-dashed curves), 4-arm star (dashed curves) and 3-arm star (solid curves) polymer fluids at $\eta_{avg} = 0.1$, and (d) 25-segment linear (dot-dashed curves), 4-arm star (dashed curves) and 3-arm star (solid curves) polymer fluids at $\eta_{avg} = 0.3$.

Figures 7.7a and b compare the average end- and mid-segments density profiles of the 4-segment linear and 3-arm star polymers. For the star polymer with only one segment in the arms, the mid-segment comprises only the articulation segment and the
Figure 7.8: Compressibility factors of the bulk star polymer fluids. (a) 3-arm star polymers with \( m = 3 \) (•) and 5 (▲), and (b) 4-arm star polymers with \( m = 3 \) (•) and 5 (▲).

end-segments comprise all the arm segments. Density of the end-segments for both the molecular topologies are higher near the surface compared to the mid-segments. On the contrary, densities of the mid-segments are enhanced at \( z = 1 \sigma \). Both the end- and mid-segment densities of the linear polymer near the surface are higher than those of the 3-arm star polymer, due to higher conformational restriction on the star polymer to pack against the surface. This is also observed in figures 7.7c and d, where the average end- and mid-segments densities near the surface of both the 3-arm and 4-arm star polymers are lower than that of the linear polymer. Comparison of the end- and mid-segments density profile of the star polymer fluids themselves, shows that as the number of arms in the star polymer increases (keeping the total number of
segments the same) both the end- and mid-segment densities of the polymer decrease near the surface.

As mentioned earlier, the contact density of the confined polymer at the hard wall is related to the pressure or the compressibility factor of the polymer fluid at the bulk density in the confinement. To test the accuracy of modified iSAFT, we calculate the compressibility factor of star polymer fluids from their contact and bulk densities in the confined space and compare with the simulation data of Yethiraj and Hall [264]. Figures 7.8a and b shows the comparison for 3-arm and 4-arm star polymer fluids. Modified iSAFT is in excellent quantitative agreement with simulation results.

7.4 Conclusions

The formulation of modified iSAFT is extended to branched polymers. The theory is applicable to polymer chains with complex branched architectures and different blocks having different chemistry. To test the accuracy of the theory, it has been applied to study the microstructure of (athermal) star polymers confined between two planar surfaces, where the width of the confinement is of the order of molecular diameter. Like athermal linear polymers, the microstructure of confined star polymers is also governed by the competition between the packing and configurational entropic effects. At lower polymer concentrations, polymer chains are depleted near the confining surface due to loss in configurational entropy. On the contrary, at higher concentrations, packing effects enhances the polymer chains near the surface. Com-
parison of the total segment density profiles of the linear and star polymers with the same total number of segments shows that the two profiles are similar with slight difference in their contact densities. However, the distribution of the individual segments in the linear and star polymers is different. The density of the mid-segments of the star polymer near the surface is lower than that of the linear polymer due to conformational constraints. These constraints are highly severe on the articulation segment of the star polymer. These theoretical results show quantitative agreement with the results from molecular simulations.

The structure of two confined star polymers having different number of arms but same total number of segments, is also compared. Again the total density profiles of the two star polymers are similar, suggesting that the total segment density profiles of the confined athermal polymers are not very sensitive to the molecular architecture. However, the distribution of the individual segments is quite different. Both the end- and mid-segment densities of the star polymer near the surface decrease as the number of arms in the star polymer increases.
Chapter 8

Self Consistent Field Theory

This chapter introduces the general formulation of Self Consistent Field Theory (SCFT) and discusses the approximations made in the theory in comparison to modified iSAFT density functional theory. There are two basic differences. The continuous gaussian chain model is employed in SCFT and instead of using a particle-based approach, a field-based approach is used.

8.1  Ideal chain model: Continuous Gaussian chain

The first description in a theoretical description of a polymeric fluid is the model describing the statistical mechanics associated with the conformational states of a single polymer chain. In a single polymer chain, the bonding constraints and the associated potentials between the neighboring segments are referred to as short-range interferences. While the interactions between the segments that are separated by
large distances along the polymer chain are referred to as long-range interactions. In previous chapters, these short-range interactions were referred to as the chain connectivity while the long-range interferences were referred to as the excluded volume effects. Also shown in these chapters, it is convenient to separate the interactions responsible for short-range and long-range interferences. This separation produces polymer theories in which the statistical mechanics of single ideal chain models with only short-range interferences play a central role.

In modified iSAFT, the underlying ideal chain model is the freely jointed chain model. In this model, the bond vectors connecting successive segments are constrained to have a fixed bond length but the orientations of the bond vectors are distributed isotropically and independently. Probability distribution of the end-to-end vector of a freely jointed chain obeys the Gaussian distribution for a very long ideal chain. In addition, since any two non-overlapping subchains of an ideal freely jointed chain are statistically independent, the end-to-end vectors of any subchain obeys the Gaussian distribution as well. Hence, a coarse-graining approach can be employed by eliminating the information concerning the microscopic details, to describe the physical properties on large scales. Several segments of the chain can be grouped to form a coarse-grained segment of the coarse-grained chain. The successive segments of this coarse-grained chain are tethered by "spring potentials", as shown in fig. 8.1a, where the spring potential is given by the Gaussian distribution. Hence, this model is known as discrete Gaussian chain model.
Figure 8.1: (a) Schematic of the coarse-grained discrete Gaussian chain model with \( N+1 \) segments and \( N \) springs. The segment positions are denoted by \( r_0, r_1, ..., r_N \), and the bond vectors are denoted by \( b_1, b_2, ..., b_N \). (b) Schematic of the continuous Gaussian chain model. The configurations of the polymer chain are described by the \( r(s) \), where \( s \in [0, N] \) is a contour parameter.

The partition function of a single chain can be expressed as

\[
Z_0 = \int \! d r^{N+1} \exp \left[ -\beta U_0(r^{N+1}) \right], \tag{8.1}
\]

where \( r^{N+1} = (r_0, r_1, ..., r_N) \) denotes the set of \( N + 1 \) segment positions and \( U_0(r^{N+1}) \) is the potential energy associated with the particular configuration of the polymer chain. An alternative representation is the set of \( N \) bond vectors, \( b^N = (b_1, b_2, ..., b_N) \), where \( b_i = r_i - r_{i-1} \).

\[
Z_0 = V \int \! d b^N \exp \left[ -\beta U_0(b^N) \right], \tag{8.2}
\]

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where $V$ is the volume of the system and

$$U_0(b^N) = \sum_{i=1}^{N} h(|b_i|). \quad (8.3)$$

$h(x)$ is the spring potential between the adjacent segments along the polymer chain, given by

$$h(x) = \frac{3kT}{2b^2} x^2, \quad (8.4)$$

where the parameter $b$ is the root-mean-square length of a bond. Like, for free jointed chain, the distribution of the segments is an important property for discrete Gaussian chain. This is defined by the reduced distribution function, $p_0(r,j)$, which represents the probability density that a polymer chain with $j + 1$ segments has its end (the segment labeled as $j$) at position $r$. This is derived by means of a Chapman-Kolmogorov equation. Assuming knowledge of the probability density of the chain with one fewer segment, $p_0(r,j - 1)$,

$$p_0(r,j) = \int db_j \Phi(b_j; r - b_j)p_0(r - b_j, j - 1). \quad (8.5)$$

$\Phi(b_j; r - b_j)$ is the conditional probability density that the bond vector connecting particles $j$ and $j - 1$ assumes a value of $b_j$, given that the segment $j - 1$ was located at position, $r - b_j$. For discrete Gaussian chain, this conditional transition probability
is independent of both the segments indices and the starting position. Hence,

\[ \Phi(b_j; r - b_j) = \Phi(b_j) = \frac{\exp[-\beta h(|b_j|)]}{\int db_i \exp[-\beta h(|b_i|)]} = \left( \frac{3}{2\pi b^2} \right)^{3/2} \exp \left[ -\frac{3|b_j|^2}{2b^2} \right]. \]

(8.6)

The eqn. 8.5 is solved using Fourier transform and the boundary condition, \( p_0(r, 0) = \delta(r) \), to obtain

\[ p_0(R, N) = \left[ \frac{3}{2\pi Nb^2} \right]^{3/2} \exp \left[ -\frac{3|R|^2}{2Nb^2} \right], \]

(8.7)

where \( R \) is the end-to-end vector of the chain, \( R = r_N - r_0 \).

In SCFT, an elegant and particularly convenient continuous Gaussian chain model is employed. This model is the continuum limit of the discrete Gaussian chain model in which the polymer chain is viewed as a continuous, linearly elastic filament. The configuration of the chain is specified by a space curve \( r(s) \) where \( s \in [0, N] \), as shown in fig. 8.1b. The continuous variable \( s \) describes the locations of a segment along the backbone of the chain. The potential energy of the continuous Gaussian chain can be written as

\[ U_0[r] = \frac{3kT}{2b^2} \int_0^N ds \left| \frac{dr(s)}{ds} \right|^2, \]

(8.8)

while the partition function is given by

\[ Z_0 = \int Dr \exp(-\beta U_0[r]), \]

(8.9)
where $\int D\mathbf{r}$ denotes a functional integration. The potential energy is now a functional of the space curve $\mathbf{r}(s)$ and partition function is calculated as a functional integral over all the possible space curves. One approach to defining the functional integration is to discretize the continuous function $\mathbf{r}(s)$ by a set of $N_s + 1$ equally spaced contour points $(\mathbf{r}_0, \mathbf{r}_1, ..., \mathbf{r}_{N_s})$. Hence,

$$Z_0 \approx \prod_{j=0}^{N_s} \int d\mathbf{r}_j \exp \left( -\frac{3}{2b^2\Delta s} \sum_{i=1}^{N_s} |\mathbf{r}_{i-1} - \mathbf{r}_i|^2 \right), \quad (8.10)$$

where $b^2\Delta s$ is the mean-squared length of one of the $N_s$ bonds, and $\Delta s = N/N_s$ is the spacing between the contour points. The quality of the approximation improves as $N_s \rightarrow \infty$. Again, the Chapman-Kolmogorov equation is used to obtain the probability density distribution of the segments.

$$p_0(\mathbf{r}, s + \Delta s) = \int d(\Delta \mathbf{r}) \Phi(\Delta \mathbf{r}) p_0(\mathbf{r} - \Delta \mathbf{r}, s), \quad (8.11)$$

where

$$\Phi(\Delta \mathbf{r}) = \left( \frac{3}{2\pi b^2 \Delta s} \right)^{3/2} \exp \left( -\frac{3|\Delta \mathbf{r}|^2}{2b^2\Delta s} \right). \quad (8.12)$$

The Chapman-Kolmogorov integral equation (8.11) can be reduced to partial differential equations, which are referred to as Fokker-Planck equations by Taylor-expanding both sides of the equation in powers of $\Delta s$ and $\Delta \mathbf{r}$ and taking $\Delta s \rightarrow 0$.

$$\frac{\partial}{\partial s} p_0(\mathbf{r}, s) = \frac{b^2}{6} \nabla^2 p_0(\mathbf{r}, s). \quad (8.13)$$
Thus, the distribution probability density for a continuous Gaussian chain takes the form of a conventional diffusion equation with a diffusion coefficient given by \( b^2/6 \). This equation is solved to obtain the probability density, instead of the integral Chapman-Kolmogorov equations with the initial condition, \( p_0(r,0) = \delta(r) \). The final distribution is given by

\[
p_0(r,s) = \left( \frac{3}{2\pi b^2} \right)^{3/2} \exp\left( -\frac{3|\mathbf{r}|^2}{2b^2} \right).
\]  

(8.14)

In SCFT, the interaction potential of the surrounding polymer segments self consistently generate the potential field on the the single polymer chain. Hence, the theoretical formulation of a Gaussian chain in an external field is presented here. The microscopic density of a Gaussian chain is given by

\[
\hat{\rho}(\mathbf{r}) = \int_0^N ds \delta(\mathbf{r} - \mathbf{r}(s)).
\]  

(8.15)

Thus, the potential due to the external field \( w(\mathbf{r}) \) acting on the chain is given by

\[
\beta U_1[\mathbf{r},w] = \int d\mathbf{r}' w(\mathbf{r}') \hat{\rho}(\mathbf{r}).
\]  

(8.16)

The partition function of the chain is

\[
Z[w] = \int D\mathbf{r} \exp\left(-\beta U_0[\mathbf{r}] - \beta U_1[\mathbf{r},w]\right).
\]  

(8.17)
However, the quantity of interest is the ratio of the partition function of the chain in the presence of an external field to the one in absence of it,

\[ Q[w] = \frac{\int D\mathbf{r} \exp \left(-\beta U_0[\mathbf{r}] - \beta U_1[\mathbf{r}, w]\right)}{\int D\mathbf{r} \exp (-\beta U_0[\mathbf{r}])}. \]  

(8.18)

This can be further approximated as

\[ Q[w] \approx \frac{1}{V} \int d\mathbf{r}^{N+1} \left[ \exp(-\Delta s w(\mathbf{r}_{N})) \Phi(\mathbf{r}_{N} - \mathbf{r}_{N-1}) \exp(-\Delta s w(\mathbf{r}_{N-1})) \Phi(\mathbf{r}_{N-1} - \mathbf{r}_{N-2}) \ldots \exp(-\Delta s w(\mathbf{r}_1)) \Phi(\mathbf{r}_1 - \mathbf{r}_0) \exp(-\Delta s w(\mathbf{r}_0)) \right]. \]  

(8.19)

Or,

\[ Q[w] = \frac{1}{V} \int d\mathbf{r} q(\mathbf{r}, N; [w]) = \frac{1}{V} \int d\mathbf{r} q(\mathbf{r}, N - s; [w]) q(s, [w]), \]  

(8.20)

where

\[ q(\mathbf{r}, 0; [w]) = \exp(-\Delta s w(\mathbf{r})) \]  

(8.21)

\[ q(\mathbf{r}, s + \Delta s; [w]) = \exp(-\Delta s w(\mathbf{r})) \int d\mathbf{r}' \Phi(\mathbf{r} - \mathbf{r}') q(\mathbf{r}', s; [w]) \]

Physically, \( q(\mathbf{r}, s; [w]) \) represents the statistical weight for a chain of length ‘s’ with its end at position \( \mathbf{r} \). This is similar to the probability density, \( p_0(\mathbf{r}, s) \) in the absence of the external field. Using this analogy, eqn. 8.21 is a Chapman-Kolmogorov equation in the presence of an external field, and the resulting Fokker-Planck equation is given
by
\[
\frac{\partial}{\partial s} q(r, s; [w]) = \frac{b^2}{6} \nabla^2 q(r, s; [w]) - w(r) q(r, s; [w]),
\]
with the initial condition, \( q(r, 0; [w]) = 1 \). The average segment density of the single chain in presence of the external field is given by

\[
\rho(r; [w]) = \langle \tilde{\rho}(r) \rangle_{[w]} = \frac{\int Dr \tilde{\rho}(r) \exp(-\beta U_0[r] - \beta U_1[r, w])}{\int Dr \exp(-\beta U_0[r] - \beta U_1[r, w])}
= \frac{1}{VQ[w]} \int_0^N ds \, q(r, N-s; [w]) q(r, s; [w]).
\]  

We can also derive the density of the segment located at the contour position, \( s \),

\[
\rho(r, s; [w]) = \frac{1}{VQ[w]} q(r, N-s; [w]) q(r, s; [w]).
\]  

These results (eqs. 8.20 and 8.23) are for linear homopolymers. The derivation can be generalized to a variety of chain structures, as shown in detail in ref. [269].

### 8.2 From particles to fields

The preliminary step in a field-based approach, such as SCFT, is to convert the standard particle-based model to a statistical field theory. This particle-to-field transformation technique for a homopolymer in an explicit solvent is discussed here in detail. The intramolecular long-range interferences and inter-molecular interactions between the segments of the polymer chains as well as the interactions with the sol-
vent molecules are parameterized with a Flory 'χ' parameter. The solution is assumed to be locally incompressible.

In the canonical ensemble, the solution consists of a mixture of $n_s$ solvent molecules and $n_P$ polymer molecules in a system of fixed volume $V$ and temperature $T$. Each polymer chain occupies a volume $v_0 N$, where $v_0$ is the volume of a statistical segment and its conformational properties are described by the continuous Gaussian chain model. The solvent molecules also occupy the same volume, $v_0$. Thus the total number density of the solution, $\rho_0 = 1/v_0$. While, the microscopic densities of the polymer segments and solvent are defined, respectively, by

$$\hat{\rho}_P(r) = \sum_{j=1}^{n_P} \int_0^N ds \, \delta(r - r_j(s)), \quad (8.25)$$

$$\hat{\rho}_S(r) = \sum_{j=1}^{n_S} \delta(r - r_j). \quad (8.26)$$

By analogy with the Flory-Huggins lattice theory, the interaction energy between the solvent molecules and the polymer segments is described by

$$\beta U_1[r^{ns+n_PN}] = v_0 \chi_{PS} \int dr \hat{\rho}_P(r) \hat{\rho}_S(r) \quad (8.27)$$

This Flory parameter $\chi_{PS}$ describes the energetic strength of local contacts between solvent molecules and polymer segments, relative to solvent-solvent and polymer-
polymer contacts. The partition function is given by

\[ Z_C(n_S, n_P, V, T) = \frac{1}{n_S!n_P!(\lambda T)^{n_S+n_P N}} \prod_{j=1}^{n_P} \int D\mathbf{r}_j \prod_{k=1}^{n_S} \int d\mathbf{r}_k \exp\left(-\beta U_0[r^{n_P N}] - \beta U_1[r^{n_S+n_P N}]\right) \delta[\mathbf{\rho}_P + \mathbf{\rho}_S - \rho_0], \quad (8.28) \]

where \( \delta[\mathbf{\rho}_P + \mathbf{\rho}_S - \rho_0] \) imposes the local incompressibility constraint. Noting this constraint, the interaction potential can be re-written as

\[ \beta U_1[r^{n_S+n_P N}] = \frac{1}{4} v_0 \chi_{PS} \int d\mathbf{r} (\rho_0^2 - [\mathbf{\rho}_P(\mathbf{r}) - \mathbf{\rho}_S(\mathbf{r})]^2). \quad (8.29) \]

Using Hubbard-Stratonovich transformation [269] gives

\[ e^{-\beta U_1} = e^{-\chi_{PS}(n_S+n_P N)/4} \int D\mathbf{w}_- \exp\left(\int d\mathbf{r} (\mathbf{\rho}_P(\mathbf{r}) - \mathbf{\rho}_S(\mathbf{r})) \mathbf{w}_- - (\rho_0/\chi_{PS})\mathbf{w}_-^2\right), \quad (8.30) \]

and from the definition of dirac delta functional

\[ \delta[\mathbf{\rho}_P + \mathbf{\rho}_S - \rho_0] = \int D\mathbf{w}_+ \exp \left(-i \int d\mathbf{r} [\mathbf{\rho}_P + \mathbf{\rho}_S - \rho_0] \mathbf{w}_+\right). \quad (8.31) \]

Here, two auxiliary fields, \( \mathbf{w}_+ \) and \( \mathbf{w}_- \), have been introduced to decouple the interactions between the solvent molecules and polymer segments. These can be viewed as fluctuating chemical potential fields. Field \( \mathbf{w}_+ \) represents the total chemical potential while \( \mathbf{w}_- \) represents the exchange chemical potential. Using these transformations,
the partition function can be written just in the terms of the fields as

$$Z_C(n_s, n_P, V, T) = Z_0 \int Dw_+ \int Dw_- \exp(-H[w_+, w_-]),$$  \hspace{1cm} (8.32)$$

where the effective Hamiltonian

$$H[w_+, w_-] = \int dr \left[ (\rho_0 / \chi_{PS})w_-^2 - i\rho_0 w_- \right] - n_P \ln Q_P[iw_+ - w_-] - n_S \ln Q_S[iw_+ + w_-].$$  \hspace{1cm} (8.33)$$

$Z_0$ represents the partition function of an ideal gas of $n_S$ solvent and $n_P$ polymer molecules in volume $V$, $Q_P$ is the normalized single-chain partition function of a polymer molecule in the complex external field $[iw_+ - w_-]$, given by eq. 8.20, and $Q_S$ is the normalized partition function of a single solvent molecule in the complex external field $[iw_+ + w_-]$, given by

$$Q_S[iw_+ + w_-] = \frac{1}{V} \int dr \exp(-[iw_+(r) + w_-(r)]).$$  \hspace{1cm} (8.34)$$

Thus, the particle-field transformation is complete. The average segment density of the polymer is given as, $(\hat{\rho}_P(r))_{w_+, w_-}$, where

$$\hat{\rho}_P(r; [iw_+ - w_-]) = -n_P \frac{\delta \ln Q_P[iw_+ - w_-]}{\delta [iw_+ - w_-]},$$  \hspace{1cm} (8.35)$$
and the average solvent density is given as, \( \langle \hat{\rho}_S(r) \rangle_{w^+, \ldots} \), where

\[
\hat{\rho}_S(r; [i\nu^+ + \nu^-]) = -n_S \frac{\delta \ln Q_S[i\nu^+ + \nu^-]}{\delta [i\nu^+ + \nu^-]}. \tag{8.36}
\]

Clearly, there are two important aspects for particle-to-field transformation. One is the introduction of the auxiliary chemical potential 'w' fields that serve to decouple the interaction among the molecules, replacing them with the interactions between each molecule and the field variables. The second aspect and the advantage of such a transformation is that the resulting field theory sidesteps the many-body problem - only the partition function of the \( Q[w] \) of a single polymer or solvent molecule experiencing the auxiliary fields need to be computed.

### 8.3 Formalism of self-consistent field theory

The field-theoretic models express the relevant partition function as a functional integral over one or more chemical potential fields, \( w(r) \),

\[
Z = \int Dw \exp(-H[w]). \tag{8.37}
\]

The observable properties are calculated as an ensemble average,

\[
\langle G[w] \rangle = Z^{-1} \int Dw G[w] \exp(-H[w]). \tag{8.38}
\]
Thus, the evaluation of the free energies and their derivatives require computing a functional integral given by eqn. 8.37 while the observable properties like the fluid structure require computing two functional integrals. In practice, for non-trivial models of three-dimensional fluids, none of these functional integrals can be evaluated in closed form. Hence, analytical approximations have been developed.

SCFT employs the most successful approximation technique known as the mean field approximation. Mean field approximation assumes that a single field configuration \( w^*(r) \) dominates the field integrals in eqs. 8.37 and 8.38. This field configuration known as the mean-field or self-consistent field, is obtained by demanding that \( H[w] \) be stationary w.r.t. variations in \( w(r) \), or

\[
\frac{\delta H[w]}{\delta w(r)} \bigg|_{w=w^*} = 0. \tag{8.39}
\]

Thus,

\[
Z \approx \exp(-H[w^*]), \tag{8.40}
\]

and

\[
\langle G[w] \rangle \approx G[w^*]. \tag{8.41}
\]

Thus, the mean field approximation neglects all “field fluctuations”. Apparently, this is a good approximation for concentrated solution or melts of high molecular wight polymers [250]. Since the effective co-ordination number of the segments in polymer melts grows as the square root of the molecular weight, the field fluctuations are
This completes the general formalism of SCFT where the polymer molecules are represented as space curves which are modeled as continuous Gaussian chains. The first step is defining the interactions between the molecules. The hard-core repulsions are crudely imposed by the incompressibility approximation while the long-range attractions are defined in terms of the Flory-Huggins $\chi$ parameter. A particle-to-field transformation follows which decouples the interactions between the molecules, replacing them with the interactions between each molecule and external fields. These fields are then obtained self-consistently with the average segment densities (microstructure) by imposing the mean-field approximation.

## 8.4 Approximations in SCFT

Previous sections introduce the formalism of SCFT. This section concludes the chapter by recapping the approximations in SCFT:

- The polymer molecules are modeled as continuous Gaussian curves. This coarse-graining suppresses all the effects related to the atomic details. Hence, the segment level information of the polymer structure and short-range effects are lost in this coarse-grained approach.

- The short-range repulsive interactions are crudely approximated by the incompressibility approximation. The incompressibility approximation neglects the
volume change on mixing, and leads to deficiencies similar to in lattice-based theories. Hence, the effect of pressure on the phase behavior of polymeric systems cannot be studied.

- The long-range attractive interactions are treated by simple contact forces similar to as in lattice-based theories. Hence, the total interaction is proportional to number of segment-segment contacts, where the proportionality constant is the Flory-Huggins $\chi$ parameter. The definition of $\chi$ is generally a convenient functional fit to describe the experimental phase behavior of the polymeric systems. These fitting approaches introduces an empirical temperature or even composition dependence of the $\chi$ parameter.

- The mean-field approximations in SCFT neglects the fluctuation effects. This approximation is incorrect for polymer solutions in the dilute or semi-dilute regimes, polymer blends near a critical point or second-order phase transition, microemulsion and micellar phases of surfactants, block copolymers near order-disorder transition, and polyelectrolyte solutions in various concentration regimes.
Chapter 9

Concluding Remarks

This dissertation presents the development of molecular models to predict the phase behavior and microstructure of bulk and inhomogeneous polymer systems. Based on Wertheim's perturbation theory (TPT1), the models expand the range of concentrations, chain structure, and chemical nature of polymer systems over which their thermodynamics and microstructure can be theoretically predicted with reasonable accuracy.

For bulk polymeric systems, a new equation of state (EOS) called SAFT-D is developed that predicts the phase behavior accurately over the whole range of polymer concentrations. For long chain alkanes, the EOS gives better estimates of the liquid densities, and critical points. The EOS improves the prediction of the phase behavior of asymmetric mixtures of long and short chain alkanes in comparison to the previous EOSs based on TPT1. The improvement is significant especially near the critical region. However, SAFT-D is not able to model low molecular weight components
such as methane with m less than 2. A possible solution to this problem is to start with a fused dimer as the reference fluid. Further developments include extending SAFT-D to copolymers, and investigating the effect of polydispersity in chain length and comonomer content on the phase behavior of these systems.

For inhomogeneous polymeric systems, a new density functional theory (DFT) called modified iSAFT is developed. Treating the polyatomic system as a mixture of associating spheres in limit of complete association, the free energy functional is derived by extending TPT1. This allows one to write the free energy functional in terms of the segment densities, leading to a segment-based DFT. Thus, the theory is easier to implement and computationally cheaper than other DFTs based on molecular densities. Furthermore, in the limit of ideal polymer chains, modified iSAFT gives the exact segment density profile and the equilibrium free energy of these ideal polymer chains (in an external field) as a function of only the segment densities. The rigor and general segment-based formulation of the theory makes it in general applicable to a range of heteronuclear as well as branched (inhomogeneous) polymer systems with advanced segment-segment and segment-surface interactions. The model is validated for heteronuclear polymers by applying it to predict the adsorption of model lipids and multi-block copolymers at a surface, and comparing the results with molecular simulations. For branched polymers, the validation is done by comparisons with molecular simulation results for the adsorption of star polymers on a surface.

A preliminary calculation for the self-assembly of lipids in aqueous medium to form
bilayers, shows the applicability of modified iSAFT for future work on self assembly of surfactant-oil-water systems and biopolymers.

In addition to the validation of modified iSAFT, two specific problems have been rigorously analyzed. First problem concerns the self-assembly of symmetric diblock copolymers to form lamellar microstructures. In bulk melts, symmetric diblock copolymers undergo order disorder transition (ODT) from a disordered homogeneous to an ordered lamellar phase as the difference in the physiochemical properties of its two blocks increases. This lamellar morphology is investigated using modified iSAFT. In comparison to previous theoretical approaches using self consistent field theory (SCFT), modified iSAFT accurately predicts the lamellar structure and the interface between two lamellae. Diblock copolymers have potential applications in development of the next generation of sub micron scale electronics and optical devices. These applications involve thin films of copolymers confined between selective surfaces. Hence, modified iSAFT is also applied to investigate the effect of confinement on the ordered lamellar phases of symmetric diblock copolymers. Again, in comparison to SCFT, modified iSAFT includes compressibility and segment-level effects which affect the relative stabilities of different lamellar phases. Future work on this area will involve more complex morphologies of block copolymers, depicted in fig. 1.1.

The second problem is the application of modified iSAFT to tethered/grafted polymers. Grafted polymers have several industrial applications in colloid stabiliza-
tion, adhesives, lubricants, modification of surface hydrophobicity, and microfluidic devices. Two important aspects of grafted polymers, namely the structure of monolayers formed by the grafted polymers and the force of interaction between two such monolayers, are harnessed in all their applications. Modified iSAFT accurately predicts the structure of the monolayers in the absence/presence of free polymer solvent. Then, the force of interaction between two monolayers is calculated. In particular, the case where the segment sizes of the free and grafted polymers are different is considered, which cannot be investigated with the previous theoretical approaches using SCFT. The force can be either purely repulsive or have an attractive minimum depending upon the relative chain lengths of free \((N_f)\) and grafted \((N_g)\) polymers. The attractive minimum is observed only when the ratio, \(\alpha = N_f/N_g\), is greater than a critical value. A scaling relation for the critical values of \(\alpha\) is proposed. In all these cases, polymers are grafted to a flat surface. With recent applications of polymer grafted nano-particles in nano-composites, the curvature of the grafting particles will come into play. Hence, future developments require implementation of modified iSAFT in 2/3 dimensions to account for the curvature effects.
Bibliography


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