INFORMATION TO USERS

This manuscript has been reproduced from the microfilm master. UMI films the text directly from the original or copy submitted. Thus, some thesis and dissertation copies are in typewriter face, while others may be from any type of computer printer.

The quality of this reproduction is dependent upon the quality of the copy submitted. Broken or indistinct print, colored or poor quality illustrations and photographs, print bleedthrough, substandard margins, and improper alignment can adversely affect reproduction.

In the unlikely event that the author did not send UMI a complete manuscript and there are missing pages, these will be noted. Also, if unauthorized copyright material had to be removed, a note will indicate the deletion.

Oversize materials (e.g., maps, drawings, charts) are reproduced by sectioning the original, beginning at the upper left-hand corner and continuing from left to right in equal sections with small overlaps. Each original is also photographed in one exposure and is included in reduced form at the back of the book.

Photographs included in the original manuscript have been reproduced xerographically in this copy. Higher quality 6” x 9” black and white photographic prints are available for any photographs or illustrations appearing in this copy for an additional charge. Contact UMI directly to order.

UMI

A Bell & Howell Information Company
300 North Zeeb Road, Ann Arbor MI 48106-1346 USA
313/761-4700 800/521-0600
RICE UNIVERSITY

Associating Fluids near Solid Surfaces

by

Chad J. Segura

A THESIS SUBMITTED
IN PARTIAL FULFILLMENT OF THE
REQUIREMENTS FOR THE DEGREE

Doctor of Philosophy

APPROVED, THESIS COMMITTEE:

Walter G. Chapman, Chair
Associate Professor of Chemical Engineering

George J. Hirasaki
Professor of Chemical Engineering

Gustavo E. Scuseria
Professor of Chemistry

Houston, Texas

December, 1997
Abstract

Associating Fluids near Solid Surfaces

by

Chad James Segura

The properties of fluids near interfaces, in particular, the fluid-solid interfaces on which this work is concentrated, are important in many processes, such as: wettability as related to oil recovery and environmental cleanup, biochemical separation, biocompatibility of materials, membrane separation, adsorption in porous solids and micro- or nanomanufacturing of thin films. However, little of the past simulation and theoretical work in the field has considered associating fluids.

In this work we perform Metropolis Monte Carlo computer simulations for one-sited (dimerizing), two-sited (linear chain forming), and four-sited (cluster forming) hard spheres against hard, smooth walls. Reported are results for density and fraction of monomers (which determines the change in Helmholtz free energy due to association according to Wertheim's theory) versus distance from the surface. Also computed are adsorption and for the four-site fluid, orientation, cluster size, and fraction of sites bonded as functions of distance from the surfaces. We also consider binary mixtures and an associating fluid near active surfaces.

Except for orientation and cluster size, results are compared (favorably, in general) against a new density functional theory, which combines elements of the Tarazona density functional for hard spheres and Wertheim's theory of association. This dissertation concludes with ideas for further work in the area.
Acknowledgments

To the members of my committee, especially Walter G. Chapman (who showed much patience with me), for their technical and financial support;

To colleagues Alejandro Garcia, Victor Perez, Mario Llano Restrepo and Dhananjay Ghonasgi, who made it a lot of fun to be in the office (especially Dhananjay, who helped me in my initial forays into Monte Carlo modeling);

To Keshawa P. Shukla, who shared his knowledge of density functional theory with me and wrote the Henderson-Plischke code;

To Frank van Swol, who lent valuable criticism to our density functional theory and told me to not lose sight of the science within the engineering, and Jacob Israelachvilli, for his insight into experimental systems;

To Eduard Vakarin, for his integral equation theory results and e-mail conversations;

To the Petroleum Research Fund, administered by the American Chemical Society, and the Robert A. Welch Foundation for financial support of this work, and to IBM for an equipment grant;

To my parents, Joseph Dulies and Gertrude Landry Segura, for my existence and for many of my values;

And most importantly, to my wife, Linda Lucita Thompson, who wholeheartedly supported this crazy idea of mine of returning to school for a Ph.D.
# Table of Contents

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0 Introduction</td>
<td>1</td>
</tr>
<tr>
<td>2.0 Association and Wertheim's Theory</td>
<td>7</td>
</tr>
<tr>
<td>3.0 Statistical Mechanical Theories of Inhomogeneous Fluids</td>
<td>16</td>
</tr>
<tr>
<td>4.0 The Associating M-site Hard Sphere Fluid against a Hard Wall</td>
<td>27</td>
</tr>
<tr>
<td>4.1 Introduction</td>
<td></td>
</tr>
<tr>
<td>4.2 Computer simulations</td>
<td></td>
</tr>
<tr>
<td>4.3 Theory</td>
<td></td>
</tr>
<tr>
<td>4.4 Results and Discussion</td>
<td></td>
</tr>
<tr>
<td>4.5 Conclusions</td>
<td></td>
</tr>
<tr>
<td>5.0 The Associating 4-site Hard Sphere Fluid</td>
<td>65</td>
</tr>
<tr>
<td>5.1 Introduction</td>
<td></td>
</tr>
<tr>
<td>5.2 Computer simulations</td>
<td></td>
</tr>
<tr>
<td>5.3 Theory</td>
<td></td>
</tr>
<tr>
<td>5.4 Results and Discussion</td>
<td></td>
</tr>
<tr>
<td>5.5 Conclusions</td>
<td></td>
</tr>
<tr>
<td>6.0 The Binary Associating Mixture against a Hard Wall</td>
<td>111</td>
</tr>
<tr>
<td>6.1 Introduction</td>
<td></td>
</tr>
<tr>
<td>6.2 Computer simulations</td>
<td></td>
</tr>
<tr>
<td>6.3 Theory</td>
<td></td>
</tr>
<tr>
<td>6.4 Results and Discussion</td>
<td></td>
</tr>
<tr>
<td>6.5 Conclusions</td>
<td></td>
</tr>
<tr>
<td>7.0 The Associating 4-site Hard Sphere Fluid near an Active Surface</td>
<td>141</td>
</tr>
<tr>
<td>7.1 Introduction</td>
<td></td>
</tr>
<tr>
<td>7.2 Computer simulations</td>
<td></td>
</tr>
<tr>
<td>7.3 Theory</td>
<td></td>
</tr>
<tr>
<td>8.0 Future Work</td>
<td>161</td>
</tr>
<tr>
<td>9.0 References</td>
<td>164</td>
</tr>
</tbody>
</table>
1. Introduction

Understanding the behavior of fluids at interfaces is the goal of much theoretical and applied research today [1-3]. Many industrial processes rely on the application of this knowledge. Despite the need for a molecular understanding of interfacial properties, only recently have simple, accurate theories been developed for even simple fluids [3]. Because of the necessity to match bulk properties, interfacial statistical mechanics has lagged theories for bulk fluids. With the recent successes of interfacial theories for simple fluids and with the advent of bulk theories for complex fluids, there has been a renewed interest in complex fluids in the interfacial region. Still, relatively few theoretical studies have included the interfacial phenomena of complex fluids such as electrolytes, polymers and associating fluids (AFs).

Associating or hydrogen bonding forces are one of the least understood of all molecular forces. Association, through strong short-range forces, gives empirical spectroscopic evidence of formation of a new molecule when several molecules of one molecular species are present together. Thus, the magnitude of the association energy, which forms relatively long-lived molecular clusters, is generally at the level of physical interactions. Therefore, association has a large effect on physical properties [4], which are important to understand due to the ubiquitous nature of these materials, especially of water.

Although associating fluids have traditionally been difficult to model, significant progress has been made in this area in recent years. Ghonasgi and Chapman [5] and Chapter 2 below briefly review theories for associating fluids in the bulk. Of the various methods for dealing with associating fluids in the bulk, we are most interested in Wertheim's theory [6] because of its relative simplicity and its high accuracy in matching
computer simulation experiments. Its result is an equation relating the change in Helmholtz free energy due to association to the fraction of unbonded molecules. Wertheim's theory accurately predicts the thermodynamic properties of hard sphere associating fluids in the bulk with 1, 2, or 4 anisotropic bonding sites per sphere [5-10]. Our goal is to take this successful theory for association of bulk fluids and adapt it toward understanding associating fluids at interfaces. The material in this thesis deals primarily with local surface properties of fluid-solid interfaces.

Surface properties can be considered to be either gross or local. For instance surface tension and adsorption would be gross surface properties of a fluid. On the other hand, local properties deal with the microscopic peculiarities of the transition region between the bulk of one phase and the surface between two phases [1]. An example would be determining molecular density of a fluid as a function of distance from its interface with a solid [11].

The subject of research in interfacial forces has a very long history [12]. Trying to explain these interfacial phenomena in terms of forces between molecules goes back to the eighteenth century. By the late nineteenth century, a purely mechanical treatment led to a simple, but very limited model. One of the major assumptions of the simple mechanical model was the stationarity of the molecules. With the development of classical thermodynamics between 1824 and 1860, and the kinetic theory of matter post 1840, this assumption could be eliminated. The work of J. Willard Gibbs led to equations for gross surface properties which used experimentally observable macroscopic properties. In the 1890's and in the early part of this century, van der Waals used a quasi-thermodynamic approach to try to understand the surface in terms of local thermodynamic functions without using statistical thermodynamics. His mean field approximations are still used in various guises in both homogeneous and inhomogeneous fluid thermodynamic studies.

These methods, although useful, stop short of illuminating what is happening at the molecular level. For this, statistical mechanical methods are required. There is a vast
literature on statistical mechanics. Rather than make an attempt at introducing the reader to it and falling well short of the goal, we will assume the reader owns a working knowledge of "stat mech." Basic references of statistical mechanics include [13-15]. For general reviews of the statistical mechanics of fluids near interfaces see [3, 13-16].

The literature in the area of applying statistical mechanics to inhomogeneous fluids near surfaces begins in the 1940's. Fisher [17] contains several references to work in this area and has an exposition on early work in the field from a Russian point of view. However, his emphasis, by far, is on vapor-liquid surfaces rather than on the local surface properties of fluid-solid surfaces, on which this work is focused. Modern approaches to inhomogeneous fluid study are generally based on integral equation or density functional theories. Reviews of previous work in these two classes of theories can be found in [3].

A plethora of methods exist for determining gross surface properties [1]. Although physical experimental methods for studying surfaces on the molecular level exist and are improving [18-20], they are expensive and suitable for only small numbers of tests. Results are generally qualitative or they quantitatively miss important structural details [21]. For formulating and testing our theory, we run computer simulation experiments, where one can more simply isolate the effects of a change in a single parameter. A short list of references for past simulation work for solid-simple fluid interfacial phenomena could include the hard sphere [22-26], hard cylinder [27], Lennard-Jones [28-30], Stockmayer [31], and hard chain [32-34] potential models. See [3, 15] for reviews and references.

The above potentials can be considered as simple models of simple fluids at interfaces. As for associating fluids at interfaces, relatively little theoretical work has been done. Certainly, there has been a fair amount of work published using partial charge models. However, these are set up for specific materials with as accurate as available interaction potentials and are much less conducive toward generating general theories. Some relatively recent work in this area include studies of water [35, 36] and methanol
Vossen and Forstmann [35] calculated the structure of liquid water in contact with a planar wall using the central force model, which models water as a 2:1 binary mixture of hydrogen and oxygen atoms with partial charges. Their integral equation results gave reasonable agreement against simulations for dielectric constant and pair distribution function for water at room temperature. Lee and Rossky [36] investigated, by way of molecular dynamics simulations, the structure and dynamics of liquid water at three types of solid surfaces: flat hydrophobic, rough hydrophobic, and hydrophilic. They found that the two hydrophobic surfaces behaved essentially the same. For the hydrophilic wall, surface activity was stronger than the bulk interaction between the molecules. In all cases, noticeable structural perturbations extended to no more than 2 or 3 molecular layers from the wall. (A careful reader of this dissertation will note that these two latter conclusions of Lee and Rossky agree qualitatively with our results in Chapter 5 at moderate densities). They reviewed research in this area and gave extensive references. Matsumoto and Kataoka [37] studied condensation and evaporation processes at a liquid surface of methanol using molecular dynamics simulations.

Research on simple models of inhomogeneous associating fluids (IAFs) has focused on two approaches, those of Wertheim [6] and Stell et al. [38-40], that have been successful in the bulk. The latter was developed for spherically symmetric AFs [38, 41] and uses the standard Ornstein-Zernike (OZ) equation with the closure adjusted for association [42]. Wertheim's theory, originally constructed for molecules with highly directional association sites, uses a fugacity expansion based on two densities: those of monomers and of the total number density.

In the past few years many papers (for example, [43-49]) have been published on the behavior of simple models of nonuniform AFs. Although they are simple models, they retain many of the essential characteristic features of real fluids and yet are simple enough for fairly general, yet accurate theories to be presented. These models can serve as references for more realistic models as complexity is added.
Many of these recent studies used integral equation (IE) theory at the singlet level [44, 45, 50, 51] to study dimerizing Cummings-Stell model [38, 41] hard spheres (or modifications thereof, [44, 45, 52]) against a hard wall. Singlet theories give at least qualitative results for density profiles but are nonetheless not very successful very close to the wall, especially at higher densities [44, 45, 52]. Henderson et. al. [43] used nonuniform Percus-Yevick (PY) theory with a PY closure, a pair theory, to successfully represent the density profile of a dimerizing fluid, but the method is numerically highly intensive [43]. We discuss integral equation theory, in general, briefly in Chapter 3 and further discuss this class of methods for IAFs in Chapter 4.

Our approach, in contrast, uses free energy density functional theory [3, 53] for a model of hard spheres with highly directional square-well sites placed on the hard core surface. Although the Cummings-Stell model is useful for spherically symmetric chemical association, the models in the following chapters include an orientation dependence that is characteristic of hydrogen bonding interactions. The accuracy of the method and speed of calculation make the free energy density functional theory more suitable for direct engineering application than integral equation theory. Also, Wertheim's first order perturbation theory is already written in the form of an association free energy functional [6, 9].

Kierlik and Rosinberg (KR) [54-57] developed a perturbational free energy density functional (DF) approach applicable to inhomogeneous fluids consisting of fully associating nonoverlapping hard spheres (i.e., tangent chains) by applying Wertheim's theory for polymerization [9, 58]. Implementation and solution can be rather difficult, however. Since, we would like to look at many different types of systems fairly quickly, we develop a simpler, but adequate DF theory. Also, the KR DF theory for AFs regards a polyatomic fluid as the complete-association limit of a model of associating particles. Thus, one sets the chain size and the number of chains in the implementation. In contrast, in our approach chains (and clusters) form as a result of the extent of association, which is
a function of temperature. We discuss the KR DF theory in further detail in the introduction of Chapter 4.

Certainly, our models are not realistic ones. However, by starting with hard spheres we can demonstrate a method which can be extended to models with long-range attractions and multipolar interactions. We demonstrate the accuracy of the method by comparing against computer simulations. Two other simulation studies [59, 60] for inhomogeneous fluids with the association potential used in this paper were reported in the same year in which we began to report our results. However, these two studies were for Lennard-Jones (LJ) fluids. These fluids, more complex than those studied here, and with a nominally more realistic potential, are too complex for an initial theoretical study.

The next chapter discusses theories of association, especially Wertheim's theory. Following that is a discussion on density functional theory, a powerful theory for inhomogeneous fluids and one of which we use to get results. The next chapter is our general theory for pure hard sphere fluids with 1 to 6 sites per molecule. A comparison is made to simulations for the one and two-site fluids for density profile, adsorption and fraction of monomers. In Chapter 5 our theory is compared for the 4-site fluid against a hard wall in a similar manner to Chapter 4. In addition, for this 4-site fluid, there are additional simulation results for cluster size, orientation and fraction of molecules bonded at one, two, three, or four sites. The final results indicate a theory that accurately predicts thermodynamic properties and structure of associating hard sphere fluids near hard, smooth walls under a wide range of conditions. The theory requires two to three orders of magnitude less computer CPU time to run than the simulations. The next two chapters give theory and simulation results for systems of simple binary associating mixtures and for an associating fluid near a hard wall which also has associating sites. We close with some comments on future work and a list of references.
2. Association and Wertheim's Theory

2.1 Association

The thermodynamic reference fluid is the ideal gas [61]. There is no interaction between the molecules. Exact thermodynamic relations can be easily calculated for the ideal gas using statistical mechanics. Most real fluids do have intermolecular interactions. At low densities, the average molecular separation is large compared to the range of interaction of the molecules; therefore, the molecules behave fairly independently of each other [62]. The behavior of these low density fluids can therefore be approximated by ideal gas relationships. At higher densities, knowledge of the nature of the intermolecular forces (and sometimes intramolecular forces) must be applied to determine the deviation from ideal gas behavior.

Some [61, 62] intermolecular forces are:

1. Electrostatic forces between charged particles and between permanent dipoles, quadrupoles, and higher multipoles. These are long-range interactions.

2. Induced forces between a permanent dipole and an induced dipole. Generally a long range force.

3. Forces of long range attraction (dispersion or induced dipole-dipole) and short range repulsion (short-range valence) between nonpolar molecules.

4. Specific (chemical) forces leading to association and complex (such as electron donor-acceptor complexes) formation; i.e., loose chemical bonds of short to intermediate range of interaction.
Real fluids can consist of molecules which show any combination of these forces. Hydrogen bonding (we will use the terms association and hydrogen bonding interchangeably) is the most common example of the fourth force. While the normal valence of hydrogen is unity, for some compounds it behaves as if it is bivalent. This occurs for molecules containing hydrogen linked to an electronegative atom. These molecules tend to associate with each other and to solvate with other molecules with accessible electronegative atoms. These bonds are an order of magnitude lower in strength than covalent bonds. However, they are strong enough to exert a large effect on physical properties.

Experimental evidence for the formation of hydrogen bonds can be seen as [61]:

1. Distances between the neighboring atoms of the two functional groups \( (X-H-Y) \) in hydrogen bonds are substantially smaller than the sum of their van der Waals radii.

2. Spectroscopic data show that the \( X-H \) stretching modes are shifted toward lower frequencies during hydrogen bonding.

3. Dipole moments are larger than those expected from vectorial addition

4. Nuclear-magnetic-resonance (NMR) chemical shifts of protons in hydrogen bonds are substantially smaller than those seen in the corresponding isolated molecules. There are reduced electron densities at protons participating in hydrogen bonding.

These four effects are not as strong in isolated dimers as they are in other hydrogen-bonded materials, indicating the importance of networks of hydrogen bonds. Because of the complex forces, associating materials such as water, hydrofluoric acid,
ammonia, and some proteins, ketones, alcohols and carboxylic acids exhibit thermodynamic properties markedly different than similar-sized molecules without hydrogen bonding [63].

Due to the ubiquitous nature of these materials, especially of water, understanding the physical properties of these materials has immense practical applications in many fields. Ghonasgi [64] mentions the inhibition of gas hydrate formation in natural gas transmission and the use of supercritical fluids in separation technologies as a couple of specific contemporary processes where better knowledge of association than which exists today would have an enormous impact. Activity coefficient approaches such as the Wilson and NRTL equations are commonly used to account for large nonidealities in mixtures. Although useful in regions where good experimental data exist, they have little predictive value outside these regions according to Galindo et. al. [65] and thus can not be safely used in extrapolation. They have no precise theoretical basis, so it is difficult to know how to improve the approach.

Theories to understand the behavior of associating fluids fall into one of three classifications: chemical theories, lattice theories, and statistical mechanics-based theories. The original chemical theory of solutions was formed by Dolezalek [66], who treated the strong associating forces as chemical reactions with corresponding equilibrium constants [61].

2.1.1 Chemical Theories of Association

Consider a solvating binary mixture of species A and B. Neither A nor B can associate with itself, but A can associate with B. In chemical theory, this solution is viewed as a ternary mixture with species A, B, and AB. In the original chemical theory, an ideal solution is formed and

\[ K = \left( x_{AB}^C \right) / \left( x_A^C x_B^C \right), \]  \hspace{1cm} (2-1)
where $K$ is the equilibrium constant and $x'_{\alpha}$ is the mole fraction of $\alpha$ in the chemical theory viewpoint. Although thermodynamically rigorous, this theory has serious drawbacks. Chapman et. al. [67] conclude that the ideal solution assumption is a poor one for binary solvating mixtures. Fugacity coefficients, therefore, are needed to describe the nonideality. However, an equation of state with certain mixing rules is needed to produce the fugacity coefficients. This chicken and the egg approach can end up being fairly cumbersome in practice, especially for less simple types of association equilibria with large clusters. Heidemann and Prausnitz [68] used chemical theory and van der Waals theory mixing rules to analytically solve for the chemical equilibria within the equation of state so that the phase equilibria could be solved directly. Ikonomou and Donohue [69] combined this approach with PACT [70] to obtain the associated perturbed anisotropic chain theory (APACT) explicitly accounting both for association and the nonsphericity of molecules. According to [65], although it has limited predictive capability, APACT has proved useful for some phase equilibria studies of water and hydrocarbons.

Economou and Donohue [71] compared a representative theory from each of the three classes of theories and obtained essentially the same results for simple cases of association with one and two bonding sites; i.e., they found that the contributions due to association are equivalent. However, in a later paper, Economou and Donohue [72] concluded that the chemical theory used, APACT, was inadequate for describing the three-dimensional structures which resulted with molecules of three or more sites.

### 2.1.2 Lattice Theories of Association

Lattice theories are based on the assumption that liquids are solid-like. This picture of liquids supposes that the molecules sit in a regular array while each molecule vibrates within a small region. Many lattice theories assume random mixtures, an assumption which should be rather poor for associating fluids. Guggenheim [73] used a
non-random mixture approach in his quasi-chemical theory. In the canonical ensemble, the Helmholtz free energy, \( A \) is written as

\[
A = -kT \ln(Q(N,V,T))
\]  

(2-2)

where \( k \) is the Boltzmann constant, \( T \) is the temperature, \( V \) is volume, \( N \) is the number of segment hole contacts, and \( P \) is the pressure, and where \( Q \) can be calculated by using [74]

\[
Q(N,V,T) = \sum_{x} \Omega(N,V,T,x) \exp\left(-\frac{E(N,V,T,x)}{kT}\right)
\]  

(2-3)

where \( E \) is the system's internal energy, \( \Omega \) is the number of configurations available to the system under constraints of volume, temperature, and number of segment hole contacts, and \( x \) is the fraction of segment-vacancy contact pairs in relation to the total number of segmental contact pairs. The sum is over all possible \( x \). The fundamental problem in lattice theory is determining \( \Omega \). Guggenheim[73, 74] used mean field theory to obtain an approximation for \( \Omega \). Sanchez and Lacombe [75] used this \( \Omega \) to develop an equation of state (EOS), which was modified to account explicitly for hydrogen bonding interactions by Panayiotou and Sanchez (the SLP EOS) [76].

Lattice theories seem useful for fluids with a regular structure such as gas hydrates [77] and for polymer solutions [61], where solutions may consist of molecules which differ greatly in size. Lattice theories, however, can deteriorate at temperatures far above the melting point [61]. Most importantly for our topic at hand, they do not seem to characterize associating solutions very well. Economou and Donohue [71] showed that the lattice theory (SLP EOS) led to the same functional of association for pure components and mixtures as chemical theory (APACT) and Wertheim's theory (see below); however, lattice theory did not do well for compressibility factor when compared to simulations [8] for hard-sphere molecules with one and two bonding sites with the error coming from the SL EOS and not from the addition of association [71]. Suresh et al. [78]
found that the SLP EOS [76] model is inaccurate for the solid-liquid equilibria of Nylon-6/2,2,2 trifluoroethanol, CO$_2$ at low Nylon-6 concentrations and low temperatures and does not represent liquid-liquid equilibrium at 373.15K. SAFT (see below), the EOS from a statistical mechanics theory, was quite accurate under the same conditions.

2.1.3 Statistical Mechanics-based Theories of Association

Statistical mechanics based theories involve introducing the association interaction into the system's potential model. Reviews of theories of this type can be found in [6(a), 67]. Association interactions are known to be highly asymmetric and directional in character [79, 80]. Andersen [79, 80] introduced the geometry of interaction at an early stage of theory development. Association was limited to a small region of the molecule called an association site. He used the Mayer cluster expansion method to determine the pair correlation functions of hydrogen-bonded fluids. By assuming that when two molecules form an association bond the repulsive cores prevent a third molecule from coming close enough to bond to either molecule, he simplified the expansion to consider only single bonds at each attractive site.

2.2 Wertheim's Theory of Association

Wertheim's theory [6] is similar in many ways to Andersen's theory. However, Wertheim's theory is based on a resummed cluster expansion made up of two densities: the total number density $\rho$, and the monomer density $\rho_\alpha$. An expansion containing both densities should be more rapidly convergent than one based solely on the total number density. After simplifying the complex graphical expansions, Wertheim ended up with a theory which relates the change in residual Helmholtz free energy due to association to the monomer density. An advantage of Wertheim's approach, as opposed to chemical theory, is that all association species are predicted by the theory. A possible disadvantage of the theory is that the parameters within Wertheim's theory are not experimentally accessible.
Initially, Wertheim dealt with pure hard-core molecules with one attractive site [6(a), 6(b)], but he later extended his theory to molecules with multiple bonding sites [6(c), 6(d)]. Wertheim's theory has been substantially extended since then. A Cornell University group extended the theory to binary mixtures of associating spherical molecules with one bonding site [7, 81]. Jackson et. al. [8] used Wertheim's theory to study hard sphere molecules with one or two bonding sites; a mean field dispersion term was added to study phase equilibria of these systems. In an analogous manner, Chapman et. al. [10] studied hard sphere chains with multiple bonding sites. Ghonasgi and Chapman [5] broadened the theory to include hard [5, 82] and Lennard-Jones (LJ) spheres [5] with four bonding sites and hard and LJ dispheres with one bonding site [83]. Extensions using a Lennard-Jones potential instead of hard spheres also include ones for Lennard-Jones spheres with one or two sites [84, 85, 86], mixtures of LJ chains [87], and one and two-sited chains of 4 LJ spheres per chain [88]. Johnson and Gubbins [89] used the theory to calculate the phase equilibria of LJ associating pure fluids and mixtures. Banaszak et. al. [90] derived EOS's for hard-core square-well chains and sticky hard chains. More recently, the Wertheim approach has been extended to deal with double bonding [91], rings (intramolecular association) [92-95], and bonding cooperativity [96]. Primarily, these studies were based on Wertheim's first-order perturbation theory, TPT1. The second order theory, which accounts for the dependence of bonding at one site on the bonding of another site [58] is difficult to calculate since it requires the appropriate three-body distribution function. As an approximation, TPT-D, developed by Ghonasgi and Chapman [97], uses dimer segments as reference molecules. Johnson uses TPT-D [97] (called TPT1-D in his paper) and intramolecular association results [92-94] to study model linear and ring polymers. The accuracy of TPT-D against simulations is greater than theories which include only monomer segments in the chain contribution, especially for longer chains [98]. TPT-D was extended to square-well chains by Taveres et. al. [99].
Being molecularly-based, Wertheim's theory can be directly compared against computer simulation [5, 7, 8, 10, 82-100].

2.2.1 Equations of State Based on Wertheim's Theory

Chapman et. al. [10] developed an accurate equation of state for pure fluids and chain molecule mixtures formed from tangent hard-sphere segments. The expression is identical to that of Wertheim [58], but it is in a different form (actual chain length versus average). This EOS is general for mixtures of associating chain molecules with multiple bonding sites, including a van der Waals one-fluid mean-field term for long-range dispersive forces. We can consider this EOS approach to be called SAFT-HS for the hard sphere version of statistical associating fluid theory. It has been used to study the behavior of model water + n-alkane [101, 102] and water + alkanol [103] mixtures and of a system which exhibits closed-loop liquid-liquid immiscibility [104]. Galindo et. al. [65] extended the previous work of Green et. al. [101] and Nezbeda et. al. [102] by using transferable fitting parameters for determining the high-pressure phase equilibria of water and n-alkanes.

A less simple, yet generally more accurate EOS for associating fluids is the original SAFT [105, 106] or recent modifications thereof. This approach treats the chain as LJ segments. This SAFT-LJ incorporates contributions from the molecular cores, the chains, the association sites, and LJ dispersion interactions.

Huang and Radosz [107] used SAFT-LJ and experimental data to obtain correlated parameters which predict the phase equilibria of many pure components and of binary mixtures. Chen et. al. [108] used SAFT to calculate properties of alternating polypropylene-polyethylene polymers in olefins. The latter work prompted the development of an improved EOS called SAFT-D (see TPT-D above) [97]. Wu and Chen [109] applied SAFT with satisfactory results in vapor-liquid calculations of polymer solutions. Suresh et al [78] found that SAFT represents the multiphase equilibrium of the
Nylon 6/TFEtOH/CO₂ system quite accurately over a wide range of conditions and compositions. Yu and Chen [110] compared the accuracy of SAFT against the UNIFAC model and the Peng-Robinson EOS with van der Waals mixing rules for the liquid-liquid equilibrium calculations of 41 binary and eight ternary mixtures, including that of associating fluids. The SAFT EOS was far superior to the other two. Others using SAFT for comparisons against experimental data include [111-114].
3. Statistical Mechanical Theories of Inhomogeneous Fluids

3.1 Introduction
The essential difference between the behavior of inhomogeneous and homogeneous fluids is in the nonlocal characteristics of the former material. Properties of the inhomogeneous fluid depend not only on the local density at position \( r \) (and of the temperature and chemical potential, which are constant throughout the fluid at equilibrium) but also on the density near \( r \). One can classify the modern approaches to these problems into integral equation theories [115] and density functional theories [53].

3.2 Integral Equation Theory
The singlet integral equation (IE) theory uses the Ornstein-Zernike (OZ) equation for solution. If we consider our wall as a giant molecule (which does not have a subscript) in a fluid of \( n \) components (including the wall we now have \( n+1 \) components), we have three OZ equations to solve [116, 117] including

\[
h_{ij} = c_{ij} + \sum_{k=1}^{n} \rho_k h_{ik} * c_{kj},
\]

which is the bulk OZ equation for mixtures, where \( h_{ij} \) is the total correlation function between components \( i \) and \( j \), \( c_{kj} \) is the bulk direct correlation function, \( \rho_k \) is the local number density of component \( k \), and \( * \) represents a convolution integral. Next,

\[
h_i = c_i + \sum_{k=1}^{n} \rho_k h_k * c_{ki},
\]
where \( h_i \) and \( c_i \) are the total and direct correlation functions, respectively, of the fluid components with the wall, and

\[
h = c + \sum_{k=1}^{n} \rho_k h_k^* c_k. \tag{3-3}
\]

where \( h \) and \( c \) are the overall total and direct correlation functions, respectively. Having a shorter range than \( h \), the bulk direct correlation function is simplest and is therefore approximated first. Equations (3-1) and (3-2) are solved by numerical iteration. Equation (3-3) can be solved directly. Once \( h_i(x) \) is known, the density profile can be obtained from

\[
\rho_i(x) = \rho_{i,\text{bulk}} \left[ 1 + h_i(x) \right], \tag{3-4}
\]

where we have assumed that the wall is flat and there is cylindrical symmetry, so we can write in terms of \( x \) instead of \( r \). To solve equations (3-1) to (3-3), one needs closure approximations. An approximation often used is the Percus-Yevick (PY) \[118\] approximation,

\[
h(r) - c(r) = y(r) - 1, \tag{3-5}
\]

where \( y(r) = (h(r) + 1) \exp[\phi(r)/kT] \) is the cavity correlation function and \( \phi(r) \) is the intermolecular pair potential. Two other approximations are the hypernetted chain approximation (HNCA),

\[
h(r) - c(r) = \ln(y(r)), \tag{3-6}
\]

and the mean spherical approximation (MSA),
\[ h(r) = -1, \quad r < 0 \]
\[ c(r) = -\beta \phi(r), \quad r > 0 \] (3-7)

of Lebowitz and Percus [119]. One can mix the approximations: therefore, one could use MSA for equation (3-1) and HNC for equation (3-2) to obtain an HNC1/MSA solution. At low densities, the PY1 and HNC1 equations are accurate against simulations [22, 23] for the hard sphere/hard wall (HSHW) system, but accuracy deteriorates markedly very close to the wall at higher densities [115, 116]. The theory does not obey the wall theorem [17], where, for any fluid near a hard wall, the bulk pressure is equal to the wall density. Accuracy, however, is at least qualitatively correct for the HSHW system. However, for some other intermolecular potentials, such as a Lennard-Jones fluid near a hard wall, results are poor [120, 121].

A more accurate integral equation approach is to generalize the OZ equation by using

\[ h(12) = c(12) + \int \rho(3) h(13) c(23) d \mathbf{r}_3, \] (3-8)

which we can call the OZ2 equation. This equation is coupled with a closure to yield the PYA2, HNCA2, or MSA2 equation. In addition to the previous equations given, these pair theories require the solution of another equation relating \( \rho(x) \) to the pair function. In pair theories, both the singlet density and the pair distribution functions are unknown (rather than, for instance, assuming the pair distribution function (PDF) is some constant such as the PDF of the bulk.) The equations used are the Born-Green (BG) equation [122], or the Lovett-Mou-Buff-Wertheim (LMBW) equation [123, 124], or modified versions of the latter. The OZ2 equation is numerically difficult and time-consuming to solve, but the LMBW equation is generally the easier of the two (BG and LMBW) to implement. Plischke and Henderson [125] solved the HSHW problem with a modified LMBW equation getting excellent results when compared against simulations. Good
success was found by Kjellander and Sarman [126] with the PY2 theory. Plischke and Henderson [127] indicate that good results can also be obtained with a Lennard-Jones fluid. Henderson and Plischke [128] developed a parametrized PY approximation that predicts the pair correlation function, g, quite well, although there is some disagreement far from the wall at high densities. For more details, check the excellent and almost exhaustive integral equation review by Henderson [115].

3.3 Density Functional Theory

3.3.1 Introduction

The idea behind the density functional method is that given a fluid intermolecular potential(s), an external potential, and the free energy of an inhomogeneous fluid, one can determine the one-body (singlet) density profile of the fluid; i.e., the minimum free energy is the appropriate functional of ρ(\mathbf{r}). Advantages [129] of using free energy DF theory [12] for inhomogeneous fluids include: (1) its accuracy against computer simulation for hard spheres, (2) its origin in the grand potential, a relatively simple concept for applying to a broad group of systems, (3) its expression as an excess Helmholtz free energy functional; therefore, all relevant thermodynamic functions can be calculated from this functional, and (4) its straightforward implementation and fast speed of calculation. These characteristics make this approach more suitable for direct engineering application than integral equation theory. However, the approximations made for the free energy functional must be accurate enough for the problem at hand.

Evans [53] reviews the history of the DF theory, the rigorous foundations of which were laid in statistical mechanics over thirty years ago. We will not attempt to repeat Evans' comprehensive effort. Much of the following is a summary of the Evans review [53] with some of my own comments.

Current effort involves forming approximate free energy DF methods. Below is a presentation of the basics of density functional theory followed by a brief review of some
of the recent approximations made for simple fluids. We begin with the definition of the
grand potential [53]:

$$\Omega = A[\rho(\mathbf{r})] + \int \rho(\mathbf{r})[\phi_w(\mathbf{r}) - \mu]d\mathbf{r}$$  \hspace{1cm} (3-9)

where $\rho$ is the singlet number density, $\phi_w$ is the external potential, and $\mu$ is the chemical
potential. The Helmholtz free energy can be broken up into a sum of ideal and excess parts as:

$$A[\rho(\mathbf{r})] = A^{id}[\rho(\mathbf{r})] + A^{ex}[\rho(\mathbf{r})]$$  \hspace{1cm} (3-10)

The ideal functional is known exactly and we can write it as:

$$A^{id}[\rho(\mathbf{r})] = \int \rho(\mathbf{r})kT[1-n\rho(\mathbf{r})-1]d\mathbf{r}.$$  \hspace{1cm} (3-11)

The excess part is somewhat unknown. However, by forming solvable approximations for
the functional, a wide variety of systems can be studied. By formally minimizing the grand
potential (at equilibrium, $\delta \Omega / \delta \rho(\mathbf{r}) = 0$), we obtain our 1st hierarchy of equations in
the form of a density functional. (By differentiating the excess Helmholtz free energy
twice, we get the direct correlation function hierarchy, with

$$c(\mathbf{r}, \mathbf{r}') = -\frac{\delta^2 A^{ex}}{kT \delta \rho(\mathbf{r}) \delta \rho(\mathbf{r}')}. \hspace{1cm} (3-12)$$

See Evans [53, 130] for more rigorous derivations.
3.3.2 Square Gradient Approximations

The key to solving the density functional, therefore, lies in the approximation to the excess Helmholtz functional. Presumably, one still minimizes the grand potential when $\tilde{A}^{\infty}$ is only an approximation to the exact functional. Crude approximations may suffice for some problems, whereas for a detailed understanding of microscopic phenomena, more sophisticated ones are necessary. The best known early approximation is the square gradient approximation [130, 131], where the density is allowed to vary by large amounts, but only over a long distance scale and

$$\tilde{A}[\rho_i] = \int d\mathbf{r} \left[ f_1(\rho(\mathbf{r})) + f_2(\rho(\mathbf{r}))(\nabla \rho(\mathbf{r}))^2 + O(\nabla \rho)^4 \right]$$  \hspace{1cm} (3-13)

Successive terms correspond to successive powers of a scaling parameter, $r_0^{-1}$. $f(\rho)$ is the Helmholtz free-energy density of a uniform fluid of density $\rho$. So eliminating all terms after the first results in the local density approximation, where the free energy is calculated as a function of the local density. These methods can determine gross features, such as adsorption [132, 133] and wetting transitions at a fluid-fluid interface [133]. The long-range nature of the methods generally preclude predicting short-range structure when there are rapidly varying density oscillations near surfaces [53].

3.3.3 Density Expansions

One can also use methods of density expansion for solving the free energy functional. Let the initial density $\rho_i(\mathbf{r})$ be $\rho_{\text{bulk}}$ at the same chemical potential. Making a two-body approximation for the direct correlation function and minimizing the resulting functional for the grand potential, one obtains the same equation as obtained by making the HNC closure of the wall-particle OZ equation [53, 115]. As noted above in Section
3.1. The equation works well for the HSHW system, but is much less satisfactory when the fluid has an attractive component.

The resulting equation can be improved by upgrading the equation to third-order from a quadratic [134, 135, 136] by approximating the three-body direct correlation function. This equation is made to obey the wall-sum rule by choosing the parameter in the third-order correctly. The third-order theory is accurate for the HSHW problem [135] and for some LJ fluids [136]. Although the second order equation can predict solid-liquid transitions in some cases [53, 137], it is unsuitable for predicting other types of phase transitions. It is uncertain how the third order theory should fare for phase transitions [53].

3.3.4 van der Waals Approximations

By taking from the example of perturbation theory for a uniform fluid, we can make the approximation for the inhomogeneous fluid of [53]:

\[ \rho^{(2)}(\phi_\alpha;r_1,r_2) = \rho(r_1)\rho(r_2) g_r(\rho^m;r_{12}), \]  

(3-14)

where \( \rho^{(2)} \) is the two-body density, \( \rho^m \) is some mean of the local densities, \( \rho(r_1) \) and \( \rho(r_2) \), \( g_r(\rho^m;r_{12}) \) is the pair correlation function of the uniform reference fluid, and \( \phi_\alpha \) is the attractive portion of the intermolecular potential. Toxvaerd [138] used the local density approximation (LDA):

\[ A_r[\rho] = A_{hs}[\rho] = \int d\mathbf{r} f_{hs}(\rho(\mathbf{r})) \]  

(3-15)
where $f_{hs}(\rho)$ is the Helmholtz free-energy density of a uniform hard-sphere fluid. (See Rowlinson and Widom [12] for a review on these methods). By ignoring structure, one can make the simpler approximation of

$$\rho^{(2)}(\phi; r_1, r_2) = \rho(r_1)\rho(r_2).$$  

(3-16)

Free energy functionals making use of this approximation and the LDA are called van der Waals theories of nonuniform fluids. These methods have been applied to an enormous number of applications including vapor-liquid interfaces, adsorption, wetting phenomena and phase transitions [139, 140, 141]. Advantages [53] include a straightforward iterative solution, simple extension to mixtures, the possibility of inverting the OZ equation and obtaining an approximation for the pairwise distribution function, and separate and simple nonlocal treatment of the attractive portion of the potential. Critical disadvantages [53] are that its mean field form can mean difficult treatment of phase transitions at interfaces and that with short-range correlations absent, the oscillatory density profiles cannot be described and the wall sum rule (wall theorem) will not be satisfied.

### 3.3.5 Smoothed Density Approximations

The idea behind weighted density (or smoothed density) approximations (WDA's) is to have the free energy depend on densities near the position $r$ as well as $\rho(r)$ itself. WDA's match the wall sum rule to the extent that the bulk equation of state is accurate [53]. The excess free energy should be well approximated by a local function of the weighted density, $\rho^w(r)$:

$$A_{ex}^{\text{ex}}[\rho] = A_{hs}^{\text{hs}}[\rho] - A_{id}^{\text{id}}[\rho] = \int \rho(r) f^{\text{ex}}(\rho(r)) dr,$$  

(3-17)
where $\bar{f}^{-\text{ex}}(\rho) = [f^{-\text{hs}}(\rho) - f^{-\text{id}}(\rho)]/\rho$ is the excess over ideal, free energy per atom. The different WDA's vary in the recipe for the weighted density. The first WDA we show is that of Nordholm et. al. [142] for which

$$\bar{\rho}(\mathbf{r}) = \int \rho(\mathbf{r'}) \omega_0(|\mathbf{r} - \mathbf{r'}|; \bar{\rho}(\mathbf{r})) d\mathbf{r'}$$  \hspace{1cm} (3-18)

with the weight function $\omega_0$ proportional to the Heaviside step function

$$\omega_0 = \frac{3}{4\pi \sigma^3} \Theta(\sigma - r)$$  \hspace{1cm} (3-19)

Using an excluded volume approximation for the hard sphere excess free energy, this WDA gives results of only qualitative accuracy for the HSHW problem [142], but with the addition of the mean field approximation, it has been found useful for phase transitions [143, 144]. Tarazona [145, 146] improved this method by using the Carnahan-Starling [147] result for the excess free energy of the hard sphere. This is Tarazona Mark I [53]. Qualitative results were obtained for the HSHW system [146]. According to Evans [53], Tarazona and Evans [146], with the mean-field approximation addition for the attractive forces, were probably the first to give a realistic description of drying at a hard wall-liquid interface.

Later Tarazona [148] developed a more sophisticated version of his WDA, termed Tarazona Mark II [53], which has a weighting function of 2nd order. More details of the method are given in the next chapter. The method is shown to be accurate for the HSHW system[148, 149] and at least qualitatively accurate for an LJ fluid at a hard wall [149]. Results for these two systems were much better than for Tarazona Mark I [149]. Tarazona et. al. [150] received realistic density profiles for an example of a wetting transition. Van Swol and Henderson [151, 152] obtained good results compared to simulations for capillary condensation [153, 154] and for systems of hard sphere binary
mixtures made of different sized spheres at a hard wall [155]. Curtin and Ashcroft [156] (CA) adapted Tarazona's method but use a less utilitarian method for obtaining a weighting function at the expense of more computational time. Results [157] are similar to Tarazona [148] for the HSHW problem.

Meister and Kroll (MK) [158] developed a WDA in which $A^{ex}$ is expressed as a functional of some slowly varying reference density $\rho_0(\mathbf{r})$, as well as of $\rho(\mathbf{r})$. The method is appealing from a theoretical nature, since it is not ad hoc [53]. However, Groot and van der Eerden [159] remedied a problem which Groot [160] earlier found with equation (3-12) and received improved results. The results are reasonable with the GvE method giving comparable results to the CA method. However, Kroll and Laird [157] in a reformulation (with a position-independent weighted density) of GvE found no solution for a crystalline phase in contrast to the position-independent form of CA (also known as the modified WDA method) which gave accurate results for hard-sphere freezing [161].

Rosenfeld [162] and then Kierlik and Rosinberg [163] gave a WDA derived specifically for hard sphere mixtures. The oscillation placements are very accurate [163] for the HSHW problem, even more so than for Tarazona Mark II or CA. The disappointment lies close to the wall. The theory satisfies the wall sum rule, but because the equation of state is the PY result, the pressure is different than the exact or Carnahan-Starling result. Also, Evans [53] states that this recipe is inherently unsuited for applications to freezing or to adsorption of liquids at strongly attractive substrates.

In contrast to the above WDA's, one can employ WDA's which do not depend on position $\mathbf{r}$. These position independent WDA's are especially well suited to freezing problems. Denton and Ashcroft [161] applied their modified WDA (MWDA) to freezing with equal success as the more demanding CA method. For fluids at surfaces, the method was found by White and Evans [164] to be equivalent to the HNC closure of the inhomogeneous OZ equation. Thus, results have both the benefits and drawbacks of that
integral equation method, which we discussed above. The generalized effective liquid
approximation (GELA) of Lutsko and Baus [165] is very accurate for hard sphere
freezing, but less accurate for inverse-power law repulsive potential freezing into fcc
crystals than the MWDA. It is less certain how accurate GELA would be for problems
other than freezing [53]. Evans [53] seems to think that the most versatile approach for
fluids at interfaces would require a position-dependent weighted density.

Evans [53] states that based on results for the three body direct correlation
function, it is difficult to choose between the methods of Rosenfeld, CA, and Tarazona
Mark II. This author, based on a less than comprehensive review of the literature
published since the review of Evans [53], sees no reason to alter this assessment. In the
past several years, these methods (especially Tarazona Mark II, which is the most widely
applied free energy DF [53]), and others, including those above, have been used for
solving many problems. The Rosenfeld [162] method has most recently been getting more
attention due to its ease of extension to mixtures (for example, see [166]). For
engineering purposes, the best method, yet to be invented, would combine the relative
simplicity and overall accuracy (widely applicable) of solution of the method of Tarazona
Mark II with the ease of extension to mixtures of the method of Rosenfeld and Kierlik and
Rosinberg.
4. The Associating M-site Hard Sphere Fluid against a Hard Wall

4.1 Introduction

Many [42-47, 50, 51, 167-172] of the previous studies of inhomogeneous AFs relied on the Cummings-Stell [38, 41] model of overlapping hard spheres (a spherically attractive shell within a hard sphere) or on modifications thereof [44, 45, 52] to study dimerizing spheres against various surfaces. Surfaces include hard wall [43-45, 47, 50, 51, 167, 170], crystalline and other associatively attractive walls [42, 167-169, 171, 172], permeable walls [46], and Lennard-Jones (LJ) [42] walls. Most of these investigations used a singlet integral equation theory including PY1 [44, 45, 50, 167, 169, 170], HNC1 [44, 45, 50, 167, 168], and combinations including PY1/EMSA [44, 51, 171, 172], HNC1/EMSA [44, 46, 51] and PY1/ARISM [42]. See [40] for ASRISM. Although each of these papers performed calculations at a limited number of conditions, some conclusions can be drawn from the works as a whole.

As might be expected, since singlet theories do not show wetting or layering transitions [47, 53], these studies did not agree with simulation results [44, 45, 51, 170, 172] for density in a narrow region next to the wall, although the results are at least qualitative and can be useful [172]. However, Trokhymchuk et. al. [172] state that for any external potential except a hard wall, [172], simple singlet theories are less successful. A pair theory (see Chapter 3), nonhomogeneous Percus-Yevick (PY) theory applied with a PY closure, did well at the two average densities studied for a dimerizing fluid, but is numerically very difficult [43]. Trokhymchuk et al. [47] used the Ornstein-Zernike equation for the wall-particle correlations with a Zhou-Stell [173] DF closure to also satisfactorily represent dimerizing hard spheres against a hard wall. The Zhou-Stell approach, however, does not consider an explicit free-energy density functional.
The most successful theory of bulk associating fluids is that of Wertheim [6]. Wertheim's theory is often written today in the form of a perturbation theory which relates excess Helmholtz free energy to the fraction of unbonded molecules; this perturbation theory was originally developed for molecules with highly directional bonding sites. Holovko et al. [49, 174] formed an associative version of the Henderson-Abraham-Barker (HAB) integral equation using Wertheim's theory to study dimerizing hard spheres against a hard wall [49] and against a sticky hard wall [174]. They later studied polymerizing hard spheres forming linear hard chains [175] against a hard wall. Their model, somewhat similar to the one we used and describe below, used nonoverlapping hard spheres with association sites of infinite depth and infinitely narrow width. Accuracy for the dimerizing hard spheres was unknown since no simulation data was provided. (Note that we make this comparison for a hard wall below.) For the hard chains, they [175] made comparisons against Monte Carlo (MC) [56] data. For triatomics the density profile was only in qualitative agreement with simulations at low densities due, in part, to ignoring intramolecular bonding. Accuracy improved markedly at higher densities. Similar results were found for longer chains. We will apply the Holovko and Vakarin approach for comparisons against our new model simulations in this work. Most recently, Kovalenko et. al. [48] and Holovko and Vakarin [176] used the associating HAB approach to theoretically determine density profiles of dimerizing hard spheres [48] and dimerizing and polymerizing hard spheres [176] near crystalline surfaces.

As stated in Chapter 1, Kierlik and Rosinberg (KR) [54-57] developed a perturbational free energy density functional (DF) approach applicable to inhomogeneous fluids consisting of fully associating nonoverlapping hard spheres (i.e., tangent chains) by applying Wertheim's theory for polymerization [9, 58]. The method uses their own [162, 163] weighted free energy DF theory for hard sphere mixtures as a reference. This reference DF theory is accurate for the hard sphere at a hard wall system. It has the advantage of being easily extended to mixtures; however, Evans [53] states that it is
unlikely to do well in freezing applications or applications of adsorption to strongly attractive substrates.

For AFs, Kierlik and Rosinberg [54-57], added Wertheim's theory for inhomogeneous fluids as a perturbation to their hard sphere fluid DF theory. Wertheim's first order thermodynamic perturbation theory (TPT1) was shown to be exact in one dimension [54]. KR self-consistently determine density profiles and inhomogeneous pair correlation functions; however, the wall density disagrees with simulation bulk pressure unless adjustable parameters are used [56]. One advantage of free energy DF theory over integral equation theory is that the thermodynamics of the system are readily available since the DF theory is written in the form of the excess Helmholtz free energy. However, for high densities and long chains, the theory of Holovko and Vakarin [175] was shown to give better results for density profiles than the DF theory of Kierlik and Rosinberg [56]. Kovalenko et al. [48] state that the extension of the KR method to crystalline surfaces is fraught with technical and numerical difficulties. Since we would also like to extend our work to more complex systems (for instance, active surfaces), we develop a simpler, but adequate DF theory. In our DF theory, we use a simple approximation for the pair distribution function and apply Wertheim's bulk theory rather than the inhomogeneous form. The KR DF theory for AFs regards a polyatomic fluid as the complete-association limit of a model of associating particles. Thus, one sets the chain size and the number of chains in the implementation. In contrast, in our approach chains (and clusters) form as a result of the extent of association, which is a function of temperature. The system is therefore polydisperse and may be characterized by number- and weighted-average chain lengths, which are both functions of position. This is the main difference between our present IE study and those cited above where theory was directed to a description of simulations of monodisperse systems.

To test the IE and DF theories, we present new Monte Carlo simulation results for dimerizing (M=1) and polymerizing (M=2) hard sphere fluids against a hard wall at several
temperatures and densities. Four other simulation studies for inhomogeneous fluids have been reported with the association potential we use in this paper. Two [59, 60] were for Lennard-Jones fluids against hard and active walls and are too complex for early theoretical studies. The third is a study for fluids of hard spheres with four sites [Chapter 5 of the present work, 177]. The fourth is a study for four site Lennard-Jones (LJ) spheres on activated carbon [178], which is also too complex for early theoretical study. In this chapter we combine Tarazona's DF theory [149, 150] with Wertheim's theory [6, 9] to form a perturbation density functional theory for fluids of hard spheres with M independent and equivalent association sites against a hard wall. We also provide results from the IE theory [179] using the association model described below. We compare adsorption and density profiles from the two theories against our simulation results. We also compare fraction of monomers for the DF theory and the simulation results. We present DF theory and simulation results for M=4 in Chapter 5.

4.2 Computer simulations

Simulations in this study were performed in the canonical (constant NVT) ensemble, using the Metropolis Monte Carlo algorithm [180]. The pair potential model is defined by

\[ \phi(r, \omega_1, \omega_2) = \phi_r(r) + \sum_A \sum_A \phi_{AA}(r, \omega_1, \omega_2), \]  

(4-1)

where \( r \) is the magnitude of the vector \( r \) connecting the centers of molecules 1 and 2 and \( \omega_1 \) and \( \omega_2 \) are the orientations of molecules 1 and 2 relative to vector \( r \) and the double sum is over all association sites on each molecule. \( \phi_r \) is the reference potential; the reference hard sphere potential is defined by
\[
\phi_R(r) = \begin{cases} 
\infty & \text{if } r < \sigma \\
0 & \text{if } r > \sigma, \end{cases} \tag{4-2}
\]

where \(\sigma\) is the hard sphere diameter. \(\phi_{AA}\) represents the association potential between a site A on molecule 1 and a site A on molecule 2. The association potential is modeled by an anisotropic short range square well. The potential of interaction due to these sites is

\[
\phi_{AA}(r, \omega_1, \omega_2) = \begin{cases} 
-\varepsilon_{AA} & \text{if } r < r_c; \theta_{A1} < \theta_c; \text{ and } \theta_{A2} < \theta_c \\
0 & \text{otherwise}, \end{cases} \tag{4-3}
\]

where \(\theta_{A1}\) is the angle made by the vector from the center of molecule 1 to site A and the vector \(r\) and \(\theta_{A2}\) is the angle made by the vector from the center of molecule 2 to site A on molecule 2 and the vector \(r\).

The one-site molecular model used in these simulations has 1 bonding site labeled A placed on a spherical core. The square well depth for association bonding is \(\varepsilon_{AA} = \varepsilon_{site}\). For the two-site model, we have two sites labeled A and B located on opposite sides of each sphere; like-labeled sites on different molecules are eligible for bonding, so our square well depth in this case is \(\varepsilon_{AA} = \varepsilon_{BB} = \varepsilon_{site}; \varepsilon_{AB} = \varepsilon_{BA} = 0\). In effect, if two eligible bonding sites on two different molecules are close enough and oriented correctly, then a bond is formed. In the simulations and in our theoretical calculations below, the radial limits of the square well association were set to \(r_c = 1.05\sigma\). The angular limit was set to \(\theta_c = 27^\circ\). See Figure 4-1.

The simulation cell consists of hard walls at \(z = 0\) and \(z = H\). See Figure 4-2. Periodic boundary conditions with boxlength \(L\) were imposed in the x and y directions. Generally, \(H = \alpha * L; \alpha > 1\), to ensure that the density oscillations died away in the central region. Therefore, the two walls did not interfere with each other. (For the results reported in Table 4-1, \(\alpha\) was 2 except at the highest average density for the one-site case.
when $\alpha$ was 3.) In addition to the pair potential on the particles, the walls exerted an external potential of

$$
\phi_w(z) = \begin{cases} 
\infty & \text{if } z \leq 0 \text{ or } z \geq H \\
0 & \text{otherwise.}
\end{cases}
$$

(4-4)

Each simulation was started by placing $N'$ hard spheres in a face-centered lattice arrangement in a cube with sides of length $L$. The particles were randomly displaced for approximately $10 \times 10^4$ configurations with a conventional Monte Carlo NVT simulation. Then in a new simulation, $(\alpha-1)$ periodic images of the resulting cell were created and placed side by side with the original cell, resulting in an elongated cell of length $H$ in the $z$ direction. The number of particles was then equal to $N = \alpha \cdot N'$. A bonding site was placed on each particle. Random orientations were given to each particle. As described by Allen and Tildesley [181] and Ghonasgi and Chapman [5], each particle was chosen in turn, displaced within the rectangular box and reoriented. The orientation and displacement parameters were chosen such that independently the two parameters each had an acceptance probability of 60 to 70%, giving an overall acceptance rate of 30 to 50%. $Z$-dependent properties were calculated by accumulating averages in slices of width of approximately $0.03\sigma$. Since these were inhomogeneous fluids the acceptance criterion of 30 to 50% was forced to hold for collections of bins along the $z$ axis, especially and including the collection of all bins within $0.25\sigma$ of either wall, where the density was highest in most of the cases run.

Systems were equilibrated for at least $5 \times 10^6$ steps at low densities with no bonding energy and for $1500 \times 10^6$ steps at the highest densities and bonding energies. Each equilibrated configuration was used as the starting configuration of a series of further
Figure 4-1. One- and two-site potential models. These can form dimers and longer linear chains, respectively.

runs. Each series consisted of 10 runs of from $5 \times 10^6$ configurations each for moderate densities and little association to $300 \times 10^6$ configurations at the higher association energies. The subaverages of properties from each run of a series were used to calculate averages. A final average was then calculated by averaging the properties of each bin on one side of the cell midpoint with its geometrically symmetrical twin.
Figure 4.2. Box of $1 \times 1 \times H$ dimensions. Periodic only in $x$ and $y$ directions.
These systems took up to a week to equilibrate on an IBM RS/6000 Model 340 workstation. No biasing scheme [182-186] was used; however, we saw no evidence of metastable configurations.

Criteria used for determining if equilibration had been reached at the end of a series of simulations were: 1) having a 5% standard deviation or less for wall densities, 2) degree of symmetry of the density profile on each side of the cell midpoint up to each wall, 3) stability of bulk density from run to run, and 4) agreement between the ensemble average simulation wall density and the theoretical bulk pressure [6-10]. Theoretical bulk pressure was calculated for the middle 40% of the cell for high temperatures and high densities to 60% of the cell for low temperatures and low densities by using the simulation bulk density and Wertheim's theory [6-10].

Densities were calculated in each slice by counting molecules in each slice and dividing by the slice volume. Wall densities were determined by extrapolating a curve fit of log density versus distance from the wall for the five slices nearest the wall. Adsorption was calculated numerically using \((\rho_{ave} \sigma^3 - \rho_{bulk} \sigma^3) * h\) where \(\rho_{ave} \sigma^3\) is the reduced average singlet number density, \(\rho_{bulk} \sigma^3\) is the reduced singlet number density in the bulk region and \(h\) is half the box length in the z direction in units of \(\sigma\). Fraction of monomers (unbonded molecules) were determined for each slice and in the bulk. Fraction of monomers at the wall were obtained from a linear curve fit of slices near the wall.
Table 4-1: NVT Monte Carlo simulation input parameters for hard spheres with one or two square well bonding site against a planar wall

<table>
<thead>
<tr>
<th>Average density, $\rho \sigma^2$</th>
<th>Number of molecules, N</th>
<th>$N_{av.} \times 10^{-6}$</th>
<th>$\varepsilon_{site}/kT$</th>
<th>H. box length in z direction, $\sigma$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-site</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.20</td>
<td>500</td>
<td>5</td>
<td>0</td>
<td>21.544</td>
</tr>
<tr>
<td>0.20</td>
<td>500</td>
<td>125</td>
<td>7</td>
<td>21.544</td>
</tr>
<tr>
<td>0.20</td>
<td>500</td>
<td>150</td>
<td>14</td>
<td>21.544</td>
</tr>
<tr>
<td>0.50</td>
<td>500</td>
<td>200</td>
<td>0</td>
<td>15.874</td>
</tr>
<tr>
<td>0.50</td>
<td>1000</td>
<td>125</td>
<td>7</td>
<td>20.0</td>
</tr>
<tr>
<td>0.50</td>
<td>1500</td>
<td>150</td>
<td>11</td>
<td>22.894</td>
</tr>
<tr>
<td>0.75</td>
<td>500</td>
<td>12</td>
<td>0</td>
<td>13.867</td>
</tr>
<tr>
<td>0.75</td>
<td>500</td>
<td>15</td>
<td>3</td>
<td>13.867</td>
</tr>
<tr>
<td>0.75</td>
<td>500</td>
<td>35</td>
<td>5</td>
<td>13.867</td>
</tr>
<tr>
<td>0.75</td>
<td>500</td>
<td>50</td>
<td>7</td>
<td>13.867</td>
</tr>
<tr>
<td>0.75</td>
<td>500</td>
<td>300</td>
<td>11</td>
<td>13.867</td>
</tr>
<tr>
<td>0.90</td>
<td>1500</td>
<td>150</td>
<td>0</td>
<td>16.441</td>
</tr>
<tr>
<td>0.90</td>
<td>1500</td>
<td>125</td>
<td>7</td>
<td>16.441</td>
</tr>
<tr>
<td>2-site</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.20</td>
<td>500</td>
<td>5</td>
<td>0</td>
<td>21.544</td>
</tr>
<tr>
<td>0.20</td>
<td>500</td>
<td>150</td>
<td>11</td>
<td>21.544</td>
</tr>
<tr>
<td>0.35</td>
<td>500</td>
<td>15</td>
<td>0</td>
<td>17.878</td>
</tr>
<tr>
<td>0.35</td>
<td>500</td>
<td>150</td>
<td>8</td>
<td>17.878</td>
</tr>
<tr>
<td>0.75</td>
<td>500</td>
<td>15</td>
<td>0</td>
<td>13.867</td>
</tr>
<tr>
<td>0.75</td>
<td>500</td>
<td>80</td>
<td>6</td>
<td>13.867</td>
</tr>
</tbody>
</table>
4.3 Theory

4.3.1 Integral Equation Theory

The previous formulation of associative HAB IE theory [149, 175] is adapted by establishing a connection between temperature and number-average chain length in the bulk of the fluid. Details can be found in [179].

4.3.2 Density Functional Theory

A thorough review of the foundations of density functional theory is given by Evans [53]. Most density functional methods are based on the idea that the free energy is a functional of the fluid density profile. All relevant thermodynamic functions can be calculated from this functional. By forming solvable approximations for the functional, a wide variety of systems can be studied. We begin with the definition of the grand potential,

\[ \Omega = A[\rho(r)] + \int \rho(r) [\phi_W(r) - \mu] \, dr, \]  \hspace{1cm} (4-5)

where \( \rho \) is the singlet number density, \( \phi_W \) is the external potential; and \( \mu \) is the chemical potential. The Helmholtz free energy can be broke up into a sum of ideal and excess parts as

\[ A[\rho(r)] = A^{id}[\rho(r)] + A^{ex}[\rho(r)]. \]  \hspace{1cm} (4-6)

The ideal functional is known exactly and we can write it as

\[ A^{id}[\rho(r)] = \int \rho(r) kT[1 + \rho(r) - 1] \, dr. \]  \hspace{1cm} (4-7)

We first describe the Tarazona [149, 150] method for hard spheres and follow with the addition of the excess free energy of association from Wertheim's theory. In particular we are interested in the Tarazona method, sometimes called Tarazona Mark II [53], the most
widely applied (according to [53]) DF theory for the HSHW problem. In Tarazona's approach, the excess free energy functional is approximated using the smoothed density approximation [150],

$$
\mathcal{A}^{\text{ex}}[\rho(r)] = \int \rho(r) f(\tilde{\rho}(r)) dr,
$$  \hspace{1cm} (4-8)

where \( f \) is the excess (over ideal gas) free energy per molecule and the smoothed density is given by

$$
\tilde{\rho}(r) = \int \rho(r') \rho(|r-r'|; \rho(r)) dr',
$$  \hspace{1cm} (4-9)

and \( w \) is the Tarazona weighting function [149, 150, Chapter 6]. The weighting function is expressed as a power series expansion with the coefficients found in [149, 150]:

$$
w(r-r', \rho) = w_0(|r-r'|) + w_1(|r-r'|) \rho + w_2(|r-r'|) \rho^2.
$$  \hspace{1cm} (4-10)

At equilibrium, \( \delta \Omega[\rho(r)] / \delta \rho(r) = 0 \). Realizing that our system is inhomogeneous only in the \( z \) direction and by formally minimizing the grand potential, we obtain

$$
\rho(z) = \exp[\beta(\mu - \phi_{HF}(z) - \lambda(z))],
$$  \hspace{1cm} (4-11)

$$
\lambda(z) = \mathcal{E}(\tilde{\rho}(z)) + \int \frac{\delta \tilde{\rho}(z')}{\delta \rho(z)} \rho(z') \mathcal{E}'(\tilde{\rho}(z')) dz',
$$  \hspace{1cm} (4-12)

$$
\mu = \mu^{\text{ex}} + \ln(\rho_{\text{bulk}}),
$$  \hspace{1cm} (4-13)

and

$$
\frac{\delta \tilde{\rho}(z')}{\delta \rho(z)} = \frac{w[|z-z'|; \rho(z')]}{1 - \rho_1(z') - 2 \rho(z') \rho_2(z')},
$$  \hspace{1cm} (4-14)
where $\beta$ is $1/kT$, $f'$ is the derivative of $f$ with respect to $\bar{\rho}$, $\mu^{\infty}$ is the excess chemical potential, and

$$
\bar{\rho}_i(z) = \int \rho(z') w_i(|z - z'|)dz'
$$

(4-15)

for $i=0, 1, 2$, and $w_i(z)$ are the coefficients of equation (4-10).

Thus far we have restated exactly the Tarazona Mark II DF theory [53] for hard spheres, though we have simplified it slightly for our problem by stating it in per square area units. This approach is very successful for hard spheres confined in hard slits [149]. We now would like to add the effects of intermolecular association.

Since the hard sphere and association interactions are of similar range, we might expect that a single weighted density could be used for both the hard sphere and association terms. Since no weighting function has been previously proposed for this case, we choose to use a weighting which is accurate in the limit of no association. If we apply Tarazona's weighting to both the bulk hard sphere and association free energy terms, our weighting is exactly the Tarazona Mark II [53] for hard spheres when there is no association. How accurate will our theory remain as the energy of association is increased? Chapman [9] indicates that the monomer-monomer pair distribution function of a fluid of associating spheres is quite similar to that of a fluid of non-associating hard spheres even when there are fewer than 60% monomers left in the association fluid. This indication of fluid structure implies some accuracy in the weighting should remain somewhat away from the limit of no association. Comparison with simulations will indicate to what degree accuracy will suffer.

Applying Tarazona's weighting to both the bulk hard sphere and association free energy terms we obtain

$$
\rho(z) = \exp[\beta(\mu - \phi_W(z) - \lambda(z))],
$$

(4-11)
\[
\lambda(z) = \bar{f}(\rho(z)) + \frac{\delta \rho(z')}{\delta \rho(z)} \rho(z') \bar{f}'(\bar{\rho}(z')) dz',
\]

(4-12)

and

\[
\mu = \mu^{\\ast, hs} + \mu^{\\ast, assoc} + kT \ln(\rho_{bulk}).
\]

(4-16)

with \( f = f_{hs} + f_{assoc} \) where \( hs \) and \( assoc \) denote the hard sphere and association terms, respectively. We use the equation of state of Carnahan and Starling [147, 187] for the hard sphere terms. For the association portion of the chemical potential, which is fixed by the bulk density and the site bonding energy, \( \varepsilon_{AA}/kT \), we have

\[
\mu^{\\ast, assoc} = M kT (\ln \chi_{AA}^{bulk} - 0.5 \chi_{AA}^{bulk} + 0.5) + M kT \rho_{bulk} \left( \frac{\partial \chi_{AA}^{bulk}}{\partial \rho_{bulk}} \right) (1/ \chi_{AA}^{bulk} - 0.5)
\]

(4-17)

where [6-10]

\[
\chi_{AA}^{bulk} = \frac{1}{1 + n \rho_{bulk} \chi_{AA}^{bulk} \Delta}.
\]

(4-18)

\( \chi_{AA}^{bulk} \) is the fraction of molecules not bonded at site \( A \), \( M \) is the number of association sites per molecule, \( n \) is the number of sites on the second molecule which one site on the first molecule is eligible to bond to, \( \Delta \) is approximately \( 4 \pi K g_{hs} (\sigma; \rho_{bulk}) f_{AA} [8] \), \( K \) is a constant that measures the volume available for bonding of the two sites on molecules 1 and 2 (here this is \( 0.25 (1 - \cos(\theta_c))^2 \sigma^2 (r_c - \sigma) \)), \( f_{AA} \) is the Mayer \( f \) function, \( \exp[\varepsilon/kT] - 1 \), and \( g_{hs}(\sigma; \rho_{bulk}) \) is the hard sphere pair correlation function at contact at the bulk density.
For the association portion of the free energy, we use the bulk relations of Wertheim's theory [6-10],

$$
\varepsilon^{assoc}[\bar{\rho}(z)] = M k T (1 + \bar{\chi}_A(z) - \bar{\chi}_A(z)/2 + 0.5)
$$
(4-19)

and

$$
\bar{\chi}_A(z) = \frac{1}{1 + n\bar{\rho}(z)\bar{\chi}_A(z)\Delta},
$$
(4-20)

where weighted reduced density, $\bar{\rho}(z)$, and weighted fraction of molecules not bonded at site A, $\bar{\chi}_A(z)$, are substituted for the normal bulk terms [6-10]. $\Delta$ is the same as above, except that $g_{hs}(\sigma;\bar{\rho}(z))$ is substituted for $g_{hs}(\sigma;\rho_{bulk})$.

Equation (4-11) was solved with a Picard type iterative method [15]. To maintain stability, less than 10 percent of the new solution was mixed with the old solution, with lower percentages used at higher average densities. Less than 500 single-loop iterations were needed for all except the highest density. To speed up calculations, the density profile for the next lowest association energy at the same density was used as the initial density profile. For the cases with no association, any good predictor of the hard sphere density at a hard wall can be used for the initial density profile. The individual terms within the integral of equation (4-12) are analytic. The integral in equation (4-12) was solved by a trapezoidal rule; a mesh width of 0.01 $\sigma$ was found to give sufficient numerical accuracy.

Once we have density as a function of distance from the surface from equation (4-11), we can use the formalism of Wertheim's theory to obtain an iterative equation for the fraction of molecules not bonded at site A. Wertheim's theory uses the approximation that only one bond can form at each association site [6c, 6d]. As in the work of Ghonasgi and Chapman [5], we will make the additional simplifying assumption that only single bonds can form between molecules. The perturbation theory solution of Wertheim's theory
includes the effect of chains and tree-like clusters on thermodynamic properties [6c]. Although also including the effect of ring-like structures may be useful for our n-site fluid when \( n > 1 \), the theory has only recently been extended for ring-like hard chains by Ghonasgi et al [92], Ghonasgi and Chapman [93] and Sear and Jackson [94, 95]; we will neglect rings. The first order perturbation theory also assumes the independence of the angles between bonding sites: thus the theory predicts that any fluid made up of molecules with the same number of bonding sites will obey the same equation of state, regardless of the angles between the sites.

If \( A \) represents the bonding sites on two interacting molecules, Wertheim's theory gives [5, 6, 9, 10]

\[
\chi_A(1) = \frac{1}{1 + \sum_A \rho(2) \chi_A(2) \Delta_{AA} d^2 2},
\]

where the sum is over all association sites, \( \chi_A(1) \) and \( \chi_A(2) \) are the fraction of molecules not bonded at site \( A \) (molecule 1) or \( A \) (molecule 2), respectively, \( \rho \) is the total singlet number density, \( d^2 = (d\omega_2 / \int d\omega_2) d\tau_2 \) denotes an angle average and a volume integral, where \( \omega_2 \) is the set of angles defining the orientation of molecule 2 and \( d\tau_2 \) is a volume element, and \( \Delta_{AA} \) is defined by

\[
\Delta_{AA} = g_R(12) f_{AA}(12),
\]

where \( g_R(12) \) is the reference fluid (hard sphere) pair correlation function and \( f_{AA} = \exp[-\phi_{AA}(12)/kT] - 1 \) is the Mayer \( f \) function.

By virtue of symmetry of the sites, the integrals in equation (4-21) are all equivalent. We can then write equation (4-21) as
\[ \chi_A(1) + n\chi_A(1)\int \chi_A(2)\rho(2)g_R(12)f_{AA}(12)d2 = 1. \] (4-23)

For planar symmetry, the density, \( \rho \), is only dependent on \( z \), the distance from the wall.

Assume \( \chi_A(1) \) is only dependent on the \( z \) direction and is not a strong function of orientation. This assumption should be strictly true in the bulk, but it may break down near the wall. Based on this assumption, we can perform an angle average over orientations of molecule 1 to obtain

\[ \frac{\int \chi_A(1)d\omega_1}{\int d\omega_1} + n\int \chi_A(1)\int \chi_A(2)\rho(2)g_R(12)f_{AA}(12)d\omega_2d\omega_1d\omega_2 = 1. \] (4-24)

If we assume \( g_R(12) \) is independent of position and direction in the inhomogeneous fluid, then \( g_R(12) = g_R(r; \rho_{bulk}) \)[22, 188]. We now have

\[ \chi_A(z_1) + n\chi_A(z_1)\int \chi_A(z_2)\rho(z_2)g_R(r)f_{AA}(12)\omega_1\omega_2 d\xi_2 = 1, \] (4-25)

where \( \langle f_{AA}(12)\rangle_{\omega_1,\omega_2} \) is an unweighted angle average of the Mayer \( f \) function. In our case, if molecules 1 and 2 are close enough to bond \( (r < r_c) \),

\[ \langle f_{AA}(12)\rangle_{\omega_1,\omega_2} = \frac{(1 - \cos(\theta_c))^2}{4}[\exp\left(\frac{\epsilon_{AA}}{kT}\right) - 1], \] (4-26)

where \( \epsilon_{AA} \) and \( \theta_c \) are as defined in Section 4-2.

Given the distance from the wall of molecule 1, \( (z_1) \), we can integrate over the range of positions for molecule 2 that allow bonding. We use the relation, \( z_2 - z_1 = r\cos\theta \) and make the change of variables from \( dr_2 \) to \( dr_{12} \).
\[ \int d\mathbf{r}_{12} = \int_0^{2\pi} d\phi \int_0^1 r_1 \cos \theta \left( \frac{r_2}{\sigma} \right) (r_{12})^2 \, dr_{12}. \quad (4-27) \]

Assume that for associating hard spheres, as Jackson et al. [8] did, that over the range of bonding, \((r_{12})^2 g(r_{12}) \approx \sigma^2 g(\sigma)\). As long as \(r_c - \sigma << 1\), we can neglect the change in \(z_2\) as \(r_{12}\) goes from 1 to \(r_c\), and integrate \(\int_{r_c}^{z_2} dr_{12} = r_c - \sigma\) and

\[ \int_{-1}^{1} d(\cos \theta) = \int_{-1}^{1} d(z_2 - z_1) \int_{-\zeta_1}^{\zeta_1} d\zeta_2. \]

Making the appropriate substitutions, Equation 4-25 becomes

\[ \chi_A(z_1) + n \chi_A(z_1) 2\pi \sigma^2 g_{\omega}(\sigma)(r_c - \sigma) \left( f_{AA}(12) \right) \int_{\omega, \omega}^{1+\zeta_1} \chi_A(z_2) \rho(z_2) \, d z_2 = 1. \quad (4-28) \]

The reference fluid radial distribution function at contact, \(g_{\omega}(\sigma)\), is obtained from the Carnahan-Starling equation of state for hard spheres[147]. We can now solve iteratively for the fraction of molecules not bonded at site A by using

\[ \chi_A^{-1}(z_1) = \frac{1}{1 + 2n \pi \sigma^2 \left( g_{\omega}(\sigma; \rho_{\text{bulk}})(r_c - \sigma) \left( f_{AA}(12) \right) \int_{\omega, \omega}^{1+\zeta_1} \chi_A(z_2) \rho(z_2) \, d z_2 \}}, \quad (4-29) \]

or in terms of equation (4-18),
\[
\chi_{A}^{i+1}(z_1) = \frac{1}{1 + 2n\pi g_{ks}(\sigma; \rho_{bulk}) K \int_{-1-z_1}^{1-z_1} \chi_{A}^{i}(z_2) \rho(z_2) dz_2}, \quad (4-30)
\]

where \(i\) is the iteration counter.

Wertheim's first order perturbation theory predicts that the activity of a site is independent of the bonding state of other sites on the same molecule. Based on this notion and the symmetry of the sites, we can write the fraction of monomers as [5, 6]

\[
\chi_0(z_1) = \chi_{A}^{M}(z_1). \quad (4-31)
\]

### 4.4 Results and discussion

Table 4-2 lists some of the major results for dimerizing spheres for density functional theory, integral equation theory and simulations. The uncertainties represent one standard deviation. The theoretical calculations used the same bulk reduced density and site association energy (which were both fixed) as the corresponding simulations. The reported bulk pressures were calculated from bulk densities using Wertheim's theory [6-9]. Also listed are average density, wall density, adsorption, and fraction of monomers at the wall. A weighted density approximation must obey the wall theorem [17]. We see that this wall sum rule was satisfied with less than a 0.5% disagreement, which was due to numerical error, for most of the cases. Theoretical adsorption was calculated numerically using \[ \int_{0}^{\rho_{bulk}} (\rho(z) \sigma^3 - \rho_{bulk} \sigma^3) dz \], where \(\rho(z)\sigma^3\) is the singlet reduced number density and \(\rho_{bulk}\sigma^3\) is the reduced number density in the bulk region and for the IE theory by an analytical representation of equation (13) in [179]. For the simulation adsorption
### Table 4-2: Theory versus Simulation for Dimerizing Hard Spheres

<table>
<thead>
<tr>
<th>Bulk density, $\rho_{bulk}$ $\sigma^3$</th>
<th>Site energy, $\epsilon_{site}$ / kT</th>
<th>Average box density, $\rho_{average}$ $\sigma^3$</th>
<th>Pressure, $P$, kT</th>
<th>Wall density, $\rho$, $\sigma^3$</th>
<th>Adsorption, $\Gamma$, $\sigma^2$</th>
<th>$\chi_0$, fraction of monomers at wall</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>simulation</td>
<td>DF theory</td>
<td>simulation</td>
<td>DF theory</td>
<td>simulation</td>
<td>theory, DF / II</td>
</tr>
<tr>
<td>0.1974</td>
<td>0</td>
<td>0.2</td>
<td>0.2099</td>
<td>0.3037</td>
<td>0.3042 ± 0.0086</td>
<td>0.0280 ± 0.0060</td>
</tr>
<tr>
<td>0.1984</td>
<td>7</td>
<td>0.2</td>
<td>0.2012</td>
<td>0.2713</td>
<td>0.2680 ± 0.0109</td>
<td>0.2718</td>
</tr>
<tr>
<td>0.1999</td>
<td>14</td>
<td>0.2</td>
<td>0.2045</td>
<td>0.1861</td>
<td>0.1892 ± 0.0075</td>
<td>0.1921</td>
</tr>
<tr>
<td>0.4844</td>
<td>0</td>
<td>0.5</td>
<td>0.5004</td>
<td>1.516</td>
<td>1.505 ± 0.018</td>
<td>1.511</td>
</tr>
<tr>
<td>0.4885</td>
<td>7</td>
<td>0.5</td>
<td>0.5031</td>
<td>1.312</td>
<td>1.332 ± 0.024</td>
<td>1.308</td>
</tr>
<tr>
<td>0.4868</td>
<td>11</td>
<td>0.5</td>
<td>0.5004</td>
<td>1.116</td>
<td>1.127 ± 0.0197</td>
<td>1.115</td>
</tr>
<tr>
<td>0.7143</td>
<td>0</td>
<td>0.75</td>
<td>0.7423</td>
<td>4.426</td>
<td>4.281 ± 0.035</td>
<td>4.228</td>
</tr>
<tr>
<td>0.7156</td>
<td>3</td>
<td>0.75</td>
<td>0.7435</td>
<td>4.123</td>
<td>4.194 ± 0.047</td>
<td>4.186</td>
</tr>
<tr>
<td>0.7167</td>
<td>5</td>
<td>0.75</td>
<td>0.7441</td>
<td>4.014</td>
<td>4.015 ± 0.045</td>
<td>3.990</td>
</tr>
<tr>
<td>0.7168</td>
<td>7</td>
<td>0.75</td>
<td>0.7435</td>
<td>3.714</td>
<td>3.771 ± 0.058</td>
<td>3.694</td>
</tr>
<tr>
<td>0.7139</td>
<td>9</td>
<td>0.75</td>
<td>0.7397</td>
<td>3.474</td>
<td>3.633 ± 0.165</td>
<td>3.452</td>
</tr>
<tr>
<td>0.8733</td>
<td>0</td>
<td>0.9</td>
<td>0.9099</td>
<td>8.580</td>
<td>8.500 ± 0.107</td>
<td>8.494</td>
</tr>
<tr>
<td>0.8761</td>
<td>7</td>
<td>0.9</td>
<td>0.9115</td>
<td>7.674</td>
<td>7.596 ± 0.102</td>
<td>7.603</td>
</tr>
</tbody>
</table>
calculations we used \((\rho_{\text{average}} \sigma^3 - \rho_{\text{bulk}} \sigma^3) \times h\), where \(h\) is half of the box length in the \(z\) direction. The theoretical and simulation values for adsorption compare well except for the highest association at a bulk density of 0.7139; the DF and IE theories are of similar accuracy for adsorption. The fraction of monomers at the wall predicted from the density functional theory is in remarkably good agreement with the simulation results.

Figures 4-3 to 4-6, compare theory against simulation results for reduced density (relative to the bulk) versus distance from the wall for the simulation average reduced number densities equal to 0.2, 0.5, 0.75, and 0.9. In Figures 4-8 through 4-10, the fraction of monomers versus distance from the wall is plotted. At each density, results are given at several site bonding energies.

Qualitatively, the simulation results behave in a well known fashion (for example, \([34, 49, 175, 185, 186\) and Chapter 5]). Briefly:

1. There are two competing effects. First, higher densities increase collision forces near the wall, increasing singlet density there.

2. As site energy increases and association rises, chain size increases. Longer chains avoid a drop in configurational entropy by avoiding the wall. Monomers suffer no drop in configurational entropy on approaching the wall, so they are affected primarily by the collision forces and tend to pile up at the wall. This effect, logically, is more pronounced for the 2-site model as opposed to the 1-site model.

3. Volume exclusion and packing effects tend to produce a layering effect at (or near at lower densities) distances of multiples of molecular diameter \(\sigma, 2\sigma, \text{etc.}\), which are dampened away as distance from the wall increases. This layering is more pronounced at higher densities and at lower amounts of association.

In Figure 4-3 we see the results for dimerizing hard spheres at a low density. The hard sphere case is presented in Figure 4-3a for comparison. Here, as in the other densities, as the temperature falls, and association increases, the theories generally follow
Figure 4-3. At a simulation average density of 0.2. Relative reduced density versus distance from a hard wall for dimerizing hard spheres from DF theory (lines), IEG theory (dashed lines) and simulations (symbols) for inverse reduced temperature of $\varepsilon_{\text{site}}/kT = 0$ (a), 7 (b), and 14 (c).
Figure 4-4. As for figure 4-3 at a simulation $\rho_{\text{average}} = 0.5$ and $\epsilon_{\text{site}}/kT = 0$ (a), 7 (b), and 11 (c).
Figure 4-5. As for figure 4-3 at a simulation $\rho_{\text{average}} = 0.75$ and $\varepsilon_{\text{site}}/kT = 0$ (a), 5 (b), 7 (c), and 9 (d).
Figure 4-6. As for figure 4-3 at a simulation $\rho_{\text{average}} = 0.9$ and $\varepsilon_{\text{site}}/kT = 0$ (a) and 7 (b).
the simulation as the wall density drops. In Figure 4-3b, the theories are both very accurate with the IE theory doing slightly better at the peak one molecular diameter from the wall. At the highest amount of association, there is desorption at the wall due to the almost complete dimerization of the fluid. At the higher densities, desorption is not possible since the higher collision energies more than make up for the entropy decrease of the dimers near the wall. Both theories are accurate at wall contact, but in Figure 1c, the DF theory fails away from the wall. Interestingly, from Table 4-2, we see that adsorption by our definition is still positive and due to cancellation of errors the DF theory is within the uncertainty of the simulation error.

At the higher densities of Figures 4-4 and 4-5, the agreement is very good to excellent. The DF theory's first peak at 1σ is slightly offset with the error increasing at higher association. At the higher density of Figure 4-5, much of the offset seems to originate with the original Tarazona Mark II DF theory for hard spheres. At the lower density the IE theory has some error at wall contact. This is to be expected since this approach reproduces the PY equation of state. Also as expected, the wall contact discrepancy increases at higher densities with a 20% error at the average density of 0.75 of Figure 4-5. Note in Figure 4-4 that for the IE theory the wall contact actually gets better at the higher amount of association. This increased success could be explained by mutual compensation of errors from the PY approximation and those from the association portion of the theory. However, the compensation is not uncontrollable, since it affects only the contact position and not the overall shape of the curves. The error of the PY approximation near contact does not prevent us from obtaining [179] accurate adsorption numbers or from predicting the enhancement-depletion transition correctly (see the tables).

At the highest density in Figure 4-6, the trends seen in Figures 4-4 and 4-5 continue. The Tarazona method for hard spheres has appreciable offset in position and magnitude in the peaks (except wall density) for the hard spheres. This offset remains
without further error when the site energy is 7 and two-thirds of the spheres are dimerized. The IE theory has almost 30% error in wall contact and there is some error at the peak of 1σ. However, the IE theory is more accurate than the DF theory at more than 0.75σ away from the wall and is very accurate beyond 1.5σ: on the whole for density profiles of dimerizing hard spheres, the DF theory is more accurate at less than 0.75σ. We must note for completeness that we could have used a semi-empirical correction [128] or adjustable parameter [56] to remedy the wall density inconsistency in the IE theory, but we neglected to do so in this comparison.

Figure 4-7 has fraction of monomers versus distance from a hard wall for the average number densities studied for dimerizing hard spheres. The symbols represent simulation data and the lines represent the DF theory from equations (4-29) and (4-31). The number of monomers is always enhanced at the walls as compared to the bulk due to lack of entropy loss on approaching the surface. The agreement is very good, except for a small error around 1σ for the high density case shown in Figure 4-7c.

The cusp in the fraction of monomers curve at z=σ is due to the nature of the integral in equation (4-29) and an approximation of bonding only at hard sphere contact. If molecule 1 is within a molecular diameter of the wall (z_1 < σ), the integrand is zero for some positions of molecule 2 due to the excluded volume of the wall.

Table 4-3 has results at a couple of average densities for M=2 and n=1. The reported bulk pressures were calculated from bulk densities using Wertheim's theory [6-8, 10]. Other results were found as described for Table 4-2 above. Qualitatively, the results are similar to that of the dimerizing spheres. Since longer chains can be formed, however, wall density depression on association is greater than that which occurs with dimerizing spheres. The wall theorem was satisfied within the uncertainty of the simulations. The theoretical and simulation values for adsorption compare well and, for the associating cases, are within one standard deviation of the simulation results. Fraction of monomers at the wall for the high density case is not very accurate, as we shall expand upon when
Figure 4-7. Fraction of monomers versus distance from a hard wall for dimerizing hard spheres from DF theory (lines) and simulations (symbols) for $\rho_{\text{average}} = 0.2$ and $\varepsilon_{\text{site}}/kT = 7$ (upper) and 14 (lower) (a), simulation $\rho_{\text{average}} = 0.75$ and $\varepsilon_{\text{site}}/kT = 5$ (upper), 7 (middle), and 9 (lower), (b), and simulation $\rho_{\text{average}} = 0.5$ and $\varepsilon_{\text{site}}/kT = 7$ (upper), 11 (lower), and for $\rho_{\text{average}} = 0.9$ and $\varepsilon_{\text{site}}/kT = 7$ (middle) (c).
Table 4-3: Theory versus Simulation for 2-Sited Hard Spheres

<table>
<thead>
<tr>
<th>Bulk density, $\rho_{bulk} \sigma^3$</th>
<th>Site energy, $\epsilon_{site} / kT$</th>
<th>Average box density, $\rho_{average} \sigma^3$</th>
<th>Bulk Pressure, $P$</th>
<th>Wall density, $\rho \sigma^3$</th>
<th>Adsorption, $\Gamma \sigma^2$</th>
<th>$\chi_0$, Fraction of monomers at wall</th>
</tr>
</thead>
<tbody>
<tr>
<td>simulation</td>
<td>DF theory</td>
<td>simulation</td>
<td>DF theory</td>
<td>simulation</td>
<td>theory, DF / II</td>
<td>simulation</td>
</tr>
<tr>
<td>0.1976</td>
<td>0</td>
<td>0.2</td>
<td>0.2011</td>
<td>0.3052</td>
<td>0.3068 ± 0.0044</td>
<td>0.0258 ± 0.0036</td>
</tr>
<tr>
<td>0.2084</td>
<td>11</td>
<td>0.2</td>
<td>0.2055</td>
<td>0.1018</td>
<td>0.0970 ± 0.0130</td>
<td>0.1027</td>
</tr>
<tr>
<td>0.3420</td>
<td>0</td>
<td>0.35</td>
<td>0.3512</td>
<td>0.7419</td>
<td>0.7455 ± 0.0083</td>
<td>0.7428</td>
</tr>
<tr>
<td>0.3449</td>
<td>8</td>
<td>0.35</td>
<td>0.3499</td>
<td>0.4475</td>
<td>0.4604 ± 0.0378</td>
<td>0.4481</td>
</tr>
<tr>
<td>0.7146</td>
<td>0</td>
<td>0.75</td>
<td>0.7427</td>
<td>4.262</td>
<td>4.276 ± 0.0482</td>
<td>4.232</td>
</tr>
<tr>
<td>0.7177</td>
<td>6</td>
<td>0.75</td>
<td>0.7435</td>
<td>3.429</td>
<td>3.456 ± 0.076</td>
<td>3.411</td>
</tr>
</tbody>
</table>
discussing Figure 4-11 below.

See Table 4-4 for the number- \((= \frac{\sum N_i l_i}{\sum N_i})\) and weighted-
\((= \frac{\sum N_i l_i^2}{\sum N_i l_i})\) average chain lengths of our two-sited fluids in the bulk. As an
input to the IE theory, the first number is more important. From Wertheim's 1st order
perturbation theory [6(d)], the number-average chain length completely determines the
Helmholtz free energy in the bulk and the chain length varies with the change in free
energy as the wall is approached.

<table>
<thead>
<tr>
<th>Bulk density (\rho_{bulk})</th>
<th>Site energy (\epsilon_{site}) / kT</th>
<th>Number-average chain length</th>
<th>Weight-average chain length</th>
</tr>
</thead>
<tbody>
<tr>
<td>(0.2084)</td>
<td>11</td>
<td>5.0674 ± 0.2326</td>
<td>11.309 ± 0.4713</td>
</tr>
<tr>
<td>(0.3449)</td>
<td>8</td>
<td>2.1938 ± 0.0696</td>
<td>3.8046 ± 0.2064</td>
</tr>
<tr>
<td>(0.7177)</td>
<td>6</td>
<td>1.7871 ± 0.0204</td>
<td>2.8619 ± 0.0833</td>
</tr>
</tbody>
</table>

Figures 4-8 to 4-10 compare theory against simulation results for reduced density
(relative to the bulk) versus distance from the wall for the simulation average reduced
number densities equal to 0.2, 0.35 and 0.75. Figure 4-11 plots the fraction of monomers
versus distance from the wall.

In Figure 4-8 we see the results for chain-forming hard spheres at a very low
density. The hard sphere case is presented in Figure 4-8a for comparison. Here, as for the
dimerizing hard spheres, as the temperature falls, and association increases, the theories
generally follow the simulation as the wall density drops. In Figure 4-8b the density is low
enough and the site energy is high enough for there to be desorption at the wall. The DF
theory is very accurate near the wall while the IE theory is inaccurate. It is difficult to
make a strong conclusion about the profiles from 0.5\(\sigma\) to 1.5\(\sigma\) away from the wall. The
density curves lie inside or near the error bars, which stand for one standard deviation,
Figure 4-8. At a simulation average density of 0.2, relative reduced density versus distance from a hard wall for 2-sited hard spheres (chain-forming) from DF theory (lines), IE theory (dashed lines) and simulations (symbols) for inverse reduced temperature of $\varepsilon_{\text{site}}/kT = 0$ (a), and 8 (b).
Figure 4-9. As for figure 4-8 at a simulation $\rho_{\text{average}} = 0.35$ and $\varepsilon_{\text{site}}/kT = 0$ (a) and 8 (b). At a simulation average density of 0.35.
Figure 4-10. As for figure 4-8 at a simulation $\rho_{\text{average}} = 0.75$ and $\varepsilon_{\text{site}}/kT = 0$ (a) and 6 (b).
Figure 4-11. Fraction of monomers versus distance from a hard wall for 2-sited hard spheres from DF theory (lines) and simulations (symbols) for $\rho_{\text{average}} = 0.2$ and $\varepsilon_{\text{site}}/kT = 11$ (lower) $\rho_{\text{average}} = 0.35$ and $\varepsilon_{\text{site}}/kT = 8$ (middle) and $\rho_{\text{average}} = 0.75$ and $\varepsilon_{\text{site}}/kT = 6$ (upper).
but the standard deviations are very high. There is some evidence that the simulation may not have reached equilibrium even after running for seven billion configurations, since the profile is changing, albeit very slowly, to push the simulation profile near $1\sigma$ up toward the theories' results. This simulation may be revisited in future work.

In Figure 4-9b, the DF theory is more accurate than the IE theory throughout most of the density profile. As found earlier [175] for monodisperse molecules of chain length of 3 or more, not accounting for intramolecular interactions may be spoiling the density profile accuracy of the IE theory at low densities. However, our DF theory, which also does not account for intramolecular interactions, is affected very little in accuracy.

At the higher density of Figure 4-10, both the IE and DF theories are fairly accurate. As for the dimerizing hard spheres at higher densities, the IE theory is inaccurate at wall contact, while the DF theory is very accurate. The other peak positions, however, are represented very accurately by the IE theory, unlike the DF theory. Part of the error of the DF theory originates with the hard sphere Tarazona method. Also, the Tarazona weighting does not account correctly for the change in structure on association. The DF theory is more accurate at less than $0.5\sigma$ (as compared to $0.75\sigma$ for dimerizing hard spheres), while the IE theory is more accurate outside that distance.

Figure 4-11 shows fraction of monomers versus distance from a hard wall for the 2-site hard sphere/hard wall problem. The lowest density case is very accurate except for the region closest to the wall. Much of this error stems from the theory density calculated from the DF theory. If the simulation densities are used as input for equation (4-29), the theory fraction of monomers at the wall is just outside one standard deviation from the simulation results. The middle density case shows very good accuracy against the DF theory. The highest density case is of only fair accuracy. The slightly low theory density for much of the first $0.4\sigma$ from the wall caused much of the overestimation of fraction of monomers near the wall. However, using simulation densities as input to equation (29) did little to improve the accuracy near the $1\sigma$ area. Note that the one dimerizing case
with the most error for fraction of monomers was also the high density, high association case.

4.5 Conclusions

We presented a perturbation density functional theory for inhomogeneous associating fluids (IAFs) consisting of \( M \) symmetrically located associating sites on hard spheres. We tested the theory for \( n = M = 1 \) and \( M = 2 \), \( n = 1 \) (\( n \) is number of bonding sites on one sphere which a site on another sphere is eligible to bond to) and obtained good to excellent agreement with computer simulations at a broad range of densities and bond energies for the density profiles of these fluids near a hard, smooth wall. This could be especially advantageous since the theory computationally runs 1000 to 10000 times faster than the simulations. We also began to evaluate the accuracy of the HAB IE theory for polydispersive systems.

For the one-site model, both theories were of very good to excellent accuracy for density profiles with the exception of the qualitative results of the DF theory when there was a slight amount of desorption. On the whole the DF theory was slightly better inside of 0.75\( \sigma \), while the IE theory had better peak positions and amplitudes outside that point. As with the Tarazona DF for hard spheres, there was some deterioration in DF theory accuracy at higher densities.

For chain-forming fluids relative accuracy of the two theories was qualitatively similar to that of the dimerizing fluid except at low densities where the HAB IE theory was of less accuracy throughout the density profile. Also, as with the dimerizing fluids, due to the PY equation of state used, IE densities at the wall did not agree with simulation bulk pressures, especially at higher densities. For the hard chains, accuracy for the IE theory against simulations for a polydisperse fluid of a certain number-average chain length in the bulk was qualitatively similar to that of the theory against simulations of a fixed chain length fluid [175] in that accuracy was fairly low at low densities and fairly
high at higher densities except at wall contact. It would be interesting to elucidate the role of polydispersity by performing simulations of monodisperse systems at the same bulk number-average density as the systems in the present work. Also, it should be noted, in fairness, that we can only be conclusive at the fairly short number-average chain-lengths of Figures 4-9 and 4-10. For longer chains, preliminary indications from Figure 4-8 are that the DF theory is very accurate inside of 0.5σ and the IE theory is of qualitative accuracy. From Figure 4-8 and some work we did at a high density (not shown here), outside of 0.5σ accuracy is at least qualitative for longer chains.

Wertheim's first order perturbation theory [6, 9] predicts that the activity of a site is independent of the bonding state of other sites on the same molecule. It would be expected that the possibility of interaction between sites on one molecule would increase as the number of sites on that molecule increases. Interestingly, in terms of the general accuracy of Wertheim's theory and the applicability of Tarazona's weighting for various structures (chains, cluster, etc.), in the DF theory used here, there was only a marginal dropoff in density profile accuracies between the one-site and 4-site theories [191]. This conclusion about the DF theory also holds in going from dimerizing hard spheres to linear chain-forming hard spheres, at least for fairly short chains. More data is needed to make a determination for longer linear hard chains (accuracy for long linear hard chains may be improved if TPT-D were used [97, 98].) If we combine these results with those for the 4-site fluid [191] at supercritical conditions, we find that the DF theory results are very good to excellent when there is adsorption. When the passage from adsorption to desorption is reached, accuracy is qualitative to fair at best. However, accuracy improves markedly and becomes very good again as desorption increases.

We also calculated fraction of monomers profiles from the DF theory and compared the results with our MC simulations. Some of the DF theory error in density is lost when calculating fraction of monomers. The key equation in calculating fraction of
monomers. Equation 4-29, is more than slightly inaccurate only near the 1σ region at high average densities.

These approaches are fairly easily implemented examples of DF and IE theories for attacking a complex fluid and yet the results should be adequate for many problems. At least a portion of the difference between the simulations and the DF theory originated in the original Tarazona Mark II [53] DF theory. Therefore, it may be advantageous to try the same procedure with other weighted DF approximations including those for more realistic potentials. The Tarazona theory for LJ spheres is also accurate [149]. For cores which can overlap, applying our weighting approach to Tarazona's LJ theory should be a fairly straightforward extension. Thus, the extension to active surfaces, which we will take up in future work, should be simpler than that attempted with other density functional theories of IAFs.
5. The Associating 4-site Hard Sphere Fluid

5.1 Introduction

We continue the work begun in Chapter 4 by studying the 4-site model. We use a particular model originally proposed by Bol [189], in which four highly anisotropic square-well sites are placed in tetrahedral symmetry on a spherical hard core surface. By far the most ubiquitous molecule which this may represent is water. Kolafa and Nezbeda [190] performed simulations for a similar model and Nezbeda et. al. [82] tested the results against Wertheim's first order perturbation theory. With more extensive testing, Gharasgi and Chapman [5] confirmed the accuracy of Wertheim's theory against simulation for Bol's model in the bulk. This model is more complex than most of the other simple associating molecular models studied, bringing in the formation of clusters as well as linear chains and rings. The density profile and structure of this fluid in the nonuniform state was recently studied theoretically by Segura et. al. [191], who used the DF theory presented below and by Vakari et. al. [192], who used an integral equation theory.

Our potential model is not a complete model for water since long range attraction and multipolar interactions have been omitted. Qualitatively, however, the model is similar to the point-charge models used in simulation studies of water and aqueous solutions [65, 101]. Therefore, we expect this model to serve either as a first approximation to real fluid behavior or as a reference for more complex, realistic fluids. For instance, very recently, Müller and Gubbins [193] used Wertheim's theory for a Lennard-Jones version of this four site model in the bulk. Dipole interactions were added as a simple perturbation. The results were accurate for water pressure, vapor and liquid density, and internal energy of vaporization except near the critical region.

In the work described here, we perform Monte Carlo simulations of the Bol model against a hard wall. We then combine the results of Tarazona with Wertheim's theory to
form two perturbation DF theories for a fluid of associating 4-sited hard spheres against a hard wall. The first method, Method 1, which we introduce here, is a density functional using the inhomogeneous form of Wertheim's theory. Method 2 is the method introduced in Chapter 4. After presenting our fluid model and theories, we compare the theoretical results for density with those from molecular simulations. We use the second method, the more accurate of the two theories near the wall, to compare density and fraction of monomers profiles and adsorption against simulations. To look at density functional accuracy versus the accuracy of our monomer fraction theory, we use our simulation densities to look at the number of molecules bonded at 0, 1, 2, 3, or 4 sites. Finally, we discuss applicability to other fluids and surfaces.

5.2 Simulations

The simulations were done in a similar manner to that described in Chapter 4. Simulations in this study were performed in the canonical (constant NVT) ensemble, using the Metropolis Monte Carlo algorithm [180]. The pair potential model is defined by [5]

\[
\phi(r, \omega_1, \omega_2) = \phi_s(r) + \sum_A \sum_C \phi_{AC} (r, \omega_1, \omega_2),
\]

(5-1)

where \( r \) is the magnitude of the vector \( r \) connecting the centers of molecules 1 and 2 and \( \omega_1 \) and \( \omega_2 \) are the orientations of molecules 1 and 2 relative to vector \( r \). \( \phi_s \) is the reference potential; the reference hard sphere potential is defined by

\[
\phi_R(r) = \begin{cases} 
0 & \text{if } r > \sigma, \\
\infty & \text{if } r < \sigma.
\end{cases}
\]

(5-2)
where \( \sigma \) is the hard sphere diameter. \( \phi_{AC} \) represents the association potential. The association potential is modeled by an anisotropic short range square well. A and C represent the sites on two interacting molecules. The potential of interaction due to these sites is

\[
\phi_{AC}(r, \omega_1, \omega_2) = \begin{cases} 
-\varepsilon_{AC} & \text{if } r < r_c; \theta_{A1} < \theta_c; \text{ and } \theta_{C2} < \theta_c \\
0, & \text{otherwise.} 
\end{cases} 
\] (5-3)

where \( \theta_{A1} \) is the angle made by the vector from the center of molecule 1 to site A and the vector \( r \) and \( \theta_{C2} \) is the angle made by the vector from the center of molecule 2 to site C and the vector \( r \). See Figure 5-1. The model selected in this work has 4 bonding sites labeled A, B, C, and D placed in tetrahedral symmetry around a spherical core. Only AC, BC, AD, and BD bonding between different molecules is allowed. The square well depth for association bonding is \( \varepsilon_{AC} = \varepsilon_{BD} = \varepsilon_{BD} = \varepsilon_{DC} \), and \( \varepsilon_{AA} = \varepsilon_{BB} = \varepsilon_{CC} = \varepsilon_{DD} = \varepsilon_{AB} = \varepsilon_{CD} = 0 \). In effect, if two eligible bonding sites are close enough and oriented correctly, then a bond is formed. The bonding in this model is therefore similar to water. In the simulations the radial limits of the square well association were set to \( r_c = 1.05\sigma \). The angular limit was set to \( \theta_c = 270^\circ \).

The simulation cell consists of hard walls at \( z = 0 \) and \( z = H \); see Figure 4-2. Periodic boundary conditions with boxlength \( L \) were imposed in the other two directions. Generally, \( H = \alpha^2 \times L; \alpha > 1 \), to ensure that the density oscillations died away in the central region. Therefore, the two walls did not interfere with each other. For the results reported in Table 5-1, \( \alpha = 2 \) except for the two highest temperature cases for the highest packing fraction of Table 5-1, where \( \alpha = 4 \). In addition to the pair potential on the particles, the walls exerted an external potential of
\[ \phi_{\text{tr}}(z) = \begin{cases} \infty & \text{if } z \leq 0 \text{ or } z \geq H \\ 0 & \text{otherwise.} \end{cases} \] (5-4)

![Diagram of a 4-site association potential model](image)

Figure 5-1. Sketch of the angular and distance dependence of the 4-site association potential model

Each simulation was started by placing \( x \) hard spheres in a face-centered lattice arrangement in a cube with sides of length \( L \). The particles were randomly displaced for approximately \( 10 \times 10^4 \) configurations with a conventional Monte Carlo NVT simulation. Then in a new simulation (\( \alpha \)-1) periodic images of the resulting cell were created and placed side by side with the original cell, resulting in an elongated cell of length \( H \) in the \( z \) direction. The number of particles was then equal to \( N = \alpha^*x \). Four bonding sites were placed on each particle in the tetrahedral symmetry mentioned earlier. Random orientations were given to each particle. As described by Allen and Tildesley [181] and
Ghonasgi and Chapman [5], each particle was chosen in turn, displaced within the rectangular box and reoriented. The orientation and displacement parameters were chosen such that the two parameters each had an acceptance probability of 60 to 70%. giving an overall acceptance rate of 30 to 50%. Z-dependent properties were calculated by accumulating averages in slices of width of approximately 0.03σ. Since these were

**Table 5-1: NVT Monte Carlo simulation input parameters for hard spheres with four square well bonding sites against a planar wall**

<table>
<thead>
<tr>
<th>Average packing fraction, n_ave</th>
<th>Average reduced density, ρσ³</th>
<th>Number of molecules, N_ave</th>
<th>x 10⁻⁵</th>
<th>ε/kT</th>
<th>H. box length in z direction, σ</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1027</td>
<td>0.2</td>
<td>500</td>
<td>5</td>
<td>0</td>
<td>21.544</td>
</tr>
<tr>
<td>0.1027</td>
<td>0.2</td>
<td>500</td>
<td>10</td>
<td>3</td>
<td>21.544</td>
</tr>
<tr>
<td>0.1027</td>
<td>0.2</td>
<td>500</td>
<td>25</td>
<td>5</td>
<td>21.544</td>
</tr>
<tr>
<td>0.1027</td>
<td>0.2</td>
<td>500</td>
<td>65</td>
<td>7</td>
<td>21.544</td>
</tr>
<tr>
<td>0.2618</td>
<td>0.5</td>
<td>500</td>
<td>15</td>
<td>0</td>
<td>15.874</td>
</tr>
<tr>
<td>0.2618</td>
<td>0.5</td>
<td>500</td>
<td>15</td>
<td>3</td>
<td>15.874</td>
</tr>
<tr>
<td>0.2618</td>
<td>0.5</td>
<td>1000</td>
<td>35</td>
<td>5</td>
<td>20.000</td>
</tr>
<tr>
<td>0.2618</td>
<td>0.5</td>
<td>1000</td>
<td>100</td>
<td>7</td>
<td>20.000</td>
</tr>
<tr>
<td>0.3927</td>
<td>0.75</td>
<td>500</td>
<td>15</td>
<td>0</td>
<td>13.867</td>
</tr>
<tr>
<td>0.3927</td>
<td>0.75</td>
<td>500</td>
<td>15</td>
<td>3</td>
<td>13.867</td>
</tr>
<tr>
<td>0.3927</td>
<td>0.75</td>
<td>500</td>
<td>35</td>
<td>5</td>
<td>13.867</td>
</tr>
<tr>
<td>0.3927</td>
<td>0.75</td>
<td>1000</td>
<td>100</td>
<td>7</td>
<td>17.472</td>
</tr>
<tr>
<td>0.493</td>
<td>0.942</td>
<td>1000</td>
<td>25</td>
<td>0</td>
<td>25.705</td>
</tr>
<tr>
<td>0.493</td>
<td>0.942</td>
<td>1000</td>
<td>30</td>
<td>3</td>
<td>25.705</td>
</tr>
<tr>
<td>0.493</td>
<td>0.942</td>
<td>500</td>
<td>75</td>
<td>5</td>
<td>12.853</td>
</tr>
<tr>
<td>0.493</td>
<td>0.942</td>
<td>1000</td>
<td>150</td>
<td>7</td>
<td>16.193</td>
</tr>
</tbody>
</table>

inhomogeneous fluids the acceptance criterion of 30 to 50% was forced to hold for collections of bins along the z axis, especially and including the collection of all bins within 0.25σ of either wall, where the density was highest in most of the cases run.

Systems were equilibrated for at least 5 x 10⁶ steps at moderate densities with no bonding energy and for 2000 x 10⁶ steps at the highest densities and bonding energies. Each equilibrated configuration was used as the starting configuration of a series of further runs. Each series consisted of 10 runs of from 5 x 10⁶ configurations each for moderate
densities and little association to $150 \times 10^6$ configurations each at the highest density with high amounts of association. The subaverages of properties from each run of a series were used to calculate averages. A final average was then calculated by averaging the properties of each bin on one side of the cell midpoint with its geometrically symmetrical twin. The number of configurations, $N_{av}$, performed for each subaverage calculation is listed in Table 5-1.

These complex systems require a very large amount of computer time to equilibrate. The longer runs took 4 to 6 weeks of CPU time on an IBM RS/6000 Model 340 workstation. We were careful to monitor the simulations for metastable states by, for example, checking the symmetry of the density profile after each subaverage calculation. Several times molecules did get stuck in one configuration, requiring a small adjustment in configuration parameters and a restart of the simulation with the metastable configuration and previous configurations being deleted from the final calculations of averages.

Criteria used for determining if equilibration had been reached at the end of a series of simulations were: 1) having a 5% standard deviation or less for wall densities. 2) degree of symmetry of the density profile on each side of the cell midpoint up to each wall, 3) stability of bulk density from run to run, 4) agreement between the ensemble average simulation wall density and the theoretical bulk pressure and 5) isotropic conditions in the bulk region as determined from the orientation tensor, $B_{j,k,k}$, which is defined below. Item 4 makes use of the relation $\rho_{wall} = P_{bulk} / kT$ [17]. Theoretical bulk pressure was calculated for the middle 20% to 40% of the cell by using the simulation bulk density and the bulk theoretical relations of Ghonasgi and Chapman [5].

Densities were calculated in each slice by counting molecules in each slice and dividing by the slice volume. Wall densities were determined by extrapolating a curve fit of log density versus distance from the wall for the five slices nearest the wall. Other wall properties were linearly curve fitted. Weighted-average cluster size, orientation factor,
and fraction of molecules bonded at n (n=0, 1, 2, 3, or 4) sites were determined for each slice and in the bulk. Weighted-average cluster size for slice s is defined as

\[ W_{c,s} = \frac{\sum_{i=1}^{N_c} n_{i,s} \cdot W_i}{N_s} \]

where \( N_c \) is the number of clusters which are wholly or partially contained in slice s, \( n_{i,s} \) is the number of molecules in slice s which make up part or all of cluster i, \( W_i \) is the total number of molecules in the simulation cell which make up cluster i, and \( N_s \) is the total number of molecules in slice s. We can define unit vectors from the center of each molecule to each of the molecule's sites in the cell-based coordinate system. The coordinates of each unit vector can be broken into x, y, and z values. The average orientation tensor for site k (A, B, C, or D) in slice s in coordinate direction j is defined as

\[ B_{j,s,k} = \frac{1}{N_s} \sum_{i=1}^{N_s} e_{i,j,s,k}^2 - \frac{1}{3} \]

where \( e_{i,j,s,k} \) is the length of the j coordinate of the unit vector to the ith k site of the molecules in slice s. Thus, for the completely random orientation expected in the bulk, we would expect \( B_{j,bulk,k} = 0 \) for any site k (A, B, C, or D).

The study was done at several packing fractions (\( \eta = \pi \rho \sigma^3 / 6 \)). At packing fractions of 0.1047, 0.2618, 0.3927, and 0.493 the association energy (square well depth) was increased from 0 to 3. 5, and then 7kT

5.3 4-site HSHW Theories

As we began the theory description in Chapter 4 and assuming our fluid is inhomogeneous in only the z direction perpendicular to the wall, the grand potential is written (here written as per unit area) [53]

\[ \Omega [\rho(z)] = A [\rho(z)] + \int \rho(z) [\phi_W(z) - \mu] dz, \]

(5-5)
where \( \rho(z) \) is the singlet molecular number density, \( A[\rho(z)] \) is the intrinsic Helmholtz free energy functional, \( \phi_W(z) \) is the external potential, and \( \mu \) is the chemical potential. We first describe the Tarazona method for hard spheres and follow with two methods for the addition of the excess free energy of association from Wertheim's theory. We introduce Method 1 first, which uses the inhomogeneous form of Wertheim's theory. We then outline Method 2, which is the DF theory given in Chapter 4, but for four sites. The intrinsic Helmholtz free energy functional can be broken into the sum of an ideal and an excess part.

\[
A[\rho(z)] = A^{id}[\rho(z)] + A^{ex}[\rho(z)].
\]  

(5-6)

The ideal functional is known exactly [149]. In Tarazona's approach, the excess free energy functional is approximated using the weighted or smoothed density approximation [150],

\[
A^{ex}[\rho(z)] = \int \rho(z) f(\tilde{\rho}(z)) dz,
\]  

(5-7)

where \( f \) is the excess (over ideal gas) free energy per molecule and the smoothed density is given by [148]

\[
\tilde{\rho}(z) = \int \rho(z') \omega(|z - z'|; \bar{\rho}(z)) dz'
\]  

(5-8)

and \( \omega \) is the Tarazona weighting function given in [148-150] and in Chapter 6. By formally minimizing the grand potential (at equilibrium, \( \delta \Omega / \delta \rho(z) = 0 \), we obtain

\[
\rho(z) = \exp[\beta(\mu - \phi_W(z) - \lambda(z))],
\]  

(5-9)

\[
\mu = \mu^{\mathrm{ex}} + kT \ln(\rho_{\mathrm{bulk}}),
\]  

(5-10)

and
\[ \lambda(z) = \tilde{f}(\bar{\rho}(z)) + \int \frac{\delta \rho(z')}{\delta \rho(z)} \rho(z') \tilde{f}'(\bar{\rho}(z')) dz'. \]  

(5-11)

where \( \beta \) is \( 1/kT \), \( \mu^{\infty} \) is the bulk excess chemical potential, \( \rho_{\text{bulk}} \) is the bulk density, and \( \tilde{f}' \) is the derivative of \( \tilde{f} \) with respect to \( \bar{\rho} \).

Thus far, we have restated exactly the Tarazona Mark II DF theory [53] for hard spheres. We do this in an almost identical manner as in Chapter 4, but we include it here for the sake of continuity. This approach is very successful for hard and LJ spheres confined in hard slits [149]. We would now like to add the effects of intermolecular association. Two methods have been studied.

**Method 1. The inhomogeneous form of Wertheim's theory.** As Chapman [9] and later Kierlik and Rosinberg [54] noted, the first order perturbation solution to Wertheim's AF theory is general for inhomogeneous fluids. We can apply Wertheim's AF functional as a perturbation to a reference fluid free energy functional, such as Tarazona's hard sphere free energy functional. As mentioned earlier, Kierlik and Rosinberg [54-57] have also used Wertheim's free energy functional, but only for the formation of chains in the limit of complete association. We are interested in the full range of association as system temperature changes. Other differences between what we are doing here and what KR did is our less accurate, although much simpler, expression for the radial distribution function at contact, and the use of the Tarazona reference DF. The excess Helmholtz free energy functional is written as [9]

\[ A^{\infty} [\rho(z)] = A^{\infty, hs} [\rho(z)] + A^{\text{assoc}} [\rho(z)], \]  

(5-12)

where \( hs \) and \( assoc \) denote the hard sphere and association terms, respectively. The hard sphere term, analogous to equation (5-7), is
\[ \mathcal{A}^{\text{assoc}}[\rho(z)] = 4kT \int \rho(z) \ln \chi_A(z) - \chi_A(z) / 2 + 0.5 \, dz, \]  
\[ \text{(5-14)} \]

For spherical molecules with four association sites, the association term is given by [5, 6, 9, 10]

\[ \mathcal{A}^{\text{assoc}}[\rho(z)] = 4kT \int \rho(z) \ln \chi_A(z) - \chi_A(z) / 2 + 0.5 \, dz, \]  
\[ \text{(5-14)} \]

where \( \chi_A(z) \) is the fraction of molecules at position \( z \) not bonded at site \( A \). For \( \chi_A(z) \) we use the iterative equation from Wertheim's theory which we derived in Chapter 4 with \( n=2 \).

\[ \chi_A^{i+1}(z_1) = \frac{1}{1 + 4 \pi K g_{hs}(\sigma; \rho_{\text{bulk}}) f_{AC} \int_{-1+z_1}^{1+z_1} \chi_A'(z_2) \rho(z_2) \, dz}, \]  
\[ \text{(5-15)} \]

where \( i \) is the iteration counter, \( K \) is a constant that measures the volume available for bonding of sites \( A \) and \( B \) on molecules 1 and 2 (here this is \( 0.25(1 - \cos(\theta_c))^2 \sigma^2 (r_c - \sigma) \)) and \( f_{AC} \) is a Mayer \( f \) function, \( \exp[e_{AC}/kT] - 1 \). In equation (5-15) we neglected the orientation dependence of \( \chi_A(z) \) and approximated the pair correlation function for the inhomogeneous fluid by assuming that \( g_{hs}(z_1, z_2, \sigma) = g_{hs}(\sigma; \rho_{\text{bulk}}) \) [22, 128, 188], where \( g_{hs}(\sigma; \rho_{\text{bulk}}) \) is the hard sphere pair correlation function at contact in the bulk. Also, we implicitly assumed that all four association sites are available for bonding regardless of the distance from the hard wall. Actually, for the 4-site fluid at least one site will be sterically unavailable for spheres very close to the wall. Due to the symmetry of the sites on the sphere, we can write the fraction of monomers from equation (4-31) as

\[ \chi_0(z_1) = \chi_A^4(z_1), \]  
\[ \text{(5-16)} \]
When we minimize the grand potential with respect to the density profile, we obtain the equations

$$\rho(z) = \exp[\beta(\mu - \phi_w(z) - \lambda(z))],$$  \hspace{1cm} (5-9)

$$\mu = \mu^{\text{hs}} + \mu^{\text{assoc}} + kT \ln(\rho_{\text{bulk}}),$$  \hspace{1cm} (5-17)

and

$$\lambda(z) = E^{\text{hs}}(\rho(z)) + \int \frac{\delta \rho(z')}{\delta \rho(z)} \rho(z') (E^{\text{hs}})'(\rho(z')) dz' + \frac{\delta A^{\text{assoc}}[\rho(z')]}{\delta \rho(z)}.$$  \hspace{1cm} (5-18)

Equations (5-17) and (5-18) are analogous to equations (5-10) and (5-11). All the hard sphere terms are calculated from the equation of state of Carnahan and Starling [147, 187]. For the association portion of the chemical potential, which is fixed by the bulk density and the site bonding energy, $\varepsilon_{AC}/kT$, we have

$$\mu^{\text{ex,assoc}} = 4kT(\ln \chi_A^{\text{bulk}} - 0.5\chi_A^{\text{bulk}} + 0.5) + 4kT \rho_{\text{bulk}} \frac{\partial \chi_A^{\text{bulk}}}{\partial \rho_{\text{bulk}}}(1/\chi_A^{\text{bulk}} - 0.5),$$  \hspace{1cm} (5-19)

where [5]

$$\chi_A^{\text{bulk}} = \frac{1}{1 + 2 \rho_{\text{bulk}} \chi_A^{\text{bulk}} \Delta}$$  \hspace{1cm} (4-18)

and $\Delta$ is approximated by $4\pi K_g^{\text{hs}}(\sigma; \rho_{\text{bulk}}) f_{AC}$.

Equation (5-9) was solved with a Picard type iterative method [15]. To maintain stability, less than 10 percent of the new solution was mixed with the old solution, with lower percentages used at higher average densities. Less than 500 iterations were needed
for all except the highest density. To speed up calculations, the density profile for the next lowest association energy at the same density was used as the initial density profile. For the cases with no association, any good predictor of the hard sphere density at a hard wall can be used for the initial density profile. We used the parametrization of Henderson and Plischke [128]. The individual terms within the integral of equation (5-18) are analytic. The integral in equation (5-18) was solved by a trapezoidal rule: a mesh width of $0.01\sigma$ was found to give sufficient numerical accuracy. The last term in equation (5-18), the functional derivative, was evaluated numerically.

**Method 2. The bulk form of Wertheim's theory with Tarazona weighting.** Method 1 requires the solution of two integral equations. A simpler approach would apply a weighted DF theory to the bulk equation of state for AF's. Since the hard sphere and association interactions are of similar range, we might expect that a single weighted density could be used for both the hard sphere and association terms. Since no weighting function has been previously proposed for this case, we choose to use a weighting which is accurate in the limit of no association. In the limit of no association, our theory is exactly Tarazona Mark II [53] for hard spheres. In our approach, we apply Tarazona's weighting to both the bulk hard sphere and association free energy terms.

We use equations (5-9), (5-11), (5-17), (5-19), and (4-18) with $\mathcal{F} = \mathcal{F}^{hs} + \mathcal{F}^{assoc}$. The hard sphere terms are obtained from an equation of state [147, 187]. For the association portion of the free energy, we use the bulk relations of Ghonasgi and Chapman [5],

$$\mathcal{F}^{assoc}[\rho(z)] = 4kT(\ln \frac{\chi_A(z)}{1 + 2\rho(z)\chi_A(z)\Delta})$$  \hspace{1cm} (5-20)

and

$$\chi_A(z) = \frac{1}{1 + 2\rho(z)\chi_A(z)\Delta}. \hspace{1cm} (5-21)$$
where weighted reduced density and weighted fraction of molecules not bonded at site A are substituted for the normal bulk terms of Ghoniasgi and Chapman [5] and \( \Delta \) this time is \( 4\pi K g_{\alpha\beta}(\sigma; \bar{\rho}(z)) f_{AC} \). The fraction of monomers is again calculated using equations (5-15) and (5-16). Wertheim's first order perturbation theory predicts that the activity of a site is independent of the bonding state of other sites on the same molecule. Based on this, Ghoniasgi and Chapman [5] have derived the following equations for \( \chi_n(z_1) \), the fraction of molecules bonded at \( n \) sites at distance \( z_1 \) from an ideal wall:

\[
\begin{align*}
\chi_0(z_1) &= \chi_0^4(z_1) & (5-16) \\
\chi_1(z_1) &= 4\chi_0^4(z_1)(1 - \chi_0(z_1)) & (5-22) \\
\chi_2(z_1) &= 6\chi_0^2(z_1)(1 - \chi_0(z_1))^2 & (5-23) \\
\chi_3(z_1) &= 4\chi_0(z_1)(1 - \chi_0(z_1))^3 & (5-24) \\
\chi_4(z_1) &= (1 - \chi_0(z_1))^4. & (5-25)
\end{align*}
\]

The same iterative scheme used for Method 1 was used to obtain the density profile in Method 2; however, with the use of bulk equations instead of the inhomogeneous form of Wertheim's theory, CPU time is greatly reduced (by as much as two orders of magnitude at some densities, so that Method 1 ran in hours and Method 2 ran in minutes versus days or weeks for the simulations). A mesh width of 0.01 \( \sigma \) was enough to obtain good numerical accuracy. For further details consult the more detailed derivation for binary mixtures in Chapter 6, from which the pure fluid case can be deduced. Chapter 4 also has the general pure fluid derivation.
5-4. Results and discussion

In the following comparisons between theory and simulation results, the same intermolecular potential and bulk density are used in the theory and simulation. In Figure 5-2, we compare Method 1 and Method 2 with simulation for relative reduced density (relative to the bulk, \( \rho(z) / \rho_{\text{bulk}} \)) versus distance from the wall for the bulk reduced number density (\( \rho_{\text{bulk}} \sigma^3 \)) equal to 0.9036 and a site bonding energy (\( \epsilon/kT = 1/T^* \)) equal to 5. Results for Method 1 are representative of the other couple of conditions looked at. Excluded volume and packing effects create a layered structure with a sharp peak near \( z = 0 \), and oscillations, which dampen with progressively smaller and more diffuse peaks at \( z = \sigma, 2\sigma \), etc. Method 1 appears to accurately predict the peak positions, but the peak heights are too high in comparison with simulation. The contact density (\( z=0 \)) in Method 1 is about 20% too high. Accuracy is improved somewhat at lower densities. Method 1 is self-consistent with the wall theorem [53, 17]; i.e., the theoretical wall density is equal to the theoretical bulk pressure. However, the wall density is incorrect compared to the simulation results due to our approximation that the pair distribution function is not a functional of \( \rho \). On the other hand, Method 2 more accurately predicts the peak heights and the contact density; however, the positions of the peaks are slightly offset from the simulation results. As will be discussed, at least some of the error in peak position can be attributed to the Tarazona DF theory for hard spheres. Since Method 2 gives more accurate contact densities and peak heights and takes significantly less computer time than Method 1, we will show further comparisons between theory and simulation only for Method 2. Once implemented for pure fluids, Method 1 has the advantage of being more easily extended to mixtures, so we will keep it in mind for future work.

In Table 5-2 we compare some of the major results from Method 2 with simulation. The uncertainties in the simulation results represent one standard deviation. The theoretical calculations used as inputs the same bulk reduced density and site
Figure 5-2. The relative reduced density is plotted versus distance from a hard wall for associating hard spheres from theory method 1 (dashed lines), theory method 2 (solid lines), and simulations (symbols) for an inverse reduced temperature of $\varepsilon / kT = 5$ and a bulk density of 0.9036. If Tarazona weighting is only applied to the hard sphere free energy (method 1), the peak densities match the simulations, but the peak heights and all density are less accurate.
association energy as the corresponding simulations. The reported bulk pressures were calculated from bulk densities using Wertheim's theory [5, 6]. Also listed are simulation average density, wall density, adsorption, and fraction of monomers at the wall. A weighted density approximation must obey the wall theorem. We see that this wall sum rule was satisfied for the theory with less than a 0.5% disagreement, which was due to numerical error, for most of the cases. See Figure 5-3, which confirms the wall theorem accuracy for the theory; several simulation results lie away from the expected line, as explained more fully later in this section. Theoretical adsorption was calculated numerically using \( \int_0^{\text{bulk}} (\rho(z) \sigma^3 - \rho_{\text{bulk}} \sigma^3) \, dz \), where \( \rho(z) \sigma^3 \) is the singlet reduced number density and \( \rho_{\text{bulk}} \sigma^3 \) is the reduced number density in the bulk region. For the simulation adsorption calculations we used \((\rho_{\text{average}} \sigma^3 - \rho_{\text{bulk}} \sigma^3) \times b\), where \( b \) is half of the box length in the \( z \) direction. The theoretical and simulation values for adsorption compare well except for the highest association at a bulk density of 0.5239. The fraction of monomers at the wall predicted from theory is in remarkably good agreement with the simulation results except at the highest site energy at the lower densities.

Figures 5-4 to 5-7 show a comparison of Method 2 with simulation results for reduced density (relative to the bulk) versus distance from the wall for the simulation average reduced number densities (\( \rho \sigma^3 \)) equal to 0.2, 0.5, 0.75, and 0.942. In Figures 5-8 to 5-12, the monomer fraction is plotted versus distance from the wall at the four average densities. At each density, results are given at site bonding energies (\( \varepsilon/kT = 1/T^* \)) equal to 0, 3, 5, and 7 (results for fraction of site bonded is not given for \( 1/T^* = 0. \) Figures 5-13 to 5-24 have fraction of \( n \) sites bonded versus distance from the wall for each density/site energy pair. Before discussing these comparisons we will review the simulation results.
Table 5-2: Density Functional Theory (Method 2) versus Simulation for Four-sited Hard Spheres

<table>
<thead>
<tr>
<th>Bulk density, $\rho_{bulk}$</th>
<th>Site energy, $\varepsilon_{site} / kT$</th>
<th>Average box density, $\rho_{ave}$</th>
<th>Pressure, $P \sigma^3/kT$</th>
<th>$\rho \sigma^3$, wall</th>
<th>$\Gamma \sigma^2$, Adsorption</th>
<th>$\chi_0$, wall</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1978</td>
<td>0</td>
<td>0.2</td>
<td>0.3059</td>
<td>0.3021±0.0108</td>
<td>0.3045</td>
<td>0.0237±0.0067</td>
</tr>
<tr>
<td>0.1977</td>
<td>3</td>
<td>0.2</td>
<td>0.2964</td>
<td>0.2956±0.0067</td>
<td>0.2960</td>
<td>0.0248±0.0066</td>
</tr>
<tr>
<td>0.1994</td>
<td>5</td>
<td>0.2</td>
<td>0.2505</td>
<td>0.2505±0.0087</td>
<td>0.2512</td>
<td>0.0065±0.0117</td>
</tr>
<tr>
<td>0.2112</td>
<td>7</td>
<td>0.2</td>
<td>0.1105</td>
<td>0.1019±0.0175</td>
<td>0.1110</td>
<td>-0.1088±0.0808</td>
</tr>
<tr>
<td>0.4861</td>
<td>0</td>
<td>0.5</td>
<td>1.528</td>
<td>1.512±0.002</td>
<td>1.523</td>
<td>0.1103±0.0081</td>
</tr>
<tr>
<td>0.4874</td>
<td>3</td>
<td>0.5</td>
<td>1.420</td>
<td>1.408±0.027</td>
<td>1.415</td>
<td>0.1000±0.0122</td>
</tr>
<tr>
<td>0.4914</td>
<td>5</td>
<td>0.5</td>
<td>1.028</td>
<td>1.028±0.058</td>
<td>1.027</td>
<td>0.086±0.0622</td>
</tr>
<tr>
<td>0.5239</td>
<td>7</td>
<td>0.5</td>
<td>0.5033</td>
<td>0.2751±0.0284</td>
<td>0.5048</td>
<td>-0.2390±0.0615</td>
</tr>
<tr>
<td>0.5246</td>
<td>9</td>
<td>0.5</td>
<td>0.0722</td>
<td>0.0747</td>
<td>-0.1249</td>
<td></td>
</tr>
<tr>
<td>0.7191</td>
<td>0</td>
<td>0.75</td>
<td>4.346</td>
<td>4.255±0.083</td>
<td>4.317</td>
<td>0.2142±0.0092</td>
</tr>
<tr>
<td>0.7191</td>
<td>3</td>
<td>0.75</td>
<td>3.864</td>
<td>3.860±0.079</td>
<td>3.841</td>
<td>0.2142±0.0152</td>
</tr>
<tr>
<td>0.7257</td>
<td>5</td>
<td>0.75</td>
<td>2.833</td>
<td>2.891±0.131</td>
<td>2.821</td>
<td>0.1685±0.0422</td>
</tr>
<tr>
<td>0.7366</td>
<td>7</td>
<td>0.75</td>
<td>1.828</td>
<td>2.413±0.1865</td>
<td>1.827</td>
<td>0.1171±0.0542</td>
</tr>
<tr>
<td>0.9156</td>
<td>0</td>
<td>0.942</td>
<td>10.376</td>
<td>10.243±0.126</td>
<td>10.263</td>
<td>0.3393±0.0096</td>
</tr>
<tr>
<td>0.9158</td>
<td>3</td>
<td>0.942</td>
<td>9.021</td>
<td>9.272±0.264</td>
<td>8.925</td>
<td>0.3367±0.0217</td>
</tr>
<tr>
<td>0.9036</td>
<td>5</td>
<td>0.942</td>
<td>6.509</td>
<td>6.971±0.149</td>
<td>6.461</td>
<td>0.2468±0.0301</td>
</tr>
<tr>
<td>0.9085</td>
<td>7</td>
<td>0.942</td>
<td>5.102</td>
<td>6.451±0.171</td>
<td>5.082</td>
<td>0.2712±0.0451</td>
</tr>
</tbody>
</table>
Figure 5-3. Demonstration of wall theorem for 4-site hard sphere fluid against a hard wall. Reduced density versus bulk pressure from simulation (symbols), DF theory Method 2 (solid line), and expected from wall theorem (dashed lines) for conditions listed in Table 5-2.

Because of the geometric definition of a bond, even when the bonding energy was zero, the simulations reported a small amount of bonding. However, in this limit, the fluid behaves as simple hard spheres and thus the results of our simulations with bonding energy equal to zero are consistent with those for simple hard spheres against a smooth, hard wall obtained in [22, 23].

Note from Table 5-2 and Figure 5-3 that the bulk pressure and simulation wall density results for pressure are in excellent agreement at all densities and low to moderately high bonding energies. Figure 5-3 demonstrates simulation wall theorem compliance for these cases. At the highest bonding energy for the three highest densities, however, the disagreement is 25%, 30%, and about 45% at packing fractions of 0.493,
0.3927, and 0.2618, respectively. Several possible reasons arise to explain the discrepancies. At the highest density, perhaps the theory is not as accurate. Ghonasgi and Chapman [5] did not test Wertheim's theory at this extremely high density. Even the Carnahan-Starling equation of state [147], which was used to develop their equation is known not to be quite as accurate at very high densities. On the other hand, perhaps there is some kind of freezing transition. The large jump in cluster sizes from high temperatures to lower temperatures seen in Table 5-3 is one indication of this. However, not very much is known about freezing transitions at solid-fluid interfaces even for simple hard spheres [26], so this explanation could be hard to prove. The numbers for adsorption do not reveal any transitions occurring. The fluid does go from adsorption to desorption between bonding energies of 5 and 7 for the 0.2618 packing fraction (Figures 5-5c,d). However, a similar passage from adsorption to desorption occurs at a 0.1027 packing fraction (Figures 5-4c,d), and yet the agreement with the theory for the wall density is fairly good. Another explanation is simply poor statistics perhaps due in part to nonattainment of equilibrium.

The first three criteria listed near the end of Section 5-2 show equilibrium to have been reached. However, the orientation tensors may provide some clues. A typical set of orientation tensors, $B_{iz}$, was about $0.0045 \pm 0.015$ near the wall and $0.0015 \pm 0.0025$ in the bulk. The average $B_{iz}$ for these three high energy cases was $0.026 \pm 0.08$ and $0.022 \pm 0.037$ near the wall and in the bulk, respectively. Granted, the high energy cases have B's near zero, but they are about one order of magnitude larger than the numbers for the other cases. Also, the bulk number is almost as large as the wall number, whereas for the equilibrated cases the wall's $B_{iz}$ was three times larger than the bulk number. Most likely, these cases have only fair statistics due to a less than complete sampling of the system space. These cases have not reached equilibrium, but are instead stuck in a metastable state. There is a low acceptance rate for clusters by our single particle moves. One solution to this problem could be using a biasing scheme which has been developed
<table>
<thead>
<tr>
<th>$\varepsilon_{\text{ave}}/kT$</th>
<th>$\rho_{\text{ave}}\sigma^3=0.5$</th>
<th>$\rho_{\text{ave}}\sigma^3=0.75$</th>
<th>$\rho_{\text{ave}}\sigma^3=0.942$</th>
</tr>
</thead>
<tbody>
<tr>
<td>wall</td>
<td>bulk</td>
<td>wall</td>
<td>bulk</td>
</tr>
<tr>
<td>0</td>
<td>$1.008 \pm 0.004$</td>
<td>$1.015 \pm 0.0002$</td>
<td>$1.034 \pm 0.001$</td>
</tr>
<tr>
<td>3</td>
<td>$1.202 \pm 0.019$</td>
<td>$1.340 \pm 0.008$</td>
<td>$1.882 \pm 0.022$</td>
</tr>
<tr>
<td>5</td>
<td>$2.744 \pm 0.124$</td>
<td>$5.85 \pm 0.51$</td>
<td>$238.2 \pm 6.4$</td>
</tr>
<tr>
<td>7</td>
<td>$386.1 \pm 25.0$</td>
<td>$484.3 \pm 1.63$</td>
<td>$497.0 \pm 0.53$</td>
</tr>
</tbody>
</table>

Table 5-3: NVT Monte Carlo simulations approximate weighted-average cluster sizes in slices near wall and in bulk (based on 500 molecules in simulation cell).
for our association potential [178-182]. However, these schemes have not been developed or tested for our more complex 4-site model.

Note in Table 5-2 that the bulk density, in general, goes up with bonding energy. Hydrogen bonding tends to cluster the molecules together and away from the wall, so more molecules are found in the bulk. Nevertheless, for any one average system density, the bulk density does not vary much.

The relative reduced density \( \frac{\eta(z)}{\eta_b} \) is plotted versus distance from the wall in Figures 5-4 to 5-7 for average system packing fractions of 0.1047, 0.2618, 0.3927, and 0.493, respectively. Note, especially at the higher densities, the sharp peak at \( z = 0 \), and the oscillations, which dampen with progressively smaller and more diffuse peaks at \( z = \sigma \), \( 2\sigma \), etc. Qualitatively, the oscillations are similar to that of the radial distribution function, \( g(r) \), of plain hard spheres in the bulk [23], so the wall creates a nearest neighbor type of effect seen at multiples of \( \sigma \). Higher average densities result in higher densities at the wall and more oscillations or layers away from the wall. Lower temperatures cause more bonds and longer-lived molecular clusters, which tend to want to stay together and reduce the wall density and reduce the magnitude of the density oscillations.

In Figures 5-8 to 5-11 the fraction of monomers are plotted as a function of distance from the wall for packing fractions of 0.1047, 0.2618, 0.3927, and 0.493, respectively. The number of monomers is always enhanced at the walls as compared to the bulk. Note that there is less structure for fraction of monomers than there was for density. The profiles at the walls show the result of two competing effects. Higher densities increase collision forces near the wall, increasing sphere density there. At higher bonding energies (or lower temperatures), configurational entropy near the wall decreases, reducing sphere density. Monomers, which suffer no drop in configurational entropy as they approach the wall, are affected only by the collision forces and tend to pile up at the wall. However, the molecular attractions cause the molecules to cluster amongst themselves rather than against the wall. The greater the cluster size, the less chance for
the cluster (and any spheres that are a part of that cluster) to be at the wall due to the decrease in configurational entropy required for the cluster to get close to wall.

Note the striking difference between Figures 5-4c and 5-4d and Figures 5-5c and 5-5d. At the highest bonding energy, there are very few monomers left in the fluid. The clusters in the fluid have difficulty approaching the wall; therefore there is a depletion in spheres against the wall.

At the highest bonding energy of 7 for the higher densities this depletion did not occur. Presumably this is due to greater collision forces in these higher densities piling up monomers and even some smaller clusters against the wall and thus overcoming to some extent the drop in configurational entropy which takes place. These two competing effects were noted for non-associating square-well chains by Yethiraj and Hall [34]. From an equation of state for this fluid [5], we calculate a critical temperature of $\varepsilon/kT_c=1/T^*=7.76$ and a critical reduced density $\rho_c \sigma^3 = 0.1717$. Therefore, our simulation results are at supercritical conditions for this model fluid. Simulation results at subcritical conditions for this fluid would be difficult, if not impossible to obtain.

In general the theory accurately predicts the effect of temperature and average density on the wall density and the magnitude of the density oscillations. In Figure 5-4 (simulation average density of 0.2), the theory for the density profile matches the simulation results except at the highest energy, where the agreement is still very good for wall density, but only fair for desorption. Table 5-2 indicates, however, a large standard deviation for adsorption in this case, with the theoretical result almost within the uncertainty of the simulation result.

At the higher densities of Figures 5-5 (simulation average density of 0.5) and 5-6 (simulation average density of 0.75), the agreement is very good with the exception in Figure 5-6d. Although the theory shows no desorption at $1/T^*$ equal to 7, it shows much desorption at $1/T^*$ equal to 9. This might not be a failure of the theory, considering the
Figure 5.4. At a simulation average density of $0.2$, the relative reduced density is plotted versus distance from a hard wall for associating hard spheres from theory method 2 (lines) and simulations (symbols) for inverse reduced temperature of $\varepsilon_{\text{LJ}} kT = 0.3$ (a), 0.5 (c), and 0.7 (d).
Figure 5-5. As for Figure 5-4 at a simulation average density of 0.5, and for inverse reduced temperature of $e_{\text{site}} / kT = 0$ (a), 3 (b), 5 (c), and 7 (theory only) (d).
Figure 5-6. As for Figure 5-4 at a simulation average density of 0.75.
Figure 5-7. As for Figure 5-4 at a simulation average density of 0.942.
strong possibility of nonattainment of equilibrium. In Figure 5-5 at the three lower energies, there is excellent agreement between theory and simulation, with the density oscillations from theory just slightly offset from the simulation oscillations. This offset is only slightly higher in Figure 5-6, but it is appreciable at the near freezing density of Figure 5-7 (simulation average density of 0.942). Comparisons between Figures 5-7a, 5-7b, and 5-7c, show that this offset has its origin in the Tarazona DF theory and not in the addition of the association theory. In Figure 5-7a, for a case of no association ($\varepsilon / kT=0$), the Tarazona Mark II theory has a slight offset in peak position compared to the simulation. As temperature is lowered and association increases in Figures 5-7(b) and 5-7(c), the offset does not change significantly. For the wall density, in particular, the agreement is very good to excellent except for the cases in Figures 5-5d, 5-6d, and 5-7d.

Figures 5-8 through 5-11 present the fraction of monomers versus distance from a hard wall. The symbols represent simulation data and the lines represent theory from equations (5-15) and (5-16). The number of monomers is always enhanced at the wall as compared to the bulk. There is very good agreement between theory and simulation. There is a small error near the wall for the high energy case of Figure 5-8. Results using the simulation densities as input into equation (15) showed little error [184]. Therefore, most of the error results from the density profile calculated from the DF theory. In Figure 5-9 for the state point of Figure 5-5d there is a significant difference for the fraction of monomers at the wall in which the simulation might not have equilibrated. At the highest density (0.942), the theory slightly underpredicts the fraction of monomers in the bulk and for the state point of Figure 5-7b, the larger offset in the peak positions of the density profile carries over into the fraction of monomers profile.

The origin of the cusp in the fraction of monomers curve at $z=\sigma$ is due to the nature of the integral in equation (5-15) and an approximation of bonding only at hard sphere contact. If molecule 1 is within a molecular diameter of the wall ($z_1 < \sigma$), the integrand is zero for some positions of molecule 2 due to the excluded volume of the wall.
Figure 5-8 Fraction of monomers versus distance from a hard wall for associating hard spheres from theory (lines) and simulations (symbols) for $\rho_\text{av}$ of 0.200 and $\epsilon_\text{site}/kT = 3$ (triangles), 5 (squares), and 7 (circles). Theory is method 2.
Figure 5-9. As for Figure 5-8 for $\rho_{av}$ of 0.5.
Figure 5-10. As for Figure 5-7 for $\rho_{av}$ of 0.75.
Figure 5-11. As for Figure 5-7 for $\rho_{av}$ of 0.942.
As found earlier [5], the theory slightly overpredicts the fraction of monomers in the bulk. This is due in part to the different definition of a monomer in the theory and in the simulation. Because of the geometric definition of a bond, a small amount of association is found for $\varepsilon / kT=0$ [5] in the simulations but not in the theory. However, in the bulk at the highest density, the fraction of monomers is underpredicted by the theory. As the density nears that of the freezing of hard spheres, some bonds which would otherwise form are broken in the simulations due to steric problems caused by the close packing. The theory does not pick up this effect.

We used equations (5-16) and (5-22 to 5-25) to calculate the fraction of $n$ sites bonded as a function of distance from the wall. We compare these theoretical numbers to simulation results in Figures 5-12 through 5-22. We use as input the density profiles from the simulation, rather than the theoretical density profiles. Accuracy varies overall from qualitatively good to quantitatively very good. Figures 5-12, 5-5-13, and 5-14 have results for an average simulation density of 0.2 at bonding energies of 3, 5, and 7, respectively. Results are generally very good with a small deterioration in accuracy at the highest bonding energy. There is a depletion at the wall in Figures 5-12 and 5-13 for all molecules which are bonded. Kinks at $1\sigma$ for all theoretical curves originate for the same reasons as given above for the fraction of monomers plots. (Of course, results for 0 sites are slightly different from the fraction of monomers plots above, since the fraction of monomer plots above used the theoretical density profiles while the plots here used the simulation density profiles as fixed inputs.) At the highest bonding energy of Figure 5-14, bonding has occurred to such a large extent that single-bonded molecules as well as monomers are enhanced at the wall as compared to the bulk. Relative to longer chains, less entropy is lost if these chain ends are nearer the wall than the bulk.

Qualitatively, at the average simulation density of 0.5, the results at the two lower bonding energies of Figures 5-15 through 5-17 are similar to Figures 5-12 through 5-14, except enhancement of dimers occurs at the bonding energy of 5, as well as at 7, due to
Figure 5-12. Fraction of singlets bonded at $n$ sites versus distance from a hard wall for associating hard spheres from theory (lines) and simulations (symbols) for $\rho_{av}$ of 0.200 and $\varepsilon_{site}/kT = 3$. Simulation densities are fixed input to theory.
Figure 5-13. Same as Figure 5-12 for $\rho_{av}$ of 0.200 and $\epsilon_{site}/kT = 5$. Simulation densities are fixed input to theory.
Figure 5-14  Same as Figure 5-12 for $\rho_{av}$ of 0.200 and $e_{site}/kT= 7$. Simulation densities are fixed input to theory.
Figure 5.15. Same as Figure 5.12 for $\rho_w$ of 0.5, 0.5 and $e_{site}/kT = 3$. Simulation densities are fixed input to theory.
Figure 5-16. Same as Figure 5-12 for $\rho_{av}$ of 0.500 and $\varepsilon_{site}/kT = 5$. Simulation densities are fixed input to theory.
Figure 5-17. Same as Figure 5-12 for $\rho_\text{av}$ of 0.500 and $\varepsilon_\text{site}/kT = 7$. Simulation densities are fixed input to theory.
Figure 5-18. Same as Figure 5-12 for $\rho_{av}$ of 0.750 and $\epsilon_{site}/kT = 3$. Simulation densities are fixed input to theory.
Figure 5-19. Same as Figure 5-12 for $\rho_{av}$ of 0.750 and $e_{site}/kT= 5$. Simulation densities are fixed input to theory.
Figure 5-20: Same as Figure 5-12 for $\rho_w$ of 0.750 and $e_{site}/kT = 7$. Simulation densities are fixed input to theory.
Figure 5.21. Same as Figure 5.12 for \( \rho_{av} \) of 0.942 and \( \epsilon_{site}/kT = 3 \). Simulation densities are fixed input to theory.
Figure 5-22. Same as Figure 5-12 for $\rho_{av}$ of 0.942 and $\epsilon_{site}/kT = 7$. Simulation densities are fixed input to theory.
the increased collision forces from the higher density. In Figure 5-17, note that even singlet molecules bonded at two sites are enhanced at the wall. Note that although almost all results in Figure 5-17 are of only qualitative accuracy, the fraction of monomers plot is still fairly accurate. Thus, the theory may miss some structural details and yet still be accurate for fraction of monomers and thus free energy.

Figure 5-17 clearly shows a feature common to Figures 5-12 through 5-22. The simulations predict the fraction bonded at 4 sites to be 0 at the wall. This makes sense from a steric point of view since every molecule next to the wall has at least one site which is directed toward the wall and therefore unavailable for bonding. However, in the theory, we assumed that $\chi_A$ is not a function of orientation, resulting in there being some molecules bonded at 4 sites at the wall in the theory; relaxing this assumption should provide better agreement.

Qualitatively, the results of Figures 5-18 through 5-22 are similar to those presented above. At these higher average simulation densities of 0.75 and 0.942, more bonding occurs (molecules more likely to be closer together). The results at the highest amount of association, Figures 5-20 and 5-22, are less than quantitatively correct, although the results for the fraction of monomers is accurate. Also, in Figure 5-22, the fraction of molecules bonded at 3 or fewer sites is enhanced at the wall. Moving way from the wall, the molecules being bonded at four sites increase rapidly.

5-5. Conclusions

We extended our perturbation density functional theory for inhomogeneous associating fluids from Chapter 4 and introduced another approach. In our Method 1 we applied the inhomogeneous form of Wertheim's associating fluid theory as a perturbation to the Tarazona weighted density functional theory for hard spheres. In our Method 2, we used the Tarazona weighting for both the hard sphere and association contributions to the
free energy functional. Method 1 is in qualitative agreement with simulation results, but Method 2 is in quantitative agreement with our simulation results.

On the whole, our DF theory (Method 2) is in good to excellent agreement with computer simulations over a broad range of densities and up to bond energies of $7kT$. The theory gives poorer results at the passage from adsorption to desorption (at least, according to the limited data we have under these conditions) and at the near freezing density of 0.942. However, these latter two conditions are rather severe tests of a theory; therefore, the method outlined here is a promising approach toward characterizing, in general, and with good accuracy, the behavior of AFs at interfaces.

At first glance, the fact that Method 2 works so well is surprising. However, we can offer an explanation for the success of Method 2 beyond those given in the theory section. Tarazona fit his weight function, $\omega$, such that equation (5-7) with equation (5-8) produces upon differentiation, the bulk hard sphere pair direct correlation function close to the PY result. The fit is accurate over a wide range of bulk densities; therefore, as Evans [53] states "one might expect the same functional to provide an accurate description of the singlet density and the free energy of an inhomogeneous fluid." Wertheim’s perturbation theory for a bulk AF assumes that the monomer-monomer pair distribution function remains the same as that in the reference fluid. In fact, the monomer-monomer distribution remains nearly the same as the hard sphere distribution even when the fluid is only 60% monomers [9]. Since Tarazona’s weighting functions reproduce the hard sphere structure, it is reasonable to expect that his weighting functions should be accurate for, at least, weak association. In general, we would expect that $\omega$ should depend on the extent of association; however, we have shown that the theory produces accurate results without additional fitting beyond the hard sphere $\omega$’s that Tarazona has supplied.

Implementation of Method 2 is straightforward. Readers who already use the Tarazona method should find it very simple to add the effects of association. At least a
portion of the difference between the simulations and the theory of Method 2 originated in the original Tarazona Mark II [53] DF theory. Therefore, it may be advantageous to try our approach with other weighted DF approximations, including those for more realistic potentials. The Tarazona method with LJ potential is accurate against simulation [149]. In the next chapters, we take up mixtures of equal size spheres and AFs against active surfaces.
6. The Binary Associating Mixture against a Hard Wall

6.1 Introduction

As a prelude to attacking more realistic systems, we would like to extend our DF theory (Method 2 of Chapter 5) to mixtures. We take a large step in that direction in this chapter by combining Tarazona's DF theory [149, 150] with Wertheim's theory [6,9] to form a perturbation density functional theory for binary associating hard sphere fluid mixtures.

Lebowitz [194] solved the PY equation (an IE equation) for bulk hard sphere mixtures of spheres of different diameters. Accurate analytical solutions for the radial distribution function using a Verlet-Weis [195] construction were obtained by Lee and Levesque [196] and Henderson and Grundke [197]. Hamad [198 and references therein] predicted with high accuracy the equimolar compressibility factor for a nonadditive binary hard-sphere mixture. His method, general for multicomponent mixtures with different size components, uses pure component equations of state and any available information on virial coefficients or unlike interaction parameters.

As reviewed by Haymet [137] the phase diagram of a binary mixture of hard spheres was studied by a number of groups using second-order perturbation theory and Denton and Ashcroft's MWDA method (see Chapter 3 and [199]). The MWDA method was slightly more accurate compared with simulations than the perturbation theory. Tan et al. [155] extended the Tarazona DF [149, 150] to binary hard sphere mixtures against a hard wall. They found reasonably accurate density profiles when compared to simulations [200] for \( \sigma_2 / \sigma_1 \leq 3 \). Rosenfeld [201] used his DF theory (see Chapter 3) to study the bulk phase behavior of asymmetric binary hard sphere mixtures. He [201] discussed possible extension to binary mixtures in external fields. See Lee [15] for work done on Lennard-Jones mixtures.
Nezbeda et al. [102] studied a binary mixture of water and a fluid of hard spheres with an attractive mean-field term. The water model [190] was a 4-site one similar to ours. They used Wertheim's theory to build phase diagrams for these mixtures within a range of values for hard-sphere size ratio and mean field strength. For the case most similar to the mixture we use, with zero mean field strength (plain hard spheres as one component), the mixture exhibited type IIId phase behavior [202, 203]. By the van Konynenburg and Scott nomenclature [202, 203], this mixture is said to exhibit gas-gas immiscibility of the first type. This is characterized by one 3-phase line associated with either a water-rich or hard sphere-rich phase. This behavior generally occurs when the self-attractive forces of one specie outweigh the self-attractive forces of the other specie and the cross-attractive forces between the species.

As stated in Chapter 4, Kierlik and Rosinberg (KR) [54-57] developed a perturbational free energy density functional (DF) approach applicable to inhomogeneous fluids consisting of fully associating nonoverlapping hard spheres (i.e., tangent chains) by applying Wertheim's theory for polymerization [9, 58]. The method uses their own [162, 163] density-independent weighted free energy DF theory for hard sphere mixtures as a reference. Those DF and IE theory approaches which use Wertheim's theory [48, 49, 54-57, 174-176, 192] for association use the number-average chain length in the bulk to determine the density profile of the inhomogeneous mixture. The work using the number-average chain length, as well as our work in Chapters 4 and 5 where different species are a result of bonding, describe what are fluid mixtures. However, in Chapter 6 we would like to control the input species as a constraint on bonding and then, as in Chapters 4 and 5, let the temperature determine the bonding. For the reasons outlined in the introduction to Chapter 4 we choose to use the Tarazona DF theory [149, 150] with Wertheim's theory, even though the extension to mixtures for Tarazona's theory is less than straightforward [53, 155].
To test our DF theory, we start with a fairly simple mixture. We present new Monte Carlo simulation results for a binary mixture of equal-sized hard spheres where some of the spheres have four associating sites placed in the Bol [189] fashion so that clusters as well as chains can form. Qualitatively, this could be a mixture of water with an inert gas. No other simulation study for an inhomogeneous fluid mixture has been reported with the current association potential. We then combine Tarazona's DF theory [149, 150] with Wertheim's theory [6, 9] to form a perturbation density functional theory for this fluid. We compare density ratio profiles (non-associating component to associating component), associating component density profiles, and fraction (of the associating component) which are monomers from the theory against our new simulation results.

6.2 Computer simulations

Simulations in this study were performed in the canonical (constant NVT) ensemble, using the Metropolis Monte Carlo algorithm [180]. The pair and wall potential models are defined as in Chapter 5. The association potential for those spheres that can associate is also defined in Chapter 5. As in Chapter 5, in the simulations and in our theoretical calculations below, the radial limits of the square well association were set to \( r_c = 1.05\sigma \). The angular limit was set to \( \theta_c = 27^\circ \). The simulation cell is the same as that shown in Figure 4-2. (For the results reported in Table 6-1, \( \alpha \), the ratio of simulation cell length to width, was 2.)

The simulations were performed as explained in Chapter 5, except that bonding sites were placed only on a certain fraction of the hard spheres. In addition, acceptance statistics were calculated separately for both the hard spheres and the 4-site hard spheres. The acceptance criterion for each specie was 20 to 50%, which was enforced within
several collections of slices, especially and including the collection of slices within 0.25 of either wall.

Systems were first equilibrated. Each equilibrated configuration was used as the starting configuration of a series of further runs. Each series consisted of 10 runs. The subaverages of properties from each run of a series were used to calculate averages. A final average was then calculated by averaging the properties of each bin on one side of the cell midpoint with its geometrically symmetrical twin. Generally, more configurations were needed at the highest amount of association, a requirement which becomes more necessary at higher densities (such as a run at an average density of 0.92, which is not yet completed). See Table 6-1.

Table 6-1: NVT Monte Carlo simulation input parameters for binary mixture of hard spheres with 4-site hard spheres against a planar wall

<table>
<thead>
<tr>
<th>Average density, $\rho \sigma^3$</th>
<th>Total number of molecules, N</th>
<th>Fraction of molecules which associate</th>
<th>$N_{eq} \times 10^6$, Equilibrium configurations</th>
<th>$N_{av} \times 10^6$, configurations in each run</th>
<th>$\epsilon_{site}/kT$</th>
<th>H, box length in z direction</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2</td>
<td>500</td>
<td>0.5</td>
<td>2250</td>
<td>150</td>
<td>7</td>
<td>21.544</td>
</tr>
<tr>
<td>0.5</td>
<td>1000</td>
<td>0.5</td>
<td>2000</td>
<td>140</td>
<td>7</td>
<td>20.000</td>
</tr>
<tr>
<td>0.75</td>
<td>500</td>
<td>0.5</td>
<td>700</td>
<td>90</td>
<td>5</td>
<td>13.864</td>
</tr>
</tbody>
</table>

Although we saw no evidence of metastable configurations, these systems take an extremely long time to equilibrate. Time to equilibrium was about one order of magnitude greater than that of the pure fluid simulations of Chapter 5.

Criteria used for determining if equilibration had been reached at the end of a series of simulations include those listed in Chapter 4. In addition, the fraction of monomers should be symmetrical on either side of the cell to within 5%. Theoretical bulk
pressure was calculated for the middle 26% (except for 40% at the average density of 0.5) of the cell by using the simulation bulk density and Wertheim’s theory [6-10].

Densities and fraction of monomers were calculated as described as in Chapter 4. Fraction of monomers are reported for those hard spheres which have association sites.

6-3. Density Functional Theory for a Binary Mixture

We begin with the definition of the grand potential

\[ \Omega = A[\rho(r)] + \int \rho(r) [\phi_w(r) - \mu] dr, \]  \hspace{1cm} (6-1)

where \( \rho \) is the singlet total number density, \( \phi_w \) is the external potential, \( \mu \) is the chemical potential, and \( A \) is the system Helmholtz free energy. The grand potential is minimized at the equilibrium density [130]. Therefore, at equilibrium, \( \delta \Omega[\rho(r)] / \delta \rho(r) = 0 \).

Generalizing to a binary mixture [204-207],

\[ \Omega(\rho_1(r), \rho_2(r)) = A[\rho_1(r), \rho_2(r)] + \sum_{i=1}^{2} \int \rho_i(r) [\phi_{w,i}(r) - \mu_i] dr, \]  \hspace{1cm} (6-2)

where the subscript \( i \) denotes species \( i \) and \( A[\rho_1(r), \rho_2(r)] = \sum_{i=1}^{2} A_i[\rho_i(r)] \). With the intermolecular potentials as defined in Section 6-2, the Helmholtz free energy can be broken up into a sum of ideal and excess parts as

\[ A_i[\rho_i(r)] = A_{i,d}^i[\rho_i(r)] + A_{i,e}^i[\rho_i(r)]. \]  \hspace{1cm} (6-3)

The ideal functional is known exactly and we can write it as
\[ A_i^{\ex} [\rho_i(r)] = \int \rho_i(r) kT [\ln \rho_i(r) - 1] dr. \] (6-4)

Also, \( A_i^{\ex, \text{hs}} = A_i^{\ex, \text{hs}} + A_i^{\ex, \text{assoc}} \), where \( \text{hs} \) and \( \text{assoc} \) denote the hard sphere and association portions of the excess (ex) Helmholtz free energy and \( kT \) is \( 1/\beta \) or the Boltzmann constant multiplied by the temperature. The excess free-energy functional can be written as [148-150, 208]

\[ A^{\ex} [\rho_1(r), \rho_2(r)] = \sum_{i=1}^{2} kT \int \rho_i(r) f_i(\bar{\rho}(r)) dr. \] (6-5)

where \( f_i(\bar{\rho}(r)) \) is the excess Helmholtz free energy per particle of species \( i \) at the smoothed total density \( \bar{\rho}(r) \) of the mixture. We define \( \bar{\rho}(r) \) later in Section 6.3.

The equilibrium density profiles \( \rho_i(r) \) are obtained by solving the coupled integral equations that result from minimizing \( \Omega \) with respect to \( \rho_i(r) \) [206, 207, 209],

\[ \frac{\delta \Omega}{\delta \rho_i(r)} = 0 \quad (i = 1, 2), \] (6-6)

to obtain

\[ \mu_i = \phi_{w,i}(r) + kT \ln \rho_i(r) + f_i[\bar{\rho}_1(r), \bar{\rho}_2(r)] + \sum_{k=1}^{2} \int \rho_k(r') \sum_{j} \frac{\partial f_k}{\partial \rho_j(r')} \frac{\delta \bar{\rho}_j(r)}{\delta \rho_i(r)} dr', \] (6-7)

where \( f_i = f_i^{\ex, \text{hs}} + f_i^{\ex, \text{assoc}} \). Realizing that our system is inhomogeneous only in the \( z \) direction and then rearranging, we have (in per square area terms)
\[ \rho_i(z) = \exp[\beta(\mu_i - \phi_{w,i}(z) - \lambda_i(z))] \] (6-8)

and

\[ \lambda_i(z) = \int \rho_i(z) \rho_2(z) + \sum_{k=1}^{2} \int \rho_k(z') \sum_{j} \frac{\partial f_k}{\partial \rho_j(z')} \frac{\delta \rho_j(z')}{\delta \rho_i(z')} dz'. \] (6-9)

6.3.1 Bulk Chemical Potential

6.3.1.1 Hard Sphere Portion

Dropping the external potential term in the fluid, since we have hard walls, we first calculate the individual chemical potentials, which at equilibrium remain constant throughout the fluid. (If we had no constant bulk density in the middle of our box, we could simply fix the potentials and then calculate our densities.) Since our species bulk densities are fixed, we can calculate the chemical potentials as

\[ \mu_i = \mu_i^{\text{ex,hs}} + \mu_i^{\text{ex,assoc}} + kT \ln(x_i \rho_{\text{bulk}}), \] (6-10)

where the last term is the ideal gas term containing the total bulk density and \( x_i \) is the fraction of species \( i \) in the bulk. The hard sphere term, which is dependent upon only the total bulk density is from Carnahan-Starling [147, 183]:

\[ \mu_i^{\text{ex,hs}} = \frac{(8\eta - 9\eta^2 + 3\eta^3)}{(1-\eta)^3}. \] (6-11)
6.3.1.2 Association Portion

The excess Helmholtz energy of association due to species $i$ is [6-10]

$$A_i^{ex,assoc} = N_i M_i kT(\ln \chi_A^{bulk,i} - 0.5 \chi_A^{bulk,i} + 0.5), \quad (6-12)$$

where $\chi_A^{bulk,i}$ is the fraction of species $i$ in the bulk not bonded at site $A$, $N_i$ is the number of total molecules of species $i$, and $M_i$ is the number of association sites per molecule of $i$ (in this chapter, $M_i = 4$ for the associating species and $M_i = 0$ for the other species). If we sum equation (6-12) for both species and differentiate the resulting equation to obtain the excess chemical potential of association for species $i$, we get for a fixed bulk density and fixed site bonding energy, $\epsilon_{AC}/kT$,

$$\mu_i^{ex,assoc} = M_i kT(\ln \chi_A^{bulk,i} - 0.5 \chi_A^{bulk,i} + 0.5) + kT \sum_{j=1}^{2} \eta_j M_j \left( \frac{\partial \chi_A^{bulk,j}}{\partial \eta_i} \right)(1/ \chi_A^{bulk,j} - 0.5). \quad (6-13)$$

If species 1 is our associating 4-site molecule and species 2 is the hard sphere then equation (6-13) becomes

$$\mu_1^{ex,assoc} = 4kT(\ln \chi_A^{bulk,1} - 0.5 \chi_A^{bulk,1} + 0.5) + 4 \eta_1 kT(\frac{\partial \chi_A^{bulk,1}}{\partial \eta_1})(1/ \chi_A^{bulk,1} - 0.5), \quad (6-14a)$$

and

$$\mu_2^{ex,assoc} = 4 \eta_2 kT(\frac{\partial \chi_A^{bulk,1}}{\partial \eta_2})(1/ \chi_A^{bulk,1} - 0.5), \quad (6-14b)$$
\( \chi_A^{bulk} = 1 \). It remains to find \( \chi_A^{bulk,i} \) and \( \frac{\partial \chi_A^{bulk,i}}{\partial \eta_i} \) to be able to solve equation (6-10). First, for associating species, from [6-10],

\[
\chi_A^{bulk,i} = \frac{1}{1 + \sum_j \rho_{bulk,j} \sum_i \chi_A^{bulk,i} \Delta_{i,j}}. \tag{6-15}
\]

Since our association sites are equal-sized and symmetric, and there is only one species which can bond, we solve the resulting quadratic equation to obtain after some rearranging,

\[
\chi_A^{bulk,i} = \frac{-1 + \sqrt{1 + 4 n \Delta \rho_{bulk,i}}}{2 n \Delta \rho_{bulk,i}}, \tag{6-16}
\]

where \( n \) is the number of sites on the second molecule which one site on the first molecule is eligible to bond to \( (n=2 \) for the 4-site species), \( \Delta \) is approximately \( 4 \pi K g_{hs}(\sigma; \rho_{bulk}) f_{AC} \) [8], \( K \) is a constant that measures the volume available for bonding of the two sites on molecules 1 and 2 (here this is \( 0.25(1 - \cos(\theta_c))^2 \sigma^2 (r_c - \sigma) \)), \( f_{AC} \) is the Mayer \( f \) function, \( \exp[\varepsilon_{AC}/kT] - 1 \), and \( g_{hs}(\sigma; \rho_{bulk}) \) is the hard sphere pair correlation function at contact at the total bulk density. From Carnahan and Starling [147, 183],

\[
g_{hs}(\sigma; \rho_{bulk}) = \frac{(1 + \eta + \eta^2 - \eta^3 - 1)}{(1 - \eta)^3} - \frac{1}{4 \eta}. \tag{6-17}
\]
We differentiate equation (6-16) by $\eta_i$ and rearrange to get

$$
\frac{\partial \chi_A^{bulk,1}}{\partial \eta_i} = \frac{-n\left(\chi_A^{bulk,1}\right)^2}{1 + 2n \rho_{bulk,1} \chi_A^{bulk,1} \Delta} \left(\Delta \frac{\partial \rho_{bulk,1}}{\partial \eta_i} + \rho_{bulk,1} \frac{\partial \Delta}{\partial \eta_i}\right),
$$

(6-18)

where $\frac{\partial \Delta}{\partial \eta_i} = 2\pi K f_{AC} (5 - 2\eta) / (1 - \eta)^4$, $\frac{\partial \rho_{bulk,1}}{\partial \eta_1} = 6/\pi$, and $\frac{\partial \rho_{bulk,1}}{\partial \eta_2} = 0$. Equation (6-10) can now be solved for the species chemical potential.

6.3.2 $\lambda_i$

6.3.2.1 Hard Sphere Portion

Adapting the expression of Carnahan-Starling [147],

$$
\xi^{\text{ex,hs}}(\tilde{\rho}(z)) = \frac{\eta(z)kT(4 - 3\eta(z))}{(1 - \eta(z))},
$$

(6-19)

and

$$
\frac{\partial f^{\text{ex,hs}}(\tilde{\rho}(z))}{\partial \tilde{\rho}_j(z)} = \frac{\pi \eta(z) f^{\text{ex,hs}}(\tilde{\rho}(z))}{3(1 - \eta(z))} + \frac{-\pi(\eta(z) - 2/3)}{(1 - \eta(z))^2},
$$

(6-20)

where

$$
\eta(z) = \frac{\pi \tilde{\rho}(z) \sigma^3}{6}.
$$

(6-21)

Analogous to the Tarazona weighting of Chapters 4 and 5, we have [149, 150, 208]
\[
\bar{\rho}(z) = \int [\rho_1(z') + \rho_2(z')]w(|z - z'|, \bar{\rho}(z))dz'
\]  
(6-22)

and \(w\) is the Tarazona weighting function [149, 150]. The weighting function, expressed as a power series expansion, is

\[
w(|z - z'|, \bar{\rho}(z)) = w_0(|z - z'|) + w_1(|z - z'|)\bar{\rho}(z) + w_2(|z - z'|)\bar{\rho}^2(z).
\]  
(6-23)

The Tarazona weighting coefficients are in [149, 150]. Since the density of the fluid varies only in the direction normal to the hard wall, we integrate over the directions parallel to the hard walls to obtain in one dimension [149],

\[
w_0(z) = \frac{3}{4\sigma}H(\sigma - z)(\sigma^2 - z^2).
\]

\[
w_1(z) = 2\pi H(2\sigma - z)H(|z| - \sigma)\left[0.288\sigma(2\sigma - z) - 0.462(4\sigma^2 - z^2) + \frac{0.764}{3\sigma}(8\sigma^3 - z^3) - \frac{0.187}{4\sigma^2}(16\sigma^4 - z^4)\right] + 2\pi H(\sigma - z)\left[\frac{0.475}{2}(\sigma^2 - z^2) - \frac{0.648}{3\sigma}0.648(\sigma^4 - z^4) + \frac{0.113}{4\sigma^2}0.288 - 1.5(0.924) + \frac{2}{3}(0.764) - \frac{15}{4}(0.187)\right],
\]

\[
w_2(z) = H(\sigma - z)\frac{10\pi^2\sigma^3}{144}\left[3(\sigma^2 - z^2) - \frac{1}{\sigma}0.648(\sigma^4 - z^4) + \frac{5}{4\sigma^2}(\sigma^4 - z^4)\right].
\]

(6-24a, 24b, 24c)

We can also write \(\bar{\rho}(z)\) as

\[
\bar{\rho}(z) = \bar{\rho}^{(0)}(z) + \bar{\rho}^{(1)}(z)\bar{\rho}(z) + \bar{\rho}^{(2)}(z)(\bar{\rho}(z))^2,
\]  
(6-25)

where

\[
\bar{\rho}^{(j)}(z) = \int \rho(z')w_j(|z - z'|)dz'.
\]  
(6-26)

Solving the quadratic equation of (6-25), the physical root we obtain is
\[ \bar{\rho}(z) = 2 \bar{\rho}^{(0)}(z) \left[ 1 - \bar{\rho}^{(1)}(z) + ((1 - \bar{\rho}^{(1)}(z))^2 - 4 \bar{\rho}^{(2)}(z) \bar{\rho}^{(0)}(z))^{0.5} \right]^{-1}. \] (6-27)

We define the individual weighted densities as

\[ \bar{\rho}_i(z) = \int \rho_i(z') w(|z - z'|; \bar{\rho}(z)) dz'. \] (6-28)

Therefore, \( \bar{\rho}(z) = \bar{\rho}_1(z) + \bar{\rho}_2(z) \). Analogous to equation (6-26), we have

\[ \bar{\rho}_i^{(j)}(z) = \int \rho_i(z') w_j(|z - z'|; \bar{\rho}(z)) dz'. \] (6-29)

We now have

\[ \bar{\rho}_i(z) = \bar{\rho}_i^{(0)}(z) + \bar{\rho}_i^{(1)}(z) \bar{\rho}(z) + \bar{\rho}_i^{(2)}(z) (\bar{\rho}(z))^2. \] (6-30)

Solve for \( \bar{\rho}(z) \) using equation (6-27) and \( \bar{\rho}_i(z) \) using equations (6-29) and (6-30). Then

\[ \bar{\rho}_2(z) = \bar{\rho}(z) - \bar{\rho}_1(z). \] (6-31)

6.3.2.2 \( \lambda_i \)-Association Portion

For the association portion of the partial excess Helmholtz free energy, we have[5-7, 10]

\[ f_{\text{assoc}}(z) = M_i kT \left( \ln \bar{X}_{A,i} - 0.5 \bar{X}_{A,i}(z) + 0.5 \right) \] (6-32)

where for multiple associating components
\[ \tilde{\chi}_{A,i}(z) = \frac{1}{1 + \sum_j \tilde{\rho}_j(z) \sum_A \tilde{\chi}_{A,j}(z) \Delta i,j}. \] 

(6-33)

For our system, for the associating component,

\[ \tilde{\chi}_{A,i}(z) = \frac{2}{1 + \sqrt{1 + 4\pi \Delta \tilde{\rho}_i(z)}}, \] 

(6-34)

where to solve equation (6-34), we substitute \( \tilde{\eta}(z) \) for \( \eta(z) \) in equation (6-17). We then have

\[ \frac{\partial f_{i}^{\text{ex, assoc}}}{\partial \tilde{\rho}_j(z)} = \frac{\pi}{6} M_i kT \left[ \frac{1}{\tilde{\chi}_{A,i}(z)} - 0.5 \right] \frac{\partial \tilde{\chi}_{A,i}(z)}{\partial \tilde{\eta}_j(z)}, \] 

(6-35)

where

\[ \frac{\partial \tilde{\chi}_{A,i}(z)}{\partial \tilde{\eta}_j(z)} = \frac{n(\tilde{\chi}_{A,i}(z))^2 \left( \frac{\partial \tilde{\rho}_j(z)}{\partial \tilde{\eta}_j(z)} + \tilde{\rho}_i(z) \frac{\partial \Delta}{\partial \tilde{\eta}_j(z)} \right)}{1 + 2n \tilde{\rho}_i(z) \tilde{\chi}_{A,i}(z) \Delta}. \] 

(6-36)

where \( \frac{\partial \Delta}{\partial \tilde{\eta}_j(z)} = 2\pi k f_{AC} (5 - 2\tilde{\eta}(z)) / (1 - \tilde{\eta}(z))^4 \) and \( \frac{\partial \tilde{\rho}_i(z)}{\partial \tilde{\eta}_j(z)} = 6/\pi \) for \( i \neq j \) and

\[ \frac{\partial \tilde{\rho}_i(z)}{\partial \tilde{\eta}_j(z)} = 0 \] for \( i \neq j \) and \( \Delta \) is as before with \( \tilde{\eta}(z) \) substituted for \( \eta(z) \) in equation (6-17). The term \( f_{i}^{\text{ex, assoc}} \) is zero for the non-associating component.
6.3.2.3 \( \lambda_i \)-Density Functional Derivatives

For the density functional derivatives, we have (see Vanderlick et al. [149] for pure fluid case)

\[
\frac{\delta \overline{\rho}_i(z')}{\delta \rho_i(z)} = w_0(|z-z'|) + w_1(|z-z'|)\overline{\rho}(z') + w_2(|z-z'|)(\overline{\rho}(z'))^2 + \frac{\rho_i^{(1)}(z')}{\rho_i(z)} \frac{\delta \overline{\rho}(z')}{\delta \rho_i(z)} + 2\frac{\rho_i^{(2)}(z')}{\rho_i(z)}(\overline{\rho}(z')) \frac{\delta \overline{\rho}(z')}{\delta \rho_i(z)}
\]  

(6-37)

for the like derivative and

\[
\frac{\delta \overline{\rho}_i(z')}{\delta \rho_j(z)} = \frac{-\rho_i^{(1)}(z')}{\rho_i(z)} \frac{\delta \overline{\rho}(z')}{\delta \rho_i(z)} + 2\frac{-\rho_i^{(2)}(z')}{\rho_i(z)}(\overline{\rho}(z')) \frac{\delta \overline{\rho}(z')}{\delta \rho_i(z)}
\]  

(6-38)

for the cross derivative. To solve these prior 2 equations,

\[
\frac{\delta \overline{\rho}(z')}{\delta \rho_i(z)} = \frac{w_0(|z-z'|) + w_1(|z-z'|)\overline{\rho}(z') + w_2(|z-z'|)(\overline{\rho}(z'))^2}{1 - \frac{-\rho_i^{(1)}(z')}{\rho_i(z)} - 2\frac{-\rho_i^{(2)}(z')}{\rho_i(z)}(\overline{\rho}(z'))}.
\]  

(6-39)

We can now solve for \( \lambda_i \).

6.3.3 Density Profiles

The iterative method of Chapters 4 and 5 was used to obtain the density profiles, with total bulk density, association site energy, and the fraction of the total bulk density made up of the species that can associate as fixed inputs to the theory. However, numerical closure was performed on each species density instead of just the total density with an average squared error of 1 x 10^{-10} for each species density. Once the density profiles were obtained, equations (5-15) and (5-16) were used to get the fraction of monomers for the associating species with \( \rho_i(z_2) \) substituted for \( \rho(z_2) \).
6.4 Results and discussion

Table 6-2 lists some of the major results for binary mixtures of hard spheres and associating 4-sited hard spheres for density functional theory and simulations. The uncertainties represent one standard deviation. The theoretical calculations used the same total bulk reduced density, site association energy, and bulk associating species density (which were all fixed) as the corresponding simulations. The reported bulk pressures were calculated from the partial bulk densities and the total density. Partial pressure for the hard spheres was calculated using the Carnahan-Starling equation [147]; partial pressure for the 4-sited hard spheres was calculated using Wertheim's theory [6-9] and added to the hard sphere partial pressure to obtain the total bulk pressure. Also listed are the bulk density of 4-sited spheres, wall density (total and 4-sited spheres), and fraction of 4-sited spheres that are monomers at the wall and in the bulk. The wall theorem [17] for the simulations was satisfied with less than 4% disagreement. The theory total wall density and the theory wall density for 4-sited spheres agreed well to near two standard deviations. The fraction of monomers at the wall obtained from theory agreed to within or close to the uncertainties of the simulations. The theoretical values for the bulk fraction monomers are higher than the simulation results at these moderate densities for the reason mentioned in Chapter 5. Note that the uncertainties for the values associated with the 4-sited spheres is greater than those values associated with all species. This is due to the lower number of 4-sited spheres as compared to the total number of spheres. The uncertainty in fraction of monomers is greater than that in Chapter 5 due to the above reason and that a greater number of configurations are possible due to there being unlike species in the mixture. We more fully explain the results below in conjunction with figure presentation.

Qualitatively, the simulation total density profiles (not shown) behave as explained in Chapters 4 and 5. Agreement with theory for singlet total densities as a function of
Table 6-2: Density Functional Theory versus Simulation for Cases of Table 6-1

<table>
<thead>
<tr>
<th>Bulk density, total/assoc.</th>
<th>Site energy, $\varepsilon_{site} / kT$</th>
<th>Bulk Pressure, $P \sigma^3 / kT$</th>
<th>Wall density, $\rho \sigma^3$, total / assoc.</th>
<th>$\chi_{0,wall}$</th>
<th>$\chi_{0,bulk}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>simulation</td>
<td>theory</td>
<td>simulation</td>
</tr>
<tr>
<td>0.1996 / 0.1014</td>
<td>7</td>
<td>0.2306</td>
<td>0.2360 ± 0.0093 / 0.0731 ± 0.0071</td>
<td>0.2356 / 0.0792</td>
<td>0.5614 ± 0.0437</td>
</tr>
<tr>
<td>0.5134 / 0.3089</td>
<td>7</td>
<td>1.112</td>
<td>1.072 ± 0.033 / 0.1584 ± 0.0474</td>
<td>1.066 / 0.145</td>
<td>0.3619 ± 0.1274</td>
</tr>
<tr>
<td>0.7173 / 0.3604</td>
<td>5</td>
<td>3.735</td>
<td>3.790 ± 0.034 / 1.444 ± 0.113</td>
<td>3.710 / 1.325</td>
<td>0.3916 ± 0.0229</td>
</tr>
</tbody>
</table>
distance from the wall was good to excellent, analogous to the situations in Chapter 5 where there was adsorption. The results in Chapter 6 are consistent with the HSHW case and the pure associating fluid case with the wall density landing between the analogous pure fluid cases of Chapter 5. On a total density basis, we have only looked here where there is adsorption, due to the presence of the nonassociating species. A more strict interpretation of our mixture results must consist of looking at the density profiles of only the 4-sited spheres or at least of the ratio of hard spheres to hard spheres that can associate.

Figures 6-1, 6-3, and 6-5 plot the ratio of hard spheres to spheres that can associate as a function of distance from the hard wall at several average densities and temperatures. At the temperature of the first two cases (Figures 6-1 and 6-3), the pure 4-site fluid at the same density in the bulk would have a temperature low enough such that the structure as determined by the radial distribution function would have a peak shift, indicative of real associating fluids [190, 210]. Figures 6-2, 6-4, and 6-6 plot the reduced density profiles of the associating species for the same conditions as Figures 6-1, 6-3, and 6-5, respectively. Figures 6-7 and 6-8 plot the fraction of 4-site spheres that are monomers as a function of distance from the hard wall. We want to compare our theory to simulations which would be extremely difficult, if not impossible, to perform at conditions where we have two phases. We relied on the phase diagram for our pure associating fluid to know that we are supercritical (and have no liquid-gas phase separation) at the conditions of our completed simulations. Furthermore, our pressures are not high enough to cause gas-gas immiscibility, [102] so we know we have one phase for our simulations. (Preliminary phase diagram work on our mixture indicates that we may have gas-gas immiscibility at $1/T^* = 7$ and a reduced density of 0.92, where we did attempt an uncompleted simulation run.)
In Figure 6-1 we see the results for a binary mixture at a low density and low temperature. The ratio of hard spheres to spheres that can associate is profiled as a function of distance from the hard wall. The theory generally lies within the uncertainty of the simulations. Accuracy is high close to the wall and then underpredicts the simulations until the bulk region is reached. Monomers are enhanced at the wall for the entropic reasons explained in Chapter 4. Monomers, spheres with no sites and unbonded 4-site spheres, are also favored at every multiple of a molecular diameter since the layering effect tends to exclude, relatively speaking, clusters, which must break some bonds to have their member spheres in the layer and will not break to avoid losing configurational entropy. This favoritism is only noticed at this low density at $1\,\sigma$, where there is a slight hitch in the ratio. This relatively flat area is also seen in Figure 6-7. Figure 6-2 shows the reduced density of the 4-site hard spheres versus distance from the wall for the same case. The simulation shows an expected desorption at the wall compared to the bulk with those spheres bonded into clusters tending to withdraw from the wall. However, very close to the wall there is first a slight decrease in singlet density before the increase takes places. Monomers are at a maximum at the wall while dimers are at a maximum at about $0.4\,\sigma$. Not until about $1\,\sigma$ are there enough longer chains and clusters allowed near the wall to make up for the decrease in monomers and dimers. The theory only picks up the overall desorption and not the dip in singlet density inside $1\,\sigma$. We see that the underprediction of the theory in Figure 6-1 is due to its overprediction of the associating species. (Except between $0.5\,\sigma$ and $1\,\sigma$ where there is 5% error in the total singlet density (not shown), the hard sphere density is underpredicted by a similar absolute amount to maintain an accurate total density profile.)

In Figure 6-3 we see the ratio of hard spheres to spheres that can associate as a function of distance from the hard wall for a binary mixture at a low temperature, but at a higher density than that of Figure 6-1. The ratio results are qualitatively similar to those
Figure 6-1. Ratio of hard spheres to 4-sited hard spheres versus distance from a hard wall for the binary mixture (50% hard spheres / 50% 4-site hard spheres in box) from DF theory (line) and simulation (symbols) for $\rho_{\text{average}} = 0.20$ and $\varepsilon_{\text{site}}/kT = 7$. 

- $1/T^* = 7$
- $\rho_{\text{bulk}}$, $\sigma^3 = 0.1996$
- $\rho_{\text{bulk, assoc}}$, $\sigma^3 = 0.1014$
Figure 6-2. Reduced density of 4-sited hard spheres versus distance from a hard wall for the same conditions as in Figure 6-1.
Box average of 50/50 mixture of equal-sized hard spheres

\[ \frac{1}{T^*} = 7 \]
\[ \rho_{\text{bulk}} \sigma^3 = 0.5134 \]
\[ \rho_{\text{bulk, assoc}} \sigma^3 = 0.3089 \]

Figure 6-3. Ratio of hard spheres to 4-sited hard spheres versus distance from a hard wall for the binary mixture (50% hard spheres / 50% 4-site hard spheres in box) from DF theory (line) and simulation (symbols) for \( \rho_{\text{average}} = 0.50 \) and \( \epsilon_{\text{site}}/kT = 7 \).
Figure 6-4. Reduced density of 4-sited hard spheres versus distance from a hard wall for the same conditions as in Figure 6-3.
Figure 6-5. Ratio of hard spheres to 4-sited hard spheres versus distance from a hard wall for the binary mixture (50% hard spheres / 50% 4-site hard spheres in box) from DF theory (line) and simulation (symbols) for $\rho_{\text{average}} = 0.75$ and $\epsilon_{\text{site}}/kT= 5$. 

- $1/T^* = 5$
- $\rho_{\text{bulk}} \sigma^3 = 0.7173$
- $\rho_{\text{bulk, assoc}} \sigma^3 = 0.3604$
Figure 6-6. Reduced density of 4-sited hard spheres versus distance from a hard wall for the same conditions as in Figure 6-5.
Figure 6-7. Fraction of 4-site hard spheres which are monomers for this binary mixture (50% hard spheres / 50% 4-site hard spheres in box) versus distance from a hard wall from DF theory (line) and simulation (symbols) for $\rho_{\text{average}} = 0.2$ and $\varepsilon_{\text{site}}/kT = 7$ (upper), and $\rho_{\text{average}} = 0.75$ and $\varepsilon_{\text{site}}/kT = 5$ (lower).
Figure 6-8. Same as in Figure 6-7 for conditions of $\rho_{\text{average}} = 0.5$ and $\varepsilon_{\text{site}}/kT = 7$. 
of Figure 6-3. The theory generally lies within the uncertainty of the simulations, but the theory underpredicts from $0.25\sigma$ until just outside the bulk region. In the small region closest to the wall, the theory is more accurate than it was at the lower density; in fact, it is highly accurate. As in Figure 6-1, there is a slight hitch in the ratio at $1\sigma$. This is reflected in the theory result with a shift in the sign of the second derivative of the ratio with respect to the distance. Figure 6-4 shows the reduced density of the 4-site hard spheres versus distance from the wall for the same case. The trough near the wall is enhanced compared with that in Figure 6-2. This time, however, the theory is fairly accurate within $1\sigma$ of the wall. Like Figure 6-2, however, the density is overpredicted throughout much of the inhomogeneous region. At this higher density, more large clusters are formed than in the case of Figure 6-2. This results in greater desorption of the associating component. The peak in dimers is pushed closer to the wall than in the case of Figure 6-2 by the higher packing forces of the higher density. This helps to deepen the trough. More simulations need to be made to determine the "path" of this trough at various conditions. We also see, as in Figure 6-1, that the underprediction of the theory in Figure 6-3 is due to its overprediction of the associating species. The hard sphere density is underpredicted by a similar absolute amount to maintain a highly accurate total density profile.

The relative "competition" error between the two species near the wall can be explained by our use of the Tarazona weighting, which gives a structure similar to the hard sphere direct correlation function (DCF). As association increases, the DCF should depart somewhat from that of a hard sphere fluid. The weighting should therefore tend to overestimate the amount of packing which the associating specie can undergo in relation to the hard spheres, hence the overprediction in Figure 6-2. Note that accuracy is improved within $0.25\sigma$ of the wall compared to the ratio accuracy further away from the wall until the bulk is reached. This region nearest the wall is also where unbonded 4-site
spheres and dimers by far outnumber multiply bonded spheres; thus, here the DCF of the associating specie must approach that of a plain hard sphere fluid.

In Figure 6-5 we see the results for a binary mixture at a high density and moderate temperature. The ratio of non-associating spheres to spheres that can associate is profiled as a function of distance from the hard wall. The theory generally lies well within the uncertainty of the simulations. Accuracy is very high within 0.25σ of the wall, drops off a little and then improves markedly. There is some offset at 1σ similar to the offset seen in the density profiles of the pure 4-site cases at high density. The ratio at the wall is lower here than in the previous mixture cases of Figures 6-1 to 6-4, since at this higher temperature the 4-site spheres are involved in smaller chains and clusters than earlier and thus compete against the spheres with no sites for wall positions on a more equitable basis. Also, there are more collision forces at this higher density to partly overcome the loss of configurational energy when a cluster approaches the wall. In Figure 6-6, we see that the 4-site sphere density prediction is highly accurate, with adsorption taking place. Adsorption takes place now due to the higher pressure (and density) of these conditions, which "pushes" longer chains against the wall and the higher temperature (than the other two cases) which favors less bonding.

In Figure 6-7 the fraction of monomers for the associating species is profiled versus distance from the hard wall for two cases. Accuracy is very high at an average reduced density of 0.75 and 1/T*=5. Some features, such as the kink in the theory at 1σ and the slight overprediction in the bulk, are in common with the results for pure 4-site fluids and are explained in Chapter 5. There is a little inaccuracy at 1σ, which seems to occur with all the associating fluids we have studied; thus far at higher densities (>0.7). For the case of average reduced density of 0.2 and 1/T*=7, there is an underprediction near the wall. By feeding the simulation densities into equations (5-15) and (5-16) and comparing against the results from an input of the theory densities, we find that most of
this underprediction error is due to the overprediction of associating species density in the density functional and not to error in equations (5-15) and (5-16). (In equations (5-15) and (5-16), \( \rho_1(z_2) \) was substituted for \( \rho(z_2) \).) Only a very small portion of the errors in density and fraction of monomers is due to assuming in the theory that \( \chi_A \) is independent of orientation when very close to the wall (which allows all four sites on a sphere to bond, which is physically impossible in the simulations) since the theory predicts few multiply bonded spheres at the wall under these conditions anyway.

In Figure 6-8 the fraction of monomers for the associating species is profiled versus distance from the hard wall for the case of an average reduced density of 0.5 and \( 1/T^* = 7 \). Results are qualitatively similar to that of the density of 0.2. Note also that the fraction of monomers at the wall for the associating specie is higher than for the pure associating fluid at the same total average density and \( 1/T^* \). See Figures 5-8 and 5-9. Fraction of monomers is comparable between the pure fluid and mixture cases when the partial densities, \( \rho_1 \), of the associating species are similar (for instance, compare Figure 5-8 to Figure 6-8).

6.5 Conclusions

We have extended our DF theory to binary mixtures of associating fluids where the reference species are both spheres of equal size. We have found that for a fluid of hard spheres with 4-site hard spheres that can associate, we can obtain reasonable accuracy for the density ratio profile of the two species. At low to moderate densities and a low temperature, accuracy was good to excellent very close to the wall, but only fair farther away from the wall. Much of the error stems from the Tarazona weighting not discerning differences in the packing of bonded and unbonded hard spheres. At higher densities and moderate temperatures, accuracy is very good to excellent throughout the profile. Accuracy under other conditions awaits the completion of further simulations. Analogous
to the pure fluid 4-site cases of Chapter 5, accuracy from highest to lowest occurs in this order: net associating species adsorption > much net associating species desorption > slight net associating species desorption.

Accuracy is of a reasonable enough quality such that we would be confident applying the theory to this mixture at subcritical conditions and receiving at least qualitative information on density profiles of the resulting phases.

Although Tarazona's theory is not conducive toward doing mixtures, we have shown that it can be done. We could extend this work to ternary mixtures (tedious, but straightforward) of equal-sized spheres or even to mixtures of unequal size components[155]. However, most researchers interested in this area would be advised to use this fairly simple density functional for quickly testing newly added features (active wall sites, for instance), rather than for investigating more complex mixtures. Other density functional methods should be more conducive toward more complex mixture investigation.
7. The Associating 4-site Hard Sphere Fluid Near an Active Surface

7.1 Introduction

We want to broaden the applicability of our density functional approach by performing Monte Carlo simulations of associating fluids against active surfaces; (e.g., hydrophilic surfaces). Many simulations of simple fluids near surfaces other than the hard wall have been performed. For a review see [3, 53]. More recently, Chmiel et al. [211] used the Tarazona density functional to theoretically study a Lennard-Jones fluid against a wall formed of parallel strips possessing different adsorbing energies. Work in the literature on associating fluids is much more sparse. Also, most [42, 48, 167-169, 171, 172, 174] of this work used IE theory (rather than DF theory) to study dimerizing spheres near crystalline and other associatively attractive walls. Holovko and Vakarin [176] used the associating HAB IE approach to study polymerizing hard spheres forming linear hard chains near crystalline surfaces. See Section 4.1 for more information.

The only other simulation studies for a system with an active external potential, using a fluid with the association potential we use, are those mentioned in Chapter 4 [59, 60, 177]. The first two listed studies are too complex for early theoretical study. Among the extensive literature performed with realistic models, we mention again the study of Lee and Rossky [36] who investigated, by way of molecular dynamics simulations, the structure and dynamics of liquid water at three types of solid surfaces: flat hydrophobic, rough hydrophobic, and hydrophilic. They found that the two hydrophobic surfaces behaved essentially the same. For the hydrophilic wall, surface activity was stronger than the bulk interaction between the molecules. In all cases, structural perturbations greatly diminished at distances greater than 2 or 3 molecular layers from the wall. These two latter conclusions of Lee and Rossky agree qualitatively with our results at moderate densities.
Presented below are outlines of our simulation method and theory. Following these are simulation results for the four site associating hard sphere model fluid next to an active wall (a wall with attractive wall sites) at several average reduced number densities and at several levels of bonding energy, including a bonding energy of zero for no bonding. Qualitatively, this study would be for water against a hydrophilic wall. Results include relative (relative to the bulk) reduced densities and fraction of monomers as a function of distance from the wall. For some of the results we report the fraction of wall sites bonded. We then show preliminary theoretical results. Finally, we conclude.

7.2 Simulations

Simulations in this study were performed in the canonical (constant NVT) ensemble, using the Metropolis Monte Carlo algorithm [180]. The fluid is the 4-site model of Chapter 5. The pair potential model is defined as is Section 5.2. As in Chapter 5, in the simulations and in our theoretical calculations below, the radial limits of the square well association were set to \( r_c = 1.05 \sigma \). The angular limit was set to \( \theta_c = 27^\circ \).

The simulation cell consists of hard walls at \( z = 0 \) and \( z = H \) with association sites on the walls; see Figures 4-2 and 7-1. For most of the cases run, the fixed active sites were placed at an area density of about \( \sigma^2 / a^2 = 0.5 \) sites per unit area. The site spacing was \( \sigma \)" and each wall was taken as a (100) plane of a face-centered cubic (FCC) lattice. This spacing was approximately \( \sigma \) for many of the runs, so if the fluid is water the site spacing is of the same order of magnitude as silica. The site energies, however, were generally much higher than silica to test the theory at a very high association energy. The sites had the same characteristic strength and radial and angular limits as the molecular sites and faced the fluid perpendicularly to the wall to which it was attached. One can visualize pseudo-molecules with centers \( 1.0 \sigma \) from the wall, each with one association site located \( 0.5 \sigma \) from the wall. Since centers of each fluid molecule can go to the wall itself,
this leaves a slight possible overlap between the fluid molecule association site and the wall site. See Figure 7-1. The wall sites can bond to any molecular site (A, B, C, or D).
The wall site runs generally ran for 50% to 200% more displacement configurations than the equivalent non wall site runs to improve the statistics. The simulations were performed in a similar manner to that detailed in Chapter 5.

Systems were first equilibrated. Each equilibrated configuration was used as the starting configuration of a series of further runs. Each series consisted of 10 runs. The subaverages of properties from each run of a series were used to calculate averages. A final average was then calculated by averaging the properties of each bin on one side of the cell midpoint with its geometrically symmetrical twin. More configurations were needed at the higher association site energies and densities to obtain acceptable statistics. More total molecules were used at the highest density to ensure against box size effects. See Table 7-1. \( \eta_{ave} \) is the average packing fraction \( \eta_{ave} = \pi \rho \sigma^3 / 6 \) of the simulation cell. \( N_{eq} \) is the total number of configurations made to reach system equilibrium. \( N_{av} \) is the number of configurations made in each run of a series or the number of steps made for each subaverage. \( E_{site} / kT \), or \( 1 / T^* \), is the site bonding energy.

Periodic boundary conditions with box length \( L \) were imposed in the other two directions. Generally, \( H = \alpha * L; \alpha \) was \( >1 \), to ensure that the density oscillations died away in the central region. Therefore, the two walls did not interfere with each other. In Table 7-1, \( \alpha \) was 2 except for the highest packing fraction, where \( \alpha \) was 3. The fluid pair potential was that of equations (5-1) through (5-3). The walls exerted an external potential of

\[
\phi(r, \omega_w, \omega_2) = \phi_{HW}(z) + \sum_{\mathcal{W}} \sum_{\mathcal{C}} \phi_{WC}(r, \omega_w, \omega_2),
\]

where \( r \) is the magnitude of the vector \( r \) connecting the centers of pseudomolecule 1 and fluid molecule 2 and \( \omega_w \) and \( \omega_2 \) are the orientations of pseudomolecule 1 and fluid
molecule 2 relative to vector \( r \). \( \phi_{HW} \) is the reference external potential; the reference hard wall potential is defined by

\[
\phi_{HW}(z) = \begin{cases} 
\infty & \text{if } z \leq 0 \text{ or } z \geq H \\
0 & \text{otherwise}.
\end{cases}
\]  

(7-2)

\( \phi_{WC} \) represents the association potential. The association potential is modeled by an anisotropic short range square well. \( C \) represents a site on a fluid molecule interacting with a wall site. The potential of interaction due to these sites is

\[
\phi_{WC}(r, \omega_1, \omega_2) = \begin{cases} 
-\varepsilon_{WC} & \text{if } r < r_c; \; \theta_{wl} < \theta_c; \text{ and } \theta_{C2} < \theta_c \\
0, & \text{otherwise},
\end{cases}
\]  

(7-3)

where \( \theta_{wl} \) is the angle made by the vector from the center of pseudo-molecule 1 to the wall site and the vector \( r \) and \( \theta_{C2} \) is the angle made by the vector from the center of molecule 2 to the molecule 2 bonding site and the vector \( r \). The square well depth for association bonding is \( \varepsilon_{WC} = \varepsilon_{WA} = \varepsilon_{WB} = \varepsilon_{WD} = \varepsilon_{wallsite} \). In effect, if a fluid molecule bonding site is close enough to a wall site and oriented correctly, then a bond is formed.

The longer runs took 4 to 6 weeks of CPU time on an IBM RS/6000 Model 360 workstation. We were careful to monitor the simulation for metastable states by, for example, checking the symmetry of the density profile after each subaverage calculation. Criteria used for determining if equilibration had been reached at the end of a series of simulations were similar to that of Chapter 5 except for the deletion of item 4; the wall theorem does not hold for active surfaces. Densities, adsorption, weighted-average cluster size, and orientation factor were also determined as in Chapter 5.
Table 7-1: NVT Monte Carlo simulation input parameters for 4-site hard spheres against an active wall

<table>
<thead>
<tr>
<th>Average density, $\rho \sigma^3$</th>
<th>Average packing fraction, $\eta_{ave}$</th>
<th>Total number of molecules, N</th>
<th>Wall site density, $\sigma^2 / \alpha^2$</th>
<th>$\varepsilon_{int}/kT$, Fluid / Wall</th>
<th>$N_{eq} \times 10^5$, Equilibrium configurations</th>
<th>$N_{av} \times 10^5$, configs. in each run</th>
<th>H. box length in z direction</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2</td>
<td>0.1027</td>
<td>500</td>
<td>0.5515</td>
<td>5 / 5</td>
<td>1000</td>
<td>75</td>
<td>21.544</td>
</tr>
<tr>
<td>0.5</td>
<td>0.2618</td>
<td>1000</td>
<td>0.4900</td>
<td>5 / 3</td>
<td>500</td>
<td>50</td>
<td>20.00</td>
</tr>
<tr>
<td>0.5</td>
<td>0.2618</td>
<td>1000</td>
<td>0.4900</td>
<td>5 / 5</td>
<td>500</td>
<td>75</td>
<td>20.00</td>
</tr>
<tr>
<td>0.5</td>
<td>0.2618</td>
<td>1000</td>
<td>0.4900</td>
<td>7 / 7</td>
<td>1000</td>
<td>150</td>
<td>20.00</td>
</tr>
<tr>
<td>0.75</td>
<td>0.3927</td>
<td>500</td>
<td>0.5200</td>
<td>0 / 0</td>
<td>150</td>
<td>15</td>
<td>13.867</td>
</tr>
<tr>
<td>0.75</td>
<td>0.3927</td>
<td>500</td>
<td>0.5200</td>
<td>3 / 3</td>
<td>200</td>
<td>25</td>
<td>13.867</td>
</tr>
<tr>
<td>0.75</td>
<td>0.3927</td>
<td>500</td>
<td>0.5200</td>
<td>5 / 3</td>
<td>1700</td>
<td>70</td>
<td>13.867</td>
</tr>
<tr>
<td>0.75</td>
<td>0.3927</td>
<td>500</td>
<td>0.5200</td>
<td>5 / 5</td>
<td>800</td>
<td>70</td>
<td>13.867</td>
</tr>
<tr>
<td>0.75</td>
<td>0.3927</td>
<td>500</td>
<td>0.1872</td>
<td>5 / 5</td>
<td>2000</td>
<td>160</td>
<td>13.867</td>
</tr>
<tr>
<td>0.75</td>
<td>0.3927</td>
<td>500</td>
<td>0.5200</td>
<td>7 / 7</td>
<td>1500</td>
<td>150</td>
<td>13.867</td>
</tr>
<tr>
<td>0.75</td>
<td>0.3927</td>
<td>500</td>
<td>0.5200</td>
<td>7 / 7</td>
<td>1000</td>
<td>160</td>
<td>13.867</td>
</tr>
<tr>
<td>0.9416</td>
<td>0.493</td>
<td>1500</td>
<td>0.5490</td>
<td>5 / 5</td>
<td>850</td>
<td>180</td>
<td>24.293</td>
</tr>
</tbody>
</table>

7.3 Theory

7.3.1 Fraction of wall sites bonded and fraction of monomers in fluid

We start with equation (4-21) for the fluid. If A and C represent the bonding sites on two interacting molecules in the fluid, Wertheim's theory gives [5, 6, 9, 10]

$$\chi_A (2) = \frac{1}{1 + \sum_C \rho(3) \chi_C (3) \Delta_{AC} d^3},$$

(4-21)
where the sum is over all association sites, \( \chi_A(2) \) and \( \chi_C(3) \) are the fraction of molecules not bonded at site A(molecule 2) or C(molecule 3), respectively, \( \rho \) is the total singlet number density, \( d3 = (d\omega_3 \int d\omega_3) d\tau_3 \) denotes an angle average and a volume integral, where \( \omega_3 \) is the set of angles defining the orientation of molecule 3 and \( d\tau_3 \) is a volume element, and \( \Delta_{AC} \) is defined by

\[
\Delta_{AC} = g_R(23)f_{AC}(23),
\]

(4-22)

where \( g_R(23) \) is the reference fluid (hard sphere) pair correlation function and \( f_{AC}(23) = \exp[-\phi_{AC}(23)/kT] - 1 \) is the Mayer \( f \) function. We now add the wall sites by adding a term analogous to the summation in equation (4-21). If we assume that \( \chi_A(2) \) is not a strong function of orientation, we can show that the fraction of orientations available for bonding is \( (1 - \cos \theta_c)/2 \). We obtain for the fluid molecules,

\[
\chi_A(2) = \frac{1}{1 + \sum_C \rho(3)\chi_C(3)\Delta_{AC}d3 + \chi_w f_{AC}(2, wall) \frac{n\pi R^2(1 - \cos \theta_c)}{2 Area}}
\]

(7-4)

where \( \chi_w \) is the fraction of wall sites not bonded, \( \frac{n}{Area} \) is the wall site density in Table 7-1, \( f_{AC}(2, wall) = f_{AC}(23) \), and \( R \) is the radius of the projected circle onto the wall from the wall site’s energy cone \( \frac{n\pi R^2}{Area} \) is thus the fraction of wall surface area available for bonding.) By geometrical calculations we can show that

\[
R^2 = (r_c^2 - (z(2)+1)^2).
\]

(7-5)
We now need $\chi_w$. Analogously to equation (4-21), but from the "viewpoint" of the wall, we have

$$
\chi_w = \frac{1}{1 + \sum_A \int \rho(2) \chi_A(2) f_wC(2, \text{wall}) d2}, \quad (7-6)
$$

where $f_wC(2, \text{wall}) = \exp[-\phi_wC(r, \omega_w, \omega_2)/kT] - 1$ and $d2 = (d\omega_2 / \int d\omega_2) d\tau_2$ denotes an angle average and a volume integral and $d\tau_2 = \text{Area} * dz_2$. There is no radial distribution function for the wall. We have defined the surface area as unity, but since not all the wall area is available for bonding we must multiply by a factor. Thus, doing an angle average (as for equation (7-4)) and multiplying by the fraction of wall area available for bonding we have

$$
\chi_w = \frac{1}{1 + \sum_A f_wC(2, \text{wall}) \frac{n\pi(1-\cos\theta_C)}{2\text{Area}} \int_0^{r^{-1}} \rho(z_2) \chi_A(z_2) R^2(z_2) dz_2}, \quad (7-7a)
$$

or

$$
\chi_w = \frac{1}{1 + 4 f_wC(2, \text{wall}) \frac{n\pi(1-\cos\theta_C)}{2\text{Area}} \int_0^{r^{-1}} \rho(z_2) \chi_A(z_2) R^2(z_2) dz_2}, \quad (7-7b)
$$

For the fluid portion of equation (7-4), the same assumptions which were made in Chapter 4 ($\chi_A(2)$ is only dependent on $z$ and is not a strong function of orientation, $g_R(23)$ is independent of position and direction, etc.) are made again to obtain the iterative equation
\[
\chi^-_{A}(z_2) = \frac{1}{1 + 4\pi \sigma^2 g_{hs}(\sigma; \rho_{\text{bulk}})(r_c - \sigma) \left( f_{AC}(23) \right) \int_{-1}^{+1} \chi'_{A}(z_3) \rho(z_3) \, dz_3 + \chi_w f_{AC}(2, \text{wall}) \frac{n\pi R^2 (1 - \cos \theta_c)}{2 \text{Area}}}.
\]

or

\[
\chi_{A}^{i+1}(z_2) = \frac{1}{1 + 4\pi K g_{hs}(\sigma; \rho_{\text{bulk}}) f_{AC} \int_{-1}^{+1} \chi'_{A}(z_3) \rho(z_3) \, dz_3 + \chi_w f_{AC}(2, \text{wall}) \frac{n\pi R^2 (1 - \cos \theta_c)}{2 \text{Area}}}.
\]

The last term in the denominator of equation (7-8) is zero when \( z \) is greater than \( r_c \). \( K \) and \( g_{hs}(\sigma; \rho_{\text{bulk}}) \) are as defined in Chapter 5.

### 7.3.2 Density Functional Theory

If one has \( \rho(z_3) \) \textit{a priori}, then one may use it directly in equation (7-7). Normally, this density profile will not be known and must first be calculated. A naive approach would be to use equation (5-9) with a nonzero \( \phi_W(z_3) \). \( \phi_W(z_3) \) would be obtained as an average field over the entire surface as

\[
\phi_W(z_3) = \begin{cases} 
-\frac{n E_w c}{\text{Area}} \pi (r_c^2 - (z_3 + 1)^2) & \text{if } z_3 < (r_c - 1) \\
0, & \text{otherwise.}
\end{cases}
\]

This method, however, would be expected to miss fine features. In fact, at an average density of 0.75 and low temperatures, the theoretical wall densities were less than one-third of the simulation wall densities. A better method may be to set \( \phi_W(z_3) \) equal to zero and adjust \( \lambda(z_3) \) of equation (5-4) using Wertheim's theory on the wall sites.
Several approaches are being developed. The most promising uses the inhomogeneous form of Wertheim's theory (similar to Method 1 of Chapter 5 with equation (7-7)) very close to the surface and the bulk form of Wertheim's theory (similar to Method 2 of Chapter 5) elsewhere.

7.4 Results and Discussion

Table 7-2 summarizes the major results of this study. \( \eta_{bulk} \) is the bulk packing fraction or the packing fraction of the middle of the simulation cell. \( \chi_{i,wall} \) is the fraction of wall sites which are bonded. \( \chi_{0,wall} \) is the fraction of monomers of the fluid at the wall. \( \eta_{wall} \) is the fluid packing fraction at the wall. \( \Gamma_{\sigma^2} \) is adsorption in reduced units. The uncertainties stand for one standard deviation. The fluid contact numbers are extrapolations of properties close to the wall. Both the fraction of monomers and density (or packing fraction) at contact are extrapolations of \( \log \chi_{\sigma} \) and \( \log \rho \), respectively. The uncertainty in the estimates for the contact values include the statistical uncertainty in the properties near the wall and the regression uncertainty of the extrapolated line. Adsorption was calculated as in the previous chapters.

The standard deviations at the wall are quite large as seen in Table 7-2. However, these numbers rapidly decrease away from the wall until the uncertainties approach those in Chapter 5.

One run was done with no bonding energy on the hard spheres or the wall. Because of the geometric definition of a bond, even when the bonding energy was zero, the simulations reported a small amount of bonding. However, in this limit, the fluid behaves as simple hard spheres and the wall as a hard wall, so the results of our simulation with bonding energy equal to zero are consistent with those for simple hard spheres against a smooth, hard wall obtained in [22, 23].
<table>
<thead>
<tr>
<th>( \frac{\sigma^2}{d^2} )</th>
<th>Wall</th>
<th>( \eta_{\text{wall}} )</th>
<th>( \eta_{\text{ave}} )</th>
<th>Fluid</th>
<th>( \eta_{\text{ave}} )</th>
<th>Fluid</th>
<th>Wall</th>
<th>Packing fraction of ( \chi_{\text{wall}} )</th>
<th>( \chi_{\text{wall}} )</th>
<th>Fluid</th>
<th>( \chi_{\text{fluid}} )</th>
<th>( d_1 )</th>
<th>( d_2 )</th>
<th>( d_3 )</th>
<th>( d_4 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0127</td>
<td>5</td>
<td>7/5</td>
<td>1.03</td>
<td>0.0469</td>
<td>0.0003</td>
<td>0.3691</td>
<td>0.1157</td>
<td>0.0094</td>
<td>0.1013</td>
<td>0.0094</td>
<td>0.0094</td>
<td>0.0094</td>
<td>0.0094</td>
<td>0.0094</td>
<td>0.0094</td>
</tr>
<tr>
<td>0.2618</td>
<td>0.0975</td>
<td>0.0114</td>
<td>0.0160</td>
<td>0.0160</td>
<td>0.0160</td>
<td>0.0160</td>
<td>0.0160</td>
<td>0.0160</td>
<td>0.0160</td>
<td>0.0160</td>
<td>0.0160</td>
<td>0.0160</td>
<td>0.0160</td>
<td>0.0160</td>
<td>0.0160</td>
</tr>
<tr>
<td>0.2618</td>
<td>0.0975</td>
<td>0.0114</td>
<td>0.0160</td>
<td>0.0160</td>
<td>0.0160</td>
<td>0.0160</td>
<td>0.0160</td>
<td>0.0160</td>
<td>0.0160</td>
<td>0.0160</td>
<td>0.0160</td>
<td>0.0160</td>
<td>0.0160</td>
<td>0.0160</td>
<td>0.0160</td>
</tr>
<tr>
<td>0.2618</td>
<td>0.0975</td>
<td>0.0114</td>
<td>0.0160</td>
<td>0.0160</td>
<td>0.0160</td>
<td>0.0160</td>
<td>0.0160</td>
<td>0.0160</td>
<td>0.0160</td>
<td>0.0160</td>
<td>0.0160</td>
<td>0.0160</td>
<td>0.0160</td>
<td>0.0160</td>
<td>0.0160</td>
</tr>
<tr>
<td>0.2618</td>
<td>0.0975</td>
<td>0.0114</td>
<td>0.0160</td>
<td>0.0160</td>
<td>0.0160</td>
<td>0.0160</td>
<td>0.0160</td>
<td>0.0160</td>
<td>0.0160</td>
<td>0.0160</td>
<td>0.0160</td>
<td>0.0160</td>
<td>0.0160</td>
<td>0.0160</td>
<td>0.0160</td>
</tr>
<tr>
<td>0.2618</td>
<td>0.0975</td>
<td>0.0114</td>
<td>0.0160</td>
<td>0.0160</td>
<td>0.0160</td>
<td>0.0160</td>
<td>0.0160</td>
<td>0.0160</td>
<td>0.0160</td>
<td>0.0160</td>
<td>0.0160</td>
<td>0.0160</td>
<td>0.0160</td>
<td>0.0160</td>
<td>0.0160</td>
</tr>
<tr>
<td>0.2618</td>
<td>0.0975</td>
<td>0.0114</td>
<td>0.0160</td>
<td>0.0160</td>
<td>0.0160</td>
<td>0.0160</td>
<td>0.0160</td>
<td>0.0160</td>
<td>0.0160</td>
<td>0.0160</td>
<td>0.0160</td>
<td>0.0160</td>
<td>0.0160</td>
<td>0.0160</td>
<td>0.0160</td>
</tr>
<tr>
<td>0.2618</td>
<td>0.0975</td>
<td>0.0114</td>
<td>0.0160</td>
<td>0.0160</td>
<td>0.0160</td>
<td>0.0160</td>
<td>0.0160</td>
<td>0.0160</td>
<td>0.0160</td>
<td>0.0160</td>
<td>0.0160</td>
<td>0.0160</td>
<td>0.0160</td>
<td>0.0160</td>
<td>0.0160</td>
</tr>
<tr>
<td>0.2618</td>
<td>0.0975</td>
<td>0.0114</td>
<td>0.0160</td>
<td>0.0160</td>
<td>0.0160</td>
<td>0.0160</td>
<td>0.0160</td>
<td>0.0160</td>
<td>0.0160</td>
<td>0.0160</td>
<td>0.0160</td>
<td>0.0160</td>
<td>0.0160</td>
<td>0.0160</td>
<td>0.0160</td>
</tr>
<tr>
<td>0.2618</td>
<td>0.0975</td>
<td>0.0114</td>
<td>0.0160</td>
<td>0.0160</td>
<td>0.0160</td>
<td>0.0160</td>
<td>0.0160</td>
<td>0.0160</td>
<td>0.0160</td>
<td>0.0160</td>
<td>0.0160</td>
<td>0.0160</td>
<td>0.0160</td>
<td>0.0160</td>
<td>0.0160</td>
</tr>
<tr>
<td>0.2618</td>
<td>0.0975</td>
<td>0.0114</td>
<td>0.0160</td>
<td>0.0160</td>
<td>0.0160</td>
<td>0.0160</td>
<td>0.0160</td>
<td>0.0160</td>
<td>0.0160</td>
<td>0.0160</td>
<td>0.0160</td>
<td>0.0160</td>
<td>0.0160</td>
<td>0.0160</td>
<td>0.0160</td>
</tr>
<tr>
<td>0.2618</td>
<td>0.0975</td>
<td>0.0114</td>
<td>0.0160</td>
<td>0.0160</td>
<td>0.0160</td>
<td>0.0160</td>
<td>0.0160</td>
<td>0.0160</td>
<td>0.0160</td>
<td>0.0160</td>
<td>0.0160</td>
<td>0.0160</td>
<td>0.0160</td>
<td>0.0160</td>
<td>0.0160</td>
</tr>
<tr>
<td>0.2618</td>
<td>0.0975</td>
<td>0.0114</td>
<td>0.0160</td>
<td>0.0160</td>
<td>0.0160</td>
<td>0.0160</td>
<td>0.0160</td>
<td>0.0160</td>
<td>0.0160</td>
<td>0.0160</td>
<td>0.0160</td>
<td>0.0160</td>
<td>0.0160</td>
<td>0.0160</td>
<td>0.0160</td>
</tr>
<tr>
<td>0.2618</td>
<td>0.0975</td>
<td>0.0114</td>
<td>0.0160</td>
<td>0.0160</td>
<td>0.0160</td>
<td>0.0160</td>
<td>0.0160</td>
<td>0.0160</td>
<td>0.0160</td>
<td>0.0160</td>
<td>0.0160</td>
<td>0.0160</td>
<td>0.0160</td>
<td>0.0160</td>
<td>0.0160</td>
</tr>
<tr>
<td>0.2618</td>
<td>0.0975</td>
<td>0.0114</td>
<td>0.0160</td>
<td>0.0160</td>
<td>0.0160</td>
<td>0.0160</td>
<td>0.0160</td>
<td>0.0160</td>
<td>0.0160</td>
<td>0.0160</td>
<td>0.0160</td>
<td>0.0160</td>
<td>0.0160</td>
<td>0.0160</td>
<td>0.0160</td>
</tr>
<tr>
<td>0.2618</td>
<td>0.0975</td>
<td>0.0114</td>
<td>0.0160</td>
<td>0.0160</td>
<td>0.0160</td>
<td>0.0160</td>
<td>0.0160</td>
<td>0.0160</td>
<td>0.0160</td>
<td>0.0160</td>
<td>0.0160</td>
<td>0.0160</td>
<td>0.0160</td>
<td>0.0160</td>
<td>0.0160</td>
</tr>
</tbody>
</table>
Note in Table 7-2 that the bulk density, in general, goes up with fluid site bonding energy if the wall site energy stays the same. Hydrogen bonding tends to cluster the molecules together and away from the wall, so more molecules are found in the bulk. When only the wall site energy increases, the fluid sites and their molecules are more attracted to the wall and bulk density decreases. At the wall site density most studied, when both the wall and fluid site energies increase at the same rate, the bulk density decreases; therefore, the wall site energy slightly dominates the fluid energy. Nevertheless, the systems are large enough that for any one average system density, the bulk density does not vary much. At the one run with a low wall site density, as would be expected, the wall fluid density is depleted compared to the equivalent run with a higher wall site spacing.

The adsorption goes up as the bonding energy of both fluid and wall increase. This is in contrast to the hard wall cases where adsorption goes down as the clusters pull away from the wall. At the wall site density of approximately 0.5, the effect of having sites on the wall overcomes the decrease in entropy which having larger clusters at the wall creates.

Figure 7-2 shows relative reduced density \( \eta(z) / \eta_b \) versus distance from a wall with wall sites for an average system packing fraction of 0.3927. Figure 7-3 is the same as Figure 7-2 for all four average densities with all sites having \( 1/T^* = 5 \). Figure 7-4 shows fraction of monomers versus distance from the wall for the same runs as illustrated in Figure 7-2. The density and fraction of monomer profiles are similar to those with hard walls in Chapter 5, except for the region very near to the wall. The wall densities are all greatly enhanced over the runs without wall sites, especially when the wall site energy is high. The effect is, however, very much localized with the effects dying away after about 0.1 \( \sigma \). This same localization occurs in the depletion of monomers near the wall for the wall site cases. This localization appears in the orientation tensors with the magnitudes appearing to be twice as high as those for the hard wall in the two slices nearest the wall.
Figure 7-2. Packing fraction of 0.3927. Relative reduced density versus distance from an active wall for associating hard spheres for $\eta_{av}$ of 0.3927 and $\epsilon_{\text{site}}/kT = \epsilon_{\text{wall}}/kT = 0$ (a), 3 (b), 5 (c), and 7 (d).
Figure 7-3. $1/T^*=5$. Relative reduced density versus distance from an active wall for associating hard spheres for $e_{site}/kT = e_{wall}/kT = 5$ and $\eta_{av}$ of 0.1047 (a), 0.2618 (b), 0.3927 (c), and 0.493 (d).
and then returning close to the factors obtained for the hard wall cases. The depletion of monomers doesn't always produce an increase in molecules bonded only to the wall. There is evidence of some cooperative effect, where two wall sites near each other each entice a molecule to bond to the wall and then these two molecules now being near each other tend to bond to each other. Table 7-3 lists the standard deviations for density and fraction of monomers for collection slices near the wall and in the bulk for the cases with active wall sites.

We present the results for average weighted cluster size in Table 7-4. These data include those wall sites which are bonded in the cluster size calculation. There were 64, 49, 25, and 36 sites on each of two walls for $\eta_{\text{ave}} = 0.1047$, 0.2618, 0.3927, and 0.493, respectively. Figure 7-5, which has average weighted cluster size versus distance from the wall at $\eta_{\text{ave}} = 0.3927$ and $1/T^* = 5$ both with and without wall sites, is typical of all the wall site simulations. The cluster size starts below the bulk cluster size and rises away from the wall until near the bulk cluster size at $z = \sigma$. There is very little apparent structure. With wall sites, the wall cluster size is higher at the wall than in the equivalent hard wall case, dropping down to a number still higher than the equivalent siteless wall cases at $0.1 \sigma$. It then rises to near the same bulk cluster size at $z = \sigma$ as the siteless wall case (although the little dip and rise is more pronounced and occurs a little sooner than in what occurs with the unattractive wall). For active walls, the bulk cluster size is smaller than the wall cluster size at low densities and high temperatures, due to the relatively high wall site density; any monomers bonding to a wall site automatically doubles cluster size there. In the runs where the wall and fluid sites had $1/T^* = 7$, the cluster size profile is relatively flat. From the standpoint of cluster size, the fluid is almost homogeneous. Having four bonds on a sphere able to bond at the wall mean that the assumption in our theory about $\chi_A$ not being a strong function of orientation should be a more accurate assumption here than in the hard wall cases.
Table 7-3: NVT Monte Carlo simulations against an active wall: approximate standard deviations in packing fraction and fraction of monomers (near wall, in bulk)

(a)

<table>
<thead>
<tr>
<th>$\varepsilon_{site}/kT$ = $\varepsilon_{wall}/kT$</th>
<th>$\eta_{ave}$=0.3927</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\eta$</td>
<td>$\chi$</td>
</tr>
<tr>
<td>0</td>
<td>$\pm(0.7-1.2, 1-2)%$</td>
</tr>
<tr>
<td>3</td>
<td>$\pm(1-2, 2-3)%$</td>
</tr>
<tr>
<td>5</td>
<td>$\pm(3-4, 2-6)%$</td>
</tr>
<tr>
<td>7</td>
<td>$\pm(4-10, 6-10)%$</td>
</tr>
</tbody>
</table>

(b)

<table>
<thead>
<tr>
<th>$\eta_{ave}$</th>
<th>$\varepsilon_{site}/kT$= $\varepsilon_{wall}/kT$=5</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\eta$</td>
<td>$\chi$</td>
</tr>
<tr>
<td>0.1047</td>
<td>$\pm(3-4, 2-3)%$</td>
</tr>
<tr>
<td>0.2618</td>
<td>$\pm(4, 2-5)%$</td>
</tr>
<tr>
<td>0.3927</td>
<td>$\pm(3-4, 2-6)%$</td>
</tr>
<tr>
<td>0.493</td>
<td>$\pm(2-4, 4-7)%$</td>
</tr>
</tbody>
</table>
Figure 7-4. Fraction of monomers versus distance from an active wall for associating hard spheres for $\eta_w$ of 0.3927 and $\epsilon_{site}/kT = \epsilon_{wall}/kT= 3$ (squares), 5 (circles), and 7 (triangles).
Table 7-4: NVT Monte Carlo simulations against an active wall: approximate weighted-average cluster sizes in slices near wall and in bulk (based on 500 molecules in simulation cell plus wall sites)

(a)

<table>
<thead>
<tr>
<th>$\varepsilon_{\text{sim}}/kT=$</th>
<th>$\eta_{\text{ave}}=0.3927$</th>
<th>$\varepsilon_{\text{wall}}/kT$</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.044±0.013</td>
<td>1.034±0.001</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>2.051±0.032</td>
<td>1.878±0.018</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>179.9±10.5</td>
<td>241.7±10.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>530.6±7.91</td>
<td>535.9±1.83</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(b)

<table>
<thead>
<tr>
<th>$\eta_{\text{ave}}$</th>
<th>$\varepsilon_{\text{sim}}/kT=\varepsilon_{\text{wall}}/kT=5$</th>
<th>$\varepsilon_{\text{wall}}/kT$</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1047</td>
<td>2.421±0.127</td>
<td>1.710±0.0147</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.2618</td>
<td>3.522±0.220</td>
<td>4.810±0.254</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.3927</td>
<td>179.9±10.5</td>
<td>241.7±10.2</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 7-5. Weighted-average cluster size versus distance from a hard wall (symbol) and an active wall (line) for $\varepsilon_{\text{site}}/kT = \varepsilon_{\text{wall}}/kT = 5$, and $\eta_{\text{av}} = 0.3927$. Data from active wall site case includes bonded wall sites in the cluster size.
In Figure 7-6 we see a preliminary result for fraction of monomers theory versus simulation for an average system packing fraction of 0.3927 and $1/T^* = 5$ for both fluid and wall sites. The simulation densities were input to equation (7-8b) to obtain the results. Equation (5-16) was also used. These results were typical for all other conditions. Higher site energies resulted in less accurate results than those shown. Lower site energies resulted in more accurate results. All theoretical results were of at least qualitative accuracy. The theory is high in the bulk as would be expected from the results in previous chapters. The theory result is also much higher than the simulation result inside $1\sigma$ for currently unknown reasons. Accuracy is quite reasonable however within $0.05\sigma$ of the wall.

**Figure 7-6.** Fraction of monomers versus distance from an active wall for 4-site associating hard spheres for $\eta_{av}$ of 0.3927 and $\epsilon_{site}/kT = \epsilon_{wall}/kT = 5$ for theory (line) and simulation (symbols). Simulation densities were used as input.
8. Future Work

We have developed a density functional theory which over a broad range of conditions model on a molecular scale the density and free energy of associating fluids near solid surfaces. Research is never completed, however, and many paths can be taken to extend this work.

One path to take would be in extending our theory to other situations besides the completion of the development our density functional theory of Chapter 7. For instance, one could test our theory with other wall potentials, obtaining information that would be useful in the study of competitive adsorption and in separations. Also, one could do simulations of confined fluids with the surfaces close enough such that there is no bulk region. The theory would be altered such that the chemical potential and the average density would be the fixed inputs. For some situations, speeding up the simulations would be advantageous. We are working on implementing an acceleration technique for 4-site or cluster simulations. We discussed over a year ago a simulation method which would include the translation and reorientation of entire clusters. We felt it would not work and did not take action. However, recent work with the mixtures of Chapter 5 demonstrated again the need for a new simulation technique.

Another path one could take would be to alter portions of our theory to improve accuracy. Our Tarazona-type density functional of Method 2 is unlikely to be the most accurate for all cases. Since Method 1 of Chapter 5 has accurate peak placements and is a simpler approach for mixtures once the pure fluid version is implemented, one can attempt instead to improve Method 1. An approach similar to that found in [56, 128] may improve the contact density. The main improvement can probably be had by introducing a more accurate radial distribution function, $g$. Once this improved method of calculating $g$ is working, one could then replace the Tarazona hard sphere density functional with the
Rosenfeld [162] hard sphere density functional to have a method even more conducive to mixtures. However, all these new approaches would suffer from heavy computation and more difficult implementation. We have recently learned of a modified Meister-Kroll [158-160] density functional [212, 213], which, with its substitution for the Tarazona DF in our Method 1 approach, could be a useful and accurate method conducive for solving mixture problems. Also, minor improvements could be made in our theory by implementing those extensions to Wertheim's theory that were mentioned in Section 2.2.

A third path would be to make direct comparisons against experimental data. However, there has been very little work done on density profiles or local thermodynamic properties. One could make initial comparisons for gross properties such as surface tension, adsorption, and disjoining pressure while the paucity of quantitative experimental data on local properties begins to be alleviated. Although the hard sphere version of SAFT [10, 65] results in fairly good thermodynamic property evaluations for bulk fluids, our hard sphere density functional theory may not be completely satisfactory for comparisons to realistic fluids. The simplest approach to take in obtaining results for realistic fluids is to add long range attraction. One can do this by means of a mean field approximation added as a perturbation in the density functional theory: In the mean field approximation the grand potential, $\Omega$, can be written as

$$\Omega = F_\text{r}[\rho(r)] + \int \rho(r)[\phi(r) - \mu] \, dr + 0.5 \int \rho(r)\rho(r')u_a(|r - r'|) \, dr \, dr'$$

where $F_\text{r}[\rho(r)]$ is the intrinsic free energy of the reference fluid with location specific density, $\rho(r)$, and $u_a$ is the attractive part of the fluid-fluid intermolecular potential. We can use the LJ version of the Tarazona density functional [149]. An approach for water may be to use the extended 4-site model of Nezbeda et al. [214, 215], which yields the liquid structure in "very good agreement" with that of real water.
Indeed, combining the Rosenfeld or Meister-Kroll DFs with techniques we have demonstrated in this work and with more realistic models could result in fairly simple, yet very accurate, means in which to study the molecular structure and thermodynamics of real associating fluids near surfaces.
9.0 References


