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PURE AND BINARY ASSOCIATING FLUIDS NEAR ACTIVE SURFACES

by

JIE ZHANG

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

APPROVED: THESIS COMMITTEE

[Signature]
Peter Nordlander, Chair
Professor
Department of Physics and Astronomy

[Signature]
Walter G. Chapman
Professor
Department of Chemical Engineering

[Signature]
Randy G. Hulet
Professor
Department of Physics and Astronomy

[Signature]
George J. Hirasaki
Professor
Department of Chemical Engineering

Houston, Texas

September, 2001
Abstract

Pure and Associating Fluids near Active Surfaces

By

Jie Zhang

The properties of associating fluids in contact with adsorbing surfaces are essential for the control of many processes of current industrial and scientific interest. Potential applications are diverse. Despite the need for a molecular understanding of interfacial properties, only in the past a few years have simple, accurate theories been developed for even simple fluids. Our group has developed a new density functional theory which applies the weighting from Tarazona's hard sphere density functional theory to Whertheim's bulk first-order perturbation theory to investigate inhomogeneous pure associating fluids confined between hard walls. This theory has been shown to be in good agreement with computer simulation results.

In this work, we extend this promising theory to binary mixtures of hard spheres and associating fluids, and apply the mixture theory to non-additive hard spheres. We have accurately predicted phase separation, critical temperature and structural properties for this model. We then extend this theory to describe the properties of associating fluids near active surfaces. Metropolis Monte Carlo computer simulations are performed for one-sited (dimerizing), two-sited (linear chain forming) and four-sited (cluster forming) molecules near active surfaces. Our theory compares favorably with simulation results for a wide range of fluid density and bonding energy for surface coverage, density profiles and fraction of monomers.
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Chapter 10 SUMMARY AND FUTURE WORK
Chapter 1 Introduction

The behavior of fluids at interfaces is of much interest in theoretical and applied research today [3,4]. Many processes of industrial interest are controlled by the interaction of complex fluids (e.g. hydrogen bonding fluids, hydrocarbons, proteins, and polymers) with active solid surfaces. Potential applications are diverse, including wettability as related to oil recovery and environmental remediation, membrane separation, adsorption in porous solids and micro- or nano-manufacturing of thin films. Efforts to model these systems have been hindered by the lack of accurate theories. During the past ten years, many significant advances have been made in applying statistical mechanics to complex fluids in the bulk. In recent developments in this group and others, extensions of these bulk theories to interfacial systems have been made. Although these are simple models of fluids, they retain many of the essential characteristic features of real fluids, but the models 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. 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 polymers and associating fluids, especially lacking in literature are studies of such complex fluids with active surfaces.
Our group recently reported a new density functional (DF) theory [40] that applies the weighting from Tarazona's hard sphere density functional theory to Wertheim's bulk first-order perturbation theory to investigate non-uniform associating fluids (AFs). This theory has been shown to be in good agreement with computer simulation results. We plan in this thesis to extend our theory to mixtures of associating fluids, and fluids near surfaces with associating sites. The goal of this research is to provide scientists and engineers with a useful theory to predict interfacial structure and thermodynamic properties of these systems.

The liquids and dense fluids are distinguished from dilute gases by the importance of the collisional process and short-range correlations and from solids by the lack of long-range order. In order to understand the behavior of fluids, it is important to study the different types of interactions that can occur in the fluid. Reed and Gubbins [41] classified these intermolecular forces as short range valence or chemical interaction; long range interactions including dispersion, polarization or induction energies and direct electrostatic energies; and short range and intermediate range forces such as hydrogen bonding. The magnitudes of hydrogen bonding are an order of magnitude lower than chemical bonding energies, and for this reason, their influence is evident in physical property behavior. Molecules exhibiting this type of interaction are called associating molecules. Charge transfer complexes present another kind of interaction that gives rise to association.
Of these interactions, associating or hydrogen bonding is the least understood. Through strong short-range forces, which are typically in the range of 8 to 40 KJ/mol, and only one order of magnitude less than that of a covalent bond, association forms relatively long-lived molecular clusters, and has a large effect on physical properties [4]. For example, association plays an important role in almost all applications which involve water. For a liquid of such a low molecular weight, water has unexpectedly high melting and boiling points and latent heat of vaporization. Another unusual property of water is its density is at maximum at 4 °C and that the solid (ice) is lighter than the liquid; this indicates that in the ice lattice the molecules prefer to be farther apart than in the liquid. Hydrogen bonds are not unique to water. They exist to varying degrees between electronegative atoms (e.g. O, N, F) and H atoms covalently bound to similar electronegative atoms. The ubiquitous nature of hydrogen bonding (associating) molecules makes the understanding of association at the molecular level particularly important.

However, associating fluids have traditionally been difficult to model, and only recently has significant progress been made in this area. Ghonasgi and Chapman [5] reviewed theories for associating fluids in the bulk. Of many methods for dealing with associating fluids in the bulk, the most promising one is Wertheim's theory [6] due to its relative simplicity and its accuracy in matching with computer simulation data. Wertheim's theory is often written in the form of a perturbation theory that relates excess Helmholtz free energy to the fraction of unbonded molecules. Wertheim's theory accurately predicts the thermodynamic properties of hard sphere associating fluids in the
bulk [5-10]. Our group has successfully extended this theory to describe associating fluids near hard walls.

The interfacial properties of fluids are determined by the presence of an external field, such as the introduction of hard or active walls. Because of broken symmetry, the fluid is inhomogeneous and it exhibits different properties than bulk fluid. This difference is important to understanding complex phenomena such as adsorption, desorption and wetting of thin films. The literature of applying classical statistical mechanics to inhomogeneous fluids near surfaces begins in 1940's. For general reviews of statistical theories of fluids near surfaces, see [13-16]. Modern approaches to inhomogeneous fluid study are generally based on integral equation or density functional theories [3].

There have been enormous growth in the use of density functional methods to inhomogeneous fluids [3]. Such systems are characterized by spatial variation of the average one-body density. Density functional methods are based on the idea that the free energy of the inhomogeneous fluid can be expressed as a functional of this one-body density. From a knowledge of this functional all the relevant thermodynamic functions can be calculated. Moreover, derivatives of the functional determine the equilibrium distribution functions that describe the microscopic structure of the inhomogeneous fluid. Many explicit approximations for the free energy functional have been made to allow calculations to be made for a variety of inhomogeneous systems. The weighted-density approximations (WDA) uses coarse-graining procedure whereby a smoothed density is constructed as an average of the true density profile over a local volume that is
determined by the range of intermolecular forces. The so called Mark II recipe of WDA from Tarazona [42] is especially appealing, because it shows excellent agreement with computer simulation experiments for hard sphere fluids at a wide range of densities. Our density functional theory for associating fluids is essentially a combination of Tarazona's Mark II recipe with Wertheim's theory for association.

Kierlik and Rosinberg (KR) [43-45] developed a perturbational free energy density function approach applicable to associating fluids consisting of fully associating hard spheres by applying Wertheim's theory for polymerization [46]. Its implementation is rather difficult. KR theory for associating fluids regards a polyatomic fluid as the complete association limit of a model of associating molecules. In our theory, as a contrast, clusters form as a result of the extent of association. Our theory is simpler to implement and has shown good agreement with simulation results.

In this work, we extend this promising theory to binary mixtures of hard spheres and associating fluids, and apply the mixture theory to non-additive hard spheres to show phase behavior of binary mixtures. We will then extend this theory to describe the properties of associating fluids near active surfaces for one-sited (dimerizing), two-sited (linear chain forming) and four-sited (cluster forming) molecules. We present a brief review of the theories and techniques that we used in this study in the next three chapters.
Chapter 2 Theories of inhomogeneous fluids

2.1 Introduction

Inhomogeneous fluids exhibit different properties than bulk fluid due to introduction of an external potential. An external field plays important roles in controlling the behavior of inhomogeneous fluids. The one-body density profile and interfacial geometry is uniquely determined by the one-body external potential. This includes the important case of confined fluids, where the interfacial properties are partially determined by the wall-fluid potential. Properties of the inhomogeneous fluid depend not only on the local density at position $r$, but also on the densities near $r$. This is the essential difference between an inhomogeneous fluid and a bulk fluid, and lead to two modern approaches towards inhomogeneous fluid theories, the integral equation theories and density functional theories.

2.2 Integral Equation Theory

Henderson [3] gave a comprehensive review of modern approaches of integral equation theory (IE). The singlet integral equation theory uses the Ornstein-Zernike (OZ) equation for direct correlation function. If we treat the wall as a giant molecule of an infinitely dilute solution, we essentially view the fluid wall system as a binary mixture, and we have three coupled OZ equations for this system [47,48], which is basically the bulk OZ equations for mixtures. We will not go into the details of IE because we will not use it in this study. However, previous works in this group have compared IE with density functional theory for pure associating fluids near a hard wall, using the
associative form of the Henderson-Abraham-Baker (HAB) equation. IE has been shown to be less accurate for lower densities and does not give correct wall contact densities due to the Percus-Yevick equation of state used.

2.3 Density functional theory

The idea behind the density functional method is that given a fluid intermolecular potential, the structure geometry of the system is uniquely determined. Systems are characterized by spatial variation of the average one-body density. The free energy of the inhomogeneous fluid can be expressed as a functional of this one-body density. From knowledge of this functional, all the relevant thermodynamic functions can be calculated. Moreover, derivatives of the functional determine the equilibrium distribution functions that describe the microscopic structure of the inhomogeneous fluid.

Advantages of using free energy density functional theory for inhomogeneous include:

1. its accuracy against computer simulation for hard spheres,

2. its origin in the grand potential, which allows it to be applied to a broad group of systems,

3. its expression in Helmholtz free energy functional and therefore all thermodynamics functions can be calculated from it, and

4. its simple implementation and fast speed of calculation.

However, determining the exact free energy functional is equivalent to solving exactly the statistical mechanics for the particular fluid under study. Explicit approximations
have to be made for the free energy functional that will allow calculations to be made for a wide variety of inhomogeneous systems.

We begin with the definition of the grand potential

\[ \Omega = A[\rho(r)] + \int \rho(r)[\phi_0(r) - \mu] \, dr, \quad (2-1) \]

where \( \rho \) is the singlet total number density, \( \phi_0 \) is the external potential; \( \mu \) is the chemical potential, and \( A \) is the system Helmholtz free energy functional.

With the intermolecular potentials as defined above, the Helmholtz free energy can be broken up into a sum of ideal and excess parts as

\[ A[\rho(r)] = A^{id}[\rho(r)] + A^{ex}[\rho(r)]. \quad (2-2) \]

The ideal functional is known exactly and can be written as

\[ A^{id}[\rho(r)] = \int \rho(r) kT [\ln \rho(r) - 1] \, dr. \quad (2-3) \]

The excess part can be calculated by forming approximations for the functional. The grand potential is minimized at the equilibrium density [49]. Therefore, at equilibrium,
\[ \Delta \mathcal{A}[\rho(r)]/\delta \rho(r) = 0 \quad (2-4) \]

we can get the direct correction function hierarchy by further differentiating the Helmholtz free energy,

\[ c(r, r') = -\frac{\delta^2 A^\text{ex}}{kT \delta \rho(r) \delta \rho(r)} \quad (2-5) \]

The key to solving the density functional lies in the approximation to the excess Helmholtz functional. Presumably, one can still minimize the grand potential when \( A^\text{ex} \) is only an approximation to the exact functional. Early approximations include square gradient approximations, which truncates the gradient expansion of \( A^\text{ex} \). One can also use methods of density expansion to solve \( A^\text{ex} \) [3]. Toxvaerd [50] pioneered the local density approximation (LDA) by using hard spheres as the reference fluid. Despite many applications of LDA, especially the van de Waals form of it, it has the fundamental flaw of giving no information about the short-range correlations that characterize a real fluid, which reflects the underlying mean-field character of the approximation. Because of the absence of short-range correlations, the LDA theory cannot describe oscillatory density profiles, nor will it give a correct description of the density at a sharp boundary such as a hard wall.

The weighted-density approximations (WDA) for \( A^\text{ex} \) is aimed to improve this defect of LDA. The idea behind WDA or smoothed density approximations was the introduction of a coarse-graining procedure whereby a smoothed density \( \bar{\rho}(r) \) is
constructed as an average of the true density profile $\rho(r)$ over a local volume that is
determined by the range of intermolecular forces. The pronounced peaks that occur in an
oscillatory profile, where the local density may exceed that for close packing, are
smoothed out in the coarse-grained density so that the excess free energy should be well
approximated by a local function of $\bar{\rho}(r)$:

$$A^e(r) = \int d\tau \rho(r) f(\bar{\rho}(r)) \quad (2-6)$$

where $f(\bar{\rho}(r))$ is the excess, over ideal, free energy per molecule. There are different
versions of WDA, based on different recipes for $\bar{\rho}(r)$.

Following the success of his Mark I WDA [3], with a weight function
proportional to a Heaviside step function, Tarazona developed a more sophisticated
version of WDA, called Mark II version [3], by constructing a smoothed density which
would lead to an accurate direct correction function $c^{(2)}(\rho;r)$ for the uniform hard sphere
fluid over a wide range of bulk densities. Tarazona's Mark II smoothed density is
constructed as,

$$\bar{\rho}(r) = \int d\tau' \omega(|r-r'|; \bar{\rho}(r)) \rho(r') \quad (2-7)$$

$\omega$ is specified by requiring (2-6) with (2-7) to produce, upon differentiation, the
hard sphere direct correlation function $c^{(2)}(\rho;r)$ close to Percus-Yevick results.
Tarazona showed that his Mark II version gave substantially better agreement with
simulation for the density profile and surface tension of hard spheres near a hard wall, as well as hard sphere freezing. By including a mean field attraction, Tarazona et. al. [51] also produced realistic density profiles for an example of a wetting transition. Van Swol and Henderson [52, 53] obtained good results compared to simulations for capillary condensation [54, 55] and for systems of hard sphere binary mixtures of unlike sized spheres at a hard wall [56]. Many other successful applications of Tarazona Mark II [57] have showed that it is a versatile and accurate approximation scheme for inhomogeneous fluids.

Other WDA recipes include the one developed by Meister and Kroll [58] and Groot and van der Eerden [59, 60], in which $A^\infty$ is expressed as a functional of some slowly varying reference density $\rho_0(r)$, as well as $\rho(r)$. It is appealing since it appears to avoid the ad hoc nature of previous recipes. We will keep this recipe in mind as an attractive alternative to Tarazona Mark II. Rosenfeld [61] and Kierlik and Rosinberg [62] gave a WDA derived specifically for hard sphere mixtures. The oscillation in the density profile are very accurate [62] for hard sphere hard wall (HSHW) system, even more so than for Tarazona Mark II. However, at wall contact, the theory satisfies wall sum rule [3], but because of its using of PY equation of state, the pressure is different than the exact Carnahan-Starling result [63]. This method, however, has the advantage of being easily extendable to mixtures.

In the past several years, many of the weighting methods mentioned above have been used to solve a wide range of problems, especially Tarazona Mark II. In earlier
studies from this group, we have successfully combined Tarazaon's Mark II with Wertheim's theory for association, which we will briefly review in next chapter, to describe associating fluids near a hard wall. This study will further extend this theory to binary mixtures and to associating fluids near an active wall.
Chapter 3  Wertheim's Theory of Association

3.1 Introduction

We have briefly discussed the nature of association and the effects that hydrogen bonding has on physical properties, especially of water. Because of the ubiquitous nature of hydrogen bonding materials, many theories have been developed for this phenomena [17,18]. Most of these theories fail in explaining all the aspects of association. Theoretical methods used to account for association are generally classified into three categories: the chemical theory, the lattice theories and statistical mechanics based theories. We will limit our discussion to statistical mechanics based theories, which are based on introducing the association interaction into the potential model of the system [6,64]. Association interactions are known to be highly asymmetric and directional in character [65,66]. Andersen [65,66] 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. Andersen used the cluster expansion method of Mayer to determine the pair correction functions of hydrogen bonded fluids. He simplified the cluster expansion by assuming that only single bonds can form at each site.

3.2 Wertheim's theory of association

Wertheim's theory of association [6a, 6b, 6c, 6d] is similar to Anderson's theory in many ways in that it introduces the geometry of interaction at an early stage. However, Wertheim's theory is based on a resummed cluster expansion that is made in terms of two densities, the total number density \( \rho \), and the monomer density \( \rho_0 \). Based on certain
careful approximations, Wertheim was able to simplify the complex graphical expansions. The final expression can be written in the form of a thermodynamic perturbation theory. He further extended his theory to molecules with more than one bonding site. Chapman [10] later extended the theory to mixtures of associating fluids.

Wertheim's first-order thermodynamic perturbation theory (TPT1) was developed for associating fluids, i.e. molecules that present highly directional and short-ranged interactions, such as hydrogen bonding. The nature of association leads to the assumption of an association site with a small volume available for bonding. TPT1 further assumes that this site allows only one other molecule to approach sufficiently close and in the correct orientation to form a bond. The second order theory accounts for the dependence of bonding at one site on the bonding of another site [46], but it is difficult to calculate since it requires the appropriate three-body distribution function.

According to Wertheim's TPT1, the change of free energy due to association for a molecule with M bonding sites, is given by,

\[ A_{asso} = \frac{A - A_{of}}{NkT} = \sum_{A_{ef}} [\ln \chi_A - \frac{\chi_A}{2} + \frac{1}{2}] \]  

(3-1)

where \( \chi_A \) is the fraction of site A on fluid molecules that are not bonded, and the sum is over all bonding sites. \( \chi_A \) is given by
\[ \chi_A = \frac{1}{1 + \rho \sum_{B \in \Gamma} \chi_{B} \Delta_{AB}} \]  

(3-2)

where \( \Delta_{AB} \) represents the association strength between a site A and a site B. This is the bulk form of Wertheim's first theory for association. Wertheim's theory has been extended to many bulk systems of associating fluids, including binary mixtures [69], hard sphere molecules with one or two bonding sites [8]. Ghonasgi and Chapman [5] broadened the theory to include hard spheres [5] and Lennard-Jonnes spheres with four bonding sites. In comparison with molecular simulation results, Wertheim's theory is highly accurate and has the advantage of being directly compared with computer simulation results, because its molecularly-based approach.

Segura and Chapman [7] have successfully combined Wertheim's first order theory of association with Tarazona's Mark II density functional theory to predict the thermodynamic properties and structure of hydrogen bonding fluids in the fluid-solid interfacial region. We will continue this work by extending this theory to mixtures and systems include active surfaces.
Chapter 4 Molecular Simulation

Molecular simulation has become an integral part of statistical mechanics since Metropolis and coworkers [67] performed the first computer simulation of a liquid. There are generally two types of molecular simulations, i.e. Monte Carlo and Molecular Dynamics. For a known interaction model, molecular simulations provides a method to perform computer experiment to calculate thermodynamic and transport properties, and can be used as a test for statistical mechanics based theories that incorporate approximations. Another advantage of molecular simulation is that it can separate many parameters that influence the properties of a system and study the effects of each one for an otherwise complex system. The results of computer simulations may also be compared with those of real experiments. Computer simulations can provide a direct route from microscopic details of a system to macroscopic properties of experimental interest, and thus offer insight to real systems. In this study, we use the technique originally developed by Metropolis to study model systems and to test our theory. A detailed account of computer simulations is given by Allen and Tildesley [68].

Metropolis et. al [67] proposed a method to sample phase space in a chosen statistical ensemble to obtain ensemble averages of properties of interest. It consists of randomly displacing and reorienting the molecules around its original position and accepting this new configuration with a probability p.
\[ p = \begin{cases} 
1, & \text{if } \exp(-(\phi_{\text{new}} - \phi_{\text{old}})/kT) > 1 \\
\exp(-(\phi_{\text{new}} - \phi_{\text{old}})/kT), & \text{otherwise}
\end{cases} \tag{4-1} \]

where \( \phi_{\text{new}} \) and \( \phi_{\text{old}} \) are the contribution of a molecule to the potential energy of the system in new and original molecule position and orientation.

The number of molecules be modeled is usually between 100 and 1000, much smaller than the quantities of any macroscopic system. To obtain a statistically meaningful result, we use a periodical boundary condition, and the system is in essence infinitely replicated by placing identical simulation cells surrounding the cell of study. By using a technique of "periodic imaging", a molecule entering the system through one side leaves the system through another side.

Euler angles are used to relate orientations in a space-fixed axis to those of a body-fixed coordinate system. Each molecule has six degrees of freedom, and each (3 in position and 3 in orientation) is displaced randomly. The maximum changes of each degree of freedom are adjusted to ensure a reasonable acceptance rate (usually 25% to 40%), so that phase space is explored efficiently.

Our simulation is done in a NVT ensemble, where the number of molecules, volume and temperature are fixed. The simulations are started from an initial configuration with no overlap for hard spheres. When an equilibrium is reached (the criteria for determining an equilibrium will be discussed in later chapters), its parameters,
such as orientations and positions of each molecule, can be saved as inputs for further runs. The ensemble averages for system properties, such as density profile, potential energy, are calculated by averaging over different configurations. Each run typically consists over 10 million configurations, and more are needed for multi-component systems as well as when interaction with active wall is included.
Chapter 5 Binary associating fluid mixtures against a hard wall

5.1. Introduction

The behavior of fluids at interfaces is of much interest in theoretical and applied research today [1,3]. Many industrial processes including adsorption and membrane separation rely on the application of this knowledge. Despite the need for a molecular understanding of interfacial properties, only in the past few years have simple, accurate theories been developed for even simple fluids [3]. Although these are simple models of fluids, they retain many of the essential characteristic features of real fluids, but the models 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. 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. We recently reported a new density functional (DF) theory [69] that applies the weighting from Tarazona’s hard sphere density functional theory to Wertheim’s bulk first-order perturbation theory to investigate non-uniform associating fluids (AFs). This theory has been shown to be in good agreement with computer simulation results. In this paper, we extend our DF theory to form a perturbation DF theory for associating hard sphere fluid mixtures.

Accompanying the development of the theories for one component homogeneous fluids, there have been many attempts to extend such theories to mixtures. Lebowitz [70]
solved the Percus-Yevick (PY) equation (an integral equation, IE) for bulk hard sphere mixtures of spheres of different diameters. Accurate analytical solutions for the radial distribution function using a Verlet-Weis [71] construction were obtained by Lee and Levesque [72] and Henderson and Grundke [73]. Hamad [74] and references therein] predicted with high accuracy the equimolar compressibility factor for a non-additive binary hard sphere mixture. His method, general for multi-component 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 [75] 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 modified weighted density approximation (MWDA) method [76]. The MWDA method was slightly more accurate compared with simulations than the perturbation theory. Tan et al. [56] extended the Tarazona DF [51] to binary hard sphere mixtures against a hard wall. They found reasonably accurate density profiles when compared to simulation [78] for size ratios $\sigma_2 / \sigma_1 \leq 3$. Rosenfeld [61] used his DF theory to study the bulk phase behavior of asymmetric binary hard sphere mixtures. He discussed possible extension to binary mixtures in external fields. (See Lee [15] and references therein) Work has also been done on Leonard-Jones mixtures.

In addition to our theory, other approaches have also been developed for associated fluids. Kierlik and Rosinberg [43-45] developed a perturbation free energy density functional approach applicable to inhomogeneous fluids consisting of fully
associated non-overlapping hard spheres (i.e., tangent chains) by applying Wertheim's theory for polymerization [46]. The method uses their own [6a,b,c,d] 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 for association use the number-average chain length in the bulk to determine the density profile of the inhomogeneous mixture. However, in this paper, we would like to control the input species as a constraint on bonding and then, let the temperature determine the extent of association.

In our approach [69], we have combined Tarazona's DF theory (Mark II) [51] with Wertheim's theory for associating fluids [6a,b,c,d] to create a perturbation density functional theory for associating fluids. Tarazona's DF theory uses weighting functions that are optimized to fit the bulk hard sphere direct correlation function. Our theory applies the weighting from Tarazona's hard sphere DF to Wertheim's bulk first order perturbation theory. We have shown this approach to be in good agreement with simulation results. Here we extend our DF theory to binary mixtures of associating fluids.

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 [79] 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 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 simulation results.

We have chosen this mixture because it shows interesting bulk phase behavior. Nezbeda et al. [80] have shown that such a mixture exhibits type IIId phase behavior. By the van Konynenburg and Scott nomenclature, this mixture is said to exhibit gas-gas immiscibility of first type.

5.2. Molecular Simulations

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

\[
\phi(r, \omega_1, \omega_2) = \phi_r(r) + \sum_A \sum_C \phi_{AC}(r, \omega_1, \omega_2), \tag{5-1}
\]

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 \(r\) 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

\[
\phi_r(r) = \begin{cases} 
  \infty & \text{if } r < \sigma, \\
  0 & \text{if } r > \sigma,
\end{cases} \tag{5-2}
\]
Where $\sigma$ is the hard sphere diameter. $\phi_{AC}$ represents the association potential between a site A on the molecule 1 and a site C on molecule 2. The association potential is modeled by an anisotropic short-range square well. The potential of interaction due to these sites is

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


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 on molecule 2 and the vector $r$. The associating component in the model selected in this work has four bonding sites, A, B, C, 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 $\varepsilon_{AC} = \varepsilon_{AD} = \varepsilon_{BC} = \varepsilon_{BD} = \varepsilon_{site}$, and $\varepsilon_{AA} = \varepsilon_{BB} = \varepsilon_{CC} = \varepsilon_{DD} = 0$. In effect, if two eligible bonding sites are close enough and oriented correctly, then a bond is formed. In the simulations and in our theoretical calculations, the radial limits of the square-well association were set to $r_c=1.05 \sigma$ and the angular limit was set to $\theta = 27^\circ$.

The nonassociating component in the mixture interacts with itself and with the associating component through the pair potential $\phi_R(r)$ defined in equation (5-2). Our mixture contains like-sized hard spheres, in which a certain fraction can self associate through the full pair potential of equation (5-1).
The simulation cell consists of hard walls at \( z = 0 \) and \( z = H \). Periodic boundary conditions with box length \( L \) were imposed in the other two directions. To ensure that the density oscillations died away in the central region, \( H = \alpha \times L \); where \( \alpha > 1 \). With this choice of \( \alpha \), the two walls did not interfere with each other and there was a bulk region in the middle of the cell. Due to adsorption at the walls, the average density in the cell is different from the bulk density in the center of the cell. The density and monomer profiles were calculated by averaging the properties of each point on one side of the cell midpoint with its geometrically symmetrical twin on the other side of the midpoint. Hence, the results appear as a function of distance from one wall in the \( z \) direction. In addition to the pair potential on the particles, the walls exerted an external potential,

\[
\phi_w(z) = \begin{cases} 
\infty & \text{if } r \leq 0 \text{ or } z \geq H, \\
0 & \text{otherwise.}
\end{cases} \tag{5-4}
\]

Acceptance statistics were calculated separately for both the hard spheres and the 4-site hard spheres. The acceptance criterion for each species was \( 20 \sim 50\% \), 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 sub-averages of properties from each run of a series were used to calculate averages. Generally, more configurations were needed at the highest amount of association, a requirement that becomes more necessary at higher densities. See Table 5-1.
Table 5-1: 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>$\varepsilon_{site}/kT$</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>

Table 5-2: Density Functional Theory versus Simulation for Cases of Table 1

<table>
<thead>
<tr>
<th>Bulk density, total/assoc. $\rho \sigma^3$</th>
<th>Site energy, $\varepsilon_{site}/kT$</th>
<th>Bulk density, Wall density, $\rho \sigma^3$, total/assoc.</th>
<th>$\chi_{0, \text{wall}}$</th>
<th>$\chi_{0, \text{bulk}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>simulation</td>
<td>theory</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±0.0003 / 0.0731±0.0071</td>
<td>0.2356 / 0.0792</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>
</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>
</tr>
</tbody>
</table>

\[ \chi_{0, \text{wall}} \]

\[ \chi_{0, \text{bulk}} \]
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 [69].

Criteria used for determining if equilibration had been reached at the end of a series of simulations include those listed in [64]. 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 [6a,b,c,d]. Densities and fractions of monomers were calculated as described in [64]. Fractions of monomers are reported for the component that has association sites.

5.3. Density Functional Theory for a Binary Mixture

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. We begin with the definition of the grand potential

$$\Omega = A[\rho(r)] + \int \rho(r)[\phi_w(r) - \mu] dr,$$

(5-5)

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 functional. The grand potential is minimized at the equilibrium density. Therefore, at equilibrium, \( \delta \Omega(\rho(r))/\delta \rho_i(r) = 0 \), where \( \rho_i(r) \) is the density of component \( i \). Generalizing to a binary mixture [5,34, 35],
\[ \Omega(\rho_1(r), \rho_2(r)) = A[\rho_1(r), \rho_2(r)] + \sum_{i=1}^{2} \int \rho_i(r) [\phi_{ii}(r) - \mu_i] \, dr, \]  

(5-6)

where the subscript \( i \) denotes species \( i \). With the intermolecular potentials as defined above, the Helmholtz free energy can be broken up into a sum of ideal and excess parts as

\[ A[\rho_1(r), \rho_2(r)] = A^{id}[\rho_1(r), \rho_2(r)] + A^{ex}[\rho_1(r), \rho_2(r)]. \]  

(5-7)

The ideal functional is known exactly and can be written as

\[ A^{id}[\rho_1(r), \rho_2(r)] = \sum_{i=1}^{2} \int \rho_i(r) kT [\ln \rho_i(r) - 1] \, dr. \]  

(5-8)

Also, \( A^{ex} = A^{ex,hs} + A^{ex,assoc} \), where \( hs \) and \( assoc \) denote the hard sphere and association portions of the excess (ex) Helmholtz free energy. For a pure hard sphere fluid with association, we have previously applied Tarazona's weighted DFT [69]. We suggested that 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 for hard spheres [51]. In our approach, we apply Tarazona's weighting to both the bulk hard sphere and association free energy terms. Here we extend this approach to our model mixture, the excess free-energy functional can be written as [51]
\[ A^{\omega}[\rho_1(\mathbf{r}), \rho_2(\mathbf{r})] = \sum_{i=1}^{2} \int \rho_i(\mathbf{r}) f_i(\bar{\rho}_i(\mathbf{r}), \bar{\rho}_2(\mathbf{r})) \, d\mathbf{r}. \quad (5-9) \]

where \( f_i(\bar{\rho}_i(\mathbf{r}), \bar{\rho}_2(\mathbf{r})) \) is given by

\[ f_i(\bar{\rho}_i(\mathbf{r}), \bar{\rho}_2(\mathbf{r})) = \frac{A^{\text{exh}}(\bar{\rho}(\mathbf{r}))}{N} + \sum_{A \in \Gamma^{(i)}} (\ln \bar{\chi}_A^{(i)}(\mathbf{r}) - \bar{\chi}_A^{(i)}(\mathbf{r})/2 + 1/2) \quad (5-10) \]

In this equation, \( \bar{\rho}_i(\mathbf{r}) \) is the smoothed density of component \( i \), \( \bar{\rho}(\mathbf{r}) \) is the smoothed total density. \( N \) is the total number of hard spheres. \( \Gamma^{(i)} \) is the set of association sites on component \( i \), and \( \bar{\chi}_A^{(i)} \) is the weighted fraction of molecules of component \( i \) not bonded at site \( A \).

We define the weighted densities for equal sized hard spheres as

\[ \bar{\rho}_i(\mathbf{r}) = \int \rho_i(\mathbf{r}') w(|\mathbf{r} - \mathbf{r}'|; \bar{\rho}(\mathbf{r})) \, d\mathbf{r}'. \quad (5-11) \]

where \( w \) is the Tarazona weighting function. The weighting function, expressed as a power series expansion, is

\[ w(|\mathbf{r} - \mathbf{r}'|; \bar{\rho}(\mathbf{r})) = w_0(|\mathbf{r} - \mathbf{r}'|) + w_1(|\mathbf{r} - \mathbf{r}'|) \bar{\rho}(\mathbf{r}) + w_2(|\mathbf{r} - \mathbf{r}'|) \bar{\rho}^2(\mathbf{r}). \quad (5-12) \]

Since, \( \bar{\rho}(\mathbf{r}) = \bar{\rho}_1(\mathbf{r}) + \bar{\rho}_2(\mathbf{r}) \).
\[
\bar{\rho}(r) = \int [\rho_1(r') + \rho_2(r')] w(|r-r'|, \bar{\rho}(r)) \, dc', \quad (5-13)
\]

The equilibrium density profiles \( \rho_i(r) \) are obtained by solving the coupled integral equations that result from formally minimizing \( \Omega, \ \partial \Omega / \partial \rho_i(r) = 0 \ (i = 1, 2) \), to obtain

\[
\mu_i = \phi_{w,i}(r) + kT \ln \rho_i(r) + \lambda_i(\bar{\rho}_1(r), \bar{\rho}_2(r)) + \sum_{k=1}^{2} \int \rho_k(r') \sum_j \frac{\partial f_k}{\partial \rho_j(r')} \frac{\partial \bar{\rho}_j(r')}{\partial \rho_i(r)} \, dc', \quad (5-14)
\]

where \( f_i = f_{i,1}^{ex,As} + f_{i,2}^{ex,assoc} \). Realizing that our system is inhomogeneous only in the \( z \) direction and then rearranging, we have (in per square area terms)

\[
\rho_i(z) = \exp[\beta(\mu_i - \phi_{w,i}(z) - \lambda_i(z))] \quad (5-15)
\]

and

\[
\lambda_i(z) = f_i(\bar{\rho}_1(z), \bar{\rho}_2(z)) + \sum_{k=1}^{2} \int \rho_k(z') \sum_j \frac{\partial f_k}{\partial \rho_j(z')} \frac{\partial \bar{\rho}_j(z')}{\partial \rho_i(z)} \, dz'. \quad (5-16)
\]

Thus far we have just extended the Tarazona Mark II DF theory for binary mixtures of equi-sized hard spheres. This approach is very successful for hard spheres confined in hard slits [51]. We now would like to add the effects of inter-molecular association.

In our earlier work, we demonstrated two approaches for including association in the grand free energy [69]. In one approach we applied the density functional form of Wertheim’s associating fluid theory. Here, follow our second approach, we apply Tarazona’s weighting to both bulk hard sphere and association free energy terms. We first calculate the individual chemical potentials, which at equilibrium remain constant
throughout the fluid. Since our species bulk densities are fixed, we can calculate the chemical potentials as

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

(5-17)

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 because the molecular diameters are the same for each components, is from Carnahan-Starling [63]. The bulk associating portion of the chemical potential, is calculated from Wertheim’s theory [6]. For a fixed bulk density and fixed site bonding energy, \( \varepsilon_{AC} / kT \) for species \( i \), we obtain

\[ \mu_i^{ex,assoc} = M_i kT (\ln(\chi_i^{bulk,i} - \chi_i^{bulk,i}/2 + 1/2) + kT \sum_{j=1}^{2} \rho_j M_j \left( \frac{\partial \chi_i^{bulk,i}}{\partial \rho_i} \right) (1/\chi_i^{bulk,i} - 1/2). \]  

(5-18)

where \( \chi_i^{bulk,i} \) is the fraction of species \( i \) in the bulk not bonded at site \( A \), \( \rho_i \) is the number density of species \( i \), and \( M_i \) is the number of association sites per molecule of \( i \).

If species 1 is our associating 4-site molecule and species 2 is the hard sphere then equation (5-18) becomes

\[ \mu_1^{ex,assoc} = 4kT (\ln(\chi_1^{bulk,1} - \chi_1^{bulk,1}/2 + 1/2) + 4 \rho_1 kT \left( \frac{\partial \chi_1^{bulk,1}}{\partial \rho_1} \right) (1/\chi_1^{bulk,1} - 1/2), \]  

(5-19)

and

\[ \mu_2^{ex,assoc} = 4 \rho_1 kT \left( \frac{\partial \chi_2^{bulk,1}}{\partial \rho_2} \right) (1/\chi_2^{bulk,1} - 1/2), \]  

(5-20)
where \( \chi_A^{\text{bulk},2} = 1 \)

\[
\chi_A^{\text{bulk},1} = \frac{1}{1 + \sum_j \rho_{\text{bulk},j} \sum_A \chi_A^{\text{bulk},j} / \Delta^{1,j}}. \quad (5-21)
\]

Although component 2 does not associate, there is a contribution to the chemical potential of component 2 due to association. This occurs since a change in mole number of component 2 affects the extent of association and thus the free energy. Since our association sites are equal-sized and symmetric, and there is only one species that can bond, we solve the resulting quadratic equation to obtain after some rearranging,

\[
\chi_A^{\text{bulk},1} = \frac{-1 + \sqrt{1 + 4n\Delta \rho_{\text{bulk},1}}}{2n\Delta \rho_{\text{bulk},1}}, \quad (5-22)
\]

where \( n \) is the number of sites on the second molecule which one site on the first molecule is eligible to bond to \((n=2 \text{ for our 4-site species})\), \( \Delta \) is approximately \( 4\pi K g_{\text{H}}(\sigma; \rho_{\text{bulk}}) f_{AC} \) [22], \( K \) is a constant that measures the volume available for bonding of the two sites on molecules 1 and 2 (here this is \( 0.25(1 - \cos(\theta_c))^2 \sigma^2(\rho - \sigma) \)), \( f_{AC} \) is the Mayer \( f \) function, \( \exp(\varepsilon_{AC}/kT) - 1 \), and \( g_{\text{H}}(\sigma; \rho_{\text{bulk}}) \) is the hard sphere pair correlation function at contact at the total bulk density.

Therefore,
\[
\frac{\partial \chi_A^{\text{bulk.1}}}{\partial \rho_i} = -n(x_A^{\text{bulk.1}})^2 \left( \Delta \frac{\partial \rho_{\text{bulk.1}}}{\partial \rho_i} + \rho_{\text{bulk.1}} \frac{\partial \Delta}{\partial \rho_i} \right) \frac{1}{1 + 2n \rho_{\text{bulk.1}} x_A^{\text{bulk.1}} \Delta},
\]  

(5-23)

where \( \frac{\partial \rho_{\text{bulk.1}}}{\partial \rho_1} = 1 \), and \( \frac{\partial \rho_{\text{bulk.1}}}{\partial \rho_2} = 0 \).

For the association portion of the excess Helmholtz free energy per particle, we have

\[ f_i^{\text{ex.assoc}}(z) = M_i kT \ln \frac{x_{A,i}(z)}{x_{A,i}(z) + 1/2}, \]  

(5-24)

where for multiple associating components

\[
\bar{x}_{A,i}(z) = \frac{1}{1 + \sum_j \bar{p}_j(z) \sum_A \bar{x}_{A,j}(z) \Delta_{ij}}. 
\]  

(5-25)

For our system, for the associating component,

\[
\bar{x}_{A,1}(z) = \frac{-1 + \sqrt{1 + 4n \Delta \bar{p}_1(z)}}{2n \Delta \bar{p}_1(z)}, 
\]  

(5-26)

where to solve equation (5-26), we substitute \( \bar{p}(z) \) for \( \rho(z) \) in equation (5-23). We then have
\[
\frac{\partial \tilde{r}_{j, \text{none}}}{\partial \bar{\rho}_j(z)} = M_i k T \left( \frac{1}{\bar{\rho}_j(z)} - 1/2 \right) \frac{\partial \bar{\rho}_{j\text{,}i}(z)}{\partial \bar{\rho}_j(z)}, \quad (5-27)
\]

where

\[
\frac{\partial \bar{\rho}_{j\text{,}i}(z)}{\partial \bar{\rho}_j(z)} = \frac{n(\bar{\rho}_{j\text{,}i}(z))^{\frac{1}{2}}}{1 + 2n \bar{\rho}_i(z) \bar{\rho}_{j\text{,}i}(z) \Delta}
\left( \frac{\partial \bar{\rho}_i(z)}{\partial \bar{\rho}_j(z)} + \bar{\rho}_i(z) \frac{\partial \Delta}{\partial \bar{\rho}_j(z)} \right), \quad (5-28)
\]

where \( \frac{\partial \Delta}{\partial \bar{\rho}_j(z)} = \frac{\partial \Delta}{\partial \bar{\rho}_j(z)} \frac{\partial \bar{\rho}_j(z)}{\partial \bar{\rho}_j(z)} \), with \( \frac{\partial \Delta}{\partial \bar{\rho}_j(z)} = 2 \pi K f_{\alpha c} (5 - 2 \bar{\eta}(z))/(1 - \bar{\eta}(z))^4 \).

\[
\frac{\partial \bar{\rho}_i(z)}{\partial \bar{\rho}_j(z)} = \pi/6 \quad \text{and} \quad \frac{\partial \bar{\rho}_i(z)}{\partial \bar{\rho}_j(z)} = 1 \quad \text{for} \quad i = j \quad \text{and} \quad \frac{\partial \bar{\rho}_i(z)}{\partial \bar{\rho}_j(z)} = 0 \quad \text{for} \quad i \neq j.
\]

For the density functional derivatives, we have (see Vanderlick et al. [77] for pure fluid case)

\[
\frac{\delta \bar{\rho}_i(z')}{\delta \rho(z)} = w_0(z - z') \bar{\rho}(z') + w_1(z - z')(\bar{\rho}(z'))^2 + \bar{\rho}_i(z') \frac{\delta \rho(z')}{\delta \rho(z)} + 2 \bar{\rho}_i(z') \frac{\delta \rho(z')}{\delta \rho(z)} \frac{\delta \rho(z')}{\delta \rho(z)},
\]

(5-29)

for the like derivative and

\[
\frac{\delta \bar{\rho}_j(z')}{\delta \rho_j(z)} = \bar{\rho}_i(z') \frac{\delta \rho(z')}{\delta \rho_j(z)} + 2 \bar{\rho}_i(z') \frac{\delta \rho(z')}{\delta \rho_j(z)} \frac{\delta \rho(z')}{\delta \rho_j(z)},
\]

(5-30)

for the cross derivative. To solve these prior 2 equations, the derivative of the total weighted density is
\[
\frac{\partial \bar{\rho}(z')}{\partial \rho_i(z)} = \frac{w_0(|z-z'|) + w_1(|z-z'|)\bar{\rho}(z') + w_2(|z-z'|)(\bar{\rho}(z'))^2}{1 - \bar{\rho}^{(1)}(z') - 2 \bar{\rho}^{(2)}(z')(\bar{\rho}(z'))}.
\] (5-31)

This completes the equations needed to solve for \( \lambda_i \).

The Picard-type iterative method 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. Numerical convergence on each species density was obtained with an average squared error of \( 1 \times 10^{-10} \) for each species density. Once the density profiles were obtained, the fraction of monomers for the associating species were calculated [69].

5.4. Results and discussion

Table 5-2 lists some of the major results for binary mixtures of hard spheres and associating 4-sited hard spheres from 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 bulk component densities using the Carnahan-Starling equation [63] and Wertheim's theory. Also listed are the bulk density of 4-sited spheres, wall density (total and 4-sited component), and fraction of 4-sited spheres that are monomers at the wall and in the bulk. The wall theorem [3] that states that the density of
Figure 5-1. 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 $\varepsilon_{\text{site}}/kT = 7$. 

Box average of 50/50 mixture of equal-sized hard spheres

$1/T^* = 7$
$\rho_{\text{bulk}} \sigma^3 = 0.1996$
$\rho_{\text{bulk, assoc}} \sigma^3 = 0.1014$

Non-associating/associating hard sphere ratio

Distance from wall, $z/\sigma$
Figure 5-2. Reduced density of 4-sited hard spheres versus distance from a hard wall for the same conditions as in Figure 6-1.
Figure 5-3. 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 $\epsilon_{\text{site}}/kT = 7$. 

Box average of 50/50 mixture of equal-sized hard spheres

- $1/T^* = 7$
- $\rho_{\text{bulk}} \sigma^3 = 0.5134$
- $\rho_{\text{bulk, assoc}} \sigma^3 = 0.3089$
Figure 5-4. Reduced density of 4-sited hard spheres versus distance from a hard wall for the same conditions as in Figure 6-3.
Figure 5-5. 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 $\epsilon_{\text{site}}/kT = 5$. 

Box average of 50/50 mixture of equal-sized hard spheres

$1/T^* = 5$

$\rho_{\text{bulk}} \sigma^3 = 0.7173$

$\rho_{\text{bulk, assoc}} \sigma^3 = 0.3604$

Distance from wall, $z / \sigma$
Box average of 50/50 mixture of equal-sized hard spheres

\[ \frac{1}{T^*} = 5 \]
\[ \rho_{\text{bulk}} \sigma^3 = 0.7173 \]
\[ \rho_{\text{bulk; assoc}} \sigma^3 = 0.3604 \]

Density of 4-sited spheres

Distance from wall, \( \frac{z}{\sigma} \)

Figure 5-6. Reduced density of 4-sited hard spheres versus distance from a hard wall for the same conditions as in Figure 6-5.
Figure 5-7. 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 5.8. Same as in Figure 6.7 for conditions of \( \rho_{\text{average}} = 0.5 \) and \( \rho_{\text{site}} / K = 7 \).
spheres at a hard wall equals the bulk pressure was satisfied with less than 4% disagreement. The theory total wall density and the theory wall density for 4-sited spheres agree with simulation results well. The fraction of monomers at the wall obtained from theory agree to within or close to the uncertainties of the simulations. The theoretical values for the bulk fraction of monomers are slightly higher than the simulation results at these moderate densities due in part to the different definition of a monomer in the theory and in the simulation [69]. Because of the geometric definition of a bond in the simulations, a small amount of association is found for $\varepsilon/\kappa T = 0$ in the simulations but not in the theory. Note that the uncertainties for quantities associated with the 4-sited spheres are greater than those values associated with all species. This is due to the smaller number of 4-sited spheres as compared to the total number of spheres. The uncertainty in fraction of monomers is greater than that in [69] due to the above reason and that a greater number of configurations are possible due to the presence of unlike species in the mixture.

Qualitatively, the simulation total density profiles behave as expected [69]. Agreement with theory for singlet total densities as a function of distance from the wall was good to excellent, analogous to the situations in [69] where there was adsorption. 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 5-1, 5-3, and 5-5 plot the ratio of hard spheres to associating spheres as a function of distance from the hard wall at several average densities and temperatures. At the temperature of the first two cases (Figures 5-1 and 5-3), the structure of the pure 4-site fluid corresponds approximately to that of room temperature water [5]. Figures 5-2, 5-4, and 5-6 plot the reduced density profiles of the associating species for the same conditions as Figures 5-1, 5-3, and 5-5, respectively. Figures 5-7 and 5-8 plot the fraction of 4-site spheres that are monomers as a function of distance from the hard wall. All calculations were performed at conditions that are above the critical temperature of each component. Furthermore, our pressures are not high enough to cause gas-gas immiscibility [80], so we know we have one phase for our simulations.

In Figure 5-1 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; however, the theory predicts that the ratio of nonassociating to associating spheres reaches its bulk value closer to the wall than observed in simulation. Monomers are enhanced at the wall due to their smaller size and thus suffer less of a drop in entropy as they approach the wall. Figure 5-2 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 0.4σ.
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 under prediction of the theory in Figure 5-1 is due to its over prediction 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 under predicted by a similar absolute amount producing an accurate total density profile.)

In Figure 5-3 we see the ratio of hard spheres to associating spheres 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 5-1. The ratio results are qualitatively similar to those of Figure 5-1. The theory generally lies within the uncertainty of the simulations, but the theory under predicts 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. As in Figure 5-1, there is a slight hitch in the ratio at $1\sigma$. This is also seen in the theory result. Figure 5-4 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 5-2. In this case, however, the theory is fairly accurate within $1\sigma$ of the wall. Like Figure 5-2, the density is over predicted throughout much of the inhomogeneous region. At this higher density, more large clusters are formed than in the case of Figure 5-2. 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 5-2 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 5-1, that the under prediction of the theory in Figure 5-3 is due to its over prediction of the density of associating species. The hard sphere density is under predicted by a similar absolute amount to maintain a highly accurate total density profile.

In Figure 5-5 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 $0.25\sigma$ of the wall, drops off a little and then improves markedly. There is some offset at $1\sigma$ 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 5-1 to 5-4, 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 5-6, we see that the 4-site sphere density prediction is highly accurate, with adsorption taking place 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 5-7 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 $1\sigma$ and the slight over prediction in the bulk, are in common with the results for pure 4-site fluids and are explained in [69]. There is a little inaccuracy at $1\sigma$, 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 under prediction near the wall. This is primarily due to over prediction by the theory of the association fluid density near the wall.

In Figure 5-8 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.

5.5 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. Considering that the density weighting functions that we have chosen were optimized for non-associating hard spheres, the agreement between simulation and theory is remarkable. 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. This approach is being extended to fluids near a hydrophilic surface; preliminary comparisons with molecular simulations have been made.
Chapter 6  Fluid-fluid phase equilibrium in a binary mixture of symmetric non-additive hard sphere fluid

6.1 Introduction

We have developed a density functional theory for binary mixtures confined between two hard walls based on Wertherim's theory for association and Tarazona weighting for hard spheres. It has been shown to be in good agreement with simulation results for a broad range of densities and bonding energies for a binary mixture of a non-associating hard sphere component and a four-site associating component in density profile, fraction of monomers and other thermodynamic properties. However, our system is an additive one (in which the distance of contact between molecules of species 1 and 2 satisfies the relation \( d_{12} = (d_{11} + d_{22})/2 \)), since we allow associating molecules to bond tangentially, and molecules of two species to come into contact. The equation of state of additive binary hard-sphere (AHS) has been studied extensively [91-95], and these mixtures exhibit a solid-fluid transition, but no fluid-fluid transition [96].

For hard sphere binary mixtures, non-additivity means that the distance of contact \( d_{12} \) between two unlike particles is different from the arithmetic mean contact distances \( d_{ii} \) between like pairs,

\[
d_{12} = \frac{d_{11} + d_{22}}{2} (1 + \Delta), \quad \text{with } \Delta \neq 0 \quad (6-1)
\]
according to the sign of $\Delta$, nonadditivity is called positive or negative. When $\Delta > 0$, the attractive part of the intermolecular forces is completely neglected and repulsive part is depicted with positively nonadditive diameters.

One of the reasons for interest in the mixtures of nonadditive hard spheres (NAHS) arises from some of their properties which are significantly different from those of the additive hard sphere system. When $\Delta > 0$, the mixtures separates into two phases at high densities, each of which consists predominantly of one species. For AHS system, like the one we studied in last chapter, it always has a negative volume of mixing, and therefore they never exhibit a fluid-fluid phase separation. However, for NAHS mixture system, the extra-repulsion between different species is able to win out over the thermal motion which tends to mix the system. If $\Delta$ is too small, the transition density may fall in the solid region and freezing occurs before the fluid-fluid phase separation happens.

The non-additive hard sphere (NAHS) mixture is probably the simplest bulk model for a binary mixture in which the fluid-fluid phase separation may occur. The interest in NAHS is motivated by the observed non-additivity in real mixtures [94] and the belief that very large non-additivities play an essential role in the structure of some liquid alloys [95]. Besides, the limiting case of NAHS model (penetrable hard spheres) can be used to describe condensation phenomena [96]. This makes the model quite flexible in many applications.
The homogeneous properties of NAHS model have been studied with a variety of approximate theoretical techniques (see Ref. 97 for review). Numerical simulation studies have been performed on NAHS system with both negative and positive non-additivity [98-103]. In spite of some success, a theory which serves reasonably well for symmetric (system with equal diameter components at equi-molar concentration) and asymmetric non-additive mixtures is still lacking.

If the NAHS mixture is located in a pore, then one deals with a problem of phase separation with a spatial confinement [104]. In principle, this concerns with an Ising-like phase transition in a restricting geometry. This problem was extensively discussed within the theory of critical phenomena (see Ref. 105 for a review). A qualitative estimation of the expected processes could be obtained, employing for instance, the Ginzburg-Landau (GL) free energy functional and minimizing with appropriate boundary conditions. Nevertheless, in application to concrete systems it is important to determine a connection of the empirical parameters appearing in GL approach and real parameters of a model of interest. Quite often this task is far from being trivial. Therefore, it seems reasonable to start directly from a concrete model and to investigate it in terms of the natural parameters.

We will apply the density functional theory developed in chapter 5 to a mixture of non-additive hard spheres (NAHS) confined between hard walls (slit pore). We will show how the fluid phase separation is affected by the restricted geometry. This NAHS model can be used as a possible candidate to be a reference for further applications to
adsorption of realistic mixtures into matrices of a complex geometry. We employ large values for the non-additivity parameter to test the theory, while in realistic mixtures studied so far it is around 0.1.

To test the theory, we compare the density functional theory results with a new mean field treatment proposed by Duda [107] and Monte Carlo simulation results performed by the same group. We will use our density functional theory to investigate the structure and the critical density of this system as a function of pore width and non-additivity parameter.

6.2 Density functional theory for NAHS binary mixtures

Our density functional (DF) methods are based on the idea that the free energy of the inhomogeneous fluid can be expressed as a functional of the one-body density \( \rho(r) \). From a knowledge of this functional all the relevant thermodynamic functions can be calculated [3]. However, the approximations made for the free energy functional must be accurate enough for the problem at hand. A widely used DF theory that is accurate for describing the density distribution of hard spheres against a hard wall is the density weighted DF theory of Tarazona (Mark II) [42], which uses weighting functions that are optimized to fit the bulk hard sphere direct correlation function. In earlier works from this group [69], we developed a perturbational density functional theory for fluids that associate with a short-range interaction by applying Tarazona weighting to Wertheim's bulk first-order associating fluid theory [6a,b,c,d]. Good agreement with computer
simulation results for a confined associating fluid was obtained over a range of temperatures and densities. Since non-additivity is also a short range perturbation, we apply the same DF theory approach to the binary NAHS mixture of equal-sized components with $0 < \Delta < 1$. Specifically, we apply Tarazona's additive hard sphere based weighting functions to relate the free energy functional of a confined non-additive hard sphere fluid to the free energy of a bulk fluid. For the bulk fluid we use the so called MIX1 approximation [91]. The MIX1 approximation consists of the following expression for the Helmholtz free energy of a homogeneous NAHS binary mixture with $\sigma_A = \sigma_B$

$$F = NkT \left[ \ln(\rho \Lambda^3) - 1 + \sum_{i=A}^{B} x_i \ln x_i + \frac{\eta(4 - 3\eta)}{1 - \eta^2} + w(\eta) x_A x_B \Delta \right]$$  \hspace{1cm} (6-2)$$

where $w(\eta) = \frac{12\eta(2 - \eta)}{(1 - \eta)^3}$, and $x_A$ and $x_B$ are the mole fraction of species A and B, $\eta$ is the total packing fraction of the mixture.

We follow the same approach as in [69] to break the Helmholtz free energy for an inhomogeneous MIX1 fluid into the sum of an ideal and an excess part:

$$F[\rho(r)] = F^{id}[\rho(r)] + F^e[\rho(r)]$$ \hspace{1cm} (6-3)$$
The ideal functional is known exactly. In Tarazona's approach \cite{3, 42}, the excess free energy functional is approximated using the weighted or smoothed density approximation as

\[
F^\text{ex}[\rho(r)] = \sum_{i=A}^{B} \int r_i(r) f(\bar{\rho}_A(r), \bar{\rho}_B(r)) \, dr \tag{6-4}
\]

where \( f \) is the excess (over ideal gas) free energy per molecule of a bulk fluid and \( \bar{\rho}(r) \) is the smoothed density using Tarazona's weighting function. The excess free energy contains two contributions: the hard sphere contribution and the perturbation due to non-additivity. Since \( \rho(r) = \rho_A(r) + \rho_B(r) \), we can rewrite \( f(\bar{\rho}_A(r), \bar{\rho}_B(r)) \) as

\[
f(\bar{\rho}_A(r), \bar{\rho}_B(r)) = f^{\text{ex,hs}}(\bar{\rho}(r)) + f^{\text{ex,MIXI}}(\bar{\rho}_A(r), \bar{\rho}_B(r)) \tag{6-5}
\]

Based on the previous work \cite{69} we define \( f^{\text{ex,MIXI}} [\bar{\rho}_A(r), \bar{\rho}_B(r)] = kT \bar{w} \bar{x}_A \bar{x}_B \Delta \) where

\[
\bar{x}_i = \frac{\bar{\rho}_i(r)}{\bar{\rho}(r)}
\]

is the weighted mole fraction for component \( i \), and \( \bar{w} \) is \( w[\bar{\eta}(r)] \), with \( \bar{\eta} \) being the weighted packing fraction \( \bar{\eta}(r) = \frac{\pi}{6} \bar{\rho}(r) \). To minimize the grand potential, we need \( \beta \frac{\delta f^{\text{ex,MIXI}}}{\delta \rho_A(r)} \) (see \cite{69}); this is given by
\[
\beta \frac{\delta f_{\text{ex,MIX1}}}{\delta \rho_a(r)} = \frac{\partial (\overline{w_A} \overline{\rho} \Delta)}{\partial \overline{\rho}_a} \frac{\partial \overline{\rho}}{\partial \rho_a} + \frac{\partial (\overline{w_A} \overline{\rho} \Delta)}{\partial \overline{\rho}_b} \frac{\partial \overline{\rho}}{\partial \rho_b} \delta \rho_a
\]

(6-6)

Using \( \overline{w_A} \overline{\rho} \Delta = \frac{1}{\rho^2(r)} \overline{\rho} \overline{\rho}_A \overline{w} \Delta \) and \( \overline{\rho}_A + \overline{\rho}_B = 1 \), we have

\[
\beta \frac{\delta f_{\text{ex,MIX1}}}{\delta \rho_A(r)} = \overline{w} \Delta \frac{\overline{\rho}_B (\overline{\rho}_B - \overline{\rho}_A)}{\overline{\rho}} \frac{\partial \overline{\rho}_A}{\partial \rho_A} + \overline{w} \Delta \frac{\overline{\rho}_A (\overline{\rho}_A - \overline{\rho}_B)}{\overline{\rho}} \frac{\partial \overline{\rho}_B}{\partial \rho_A} + \overline{\rho}_A \overline{\rho}_B \Delta \frac{\partial \overline{w}}{\partial \overline{\rho}} \frac{\partial \overline{\rho}}{\partial \rho_A}
\]

(6-7)

and similarly,

\[
\beta \frac{\delta f_{\text{ex,MIX1}}}{\delta \rho_B(r)} = \overline{w} \Delta \frac{\overline{\rho}_B (\overline{\rho}_B - \overline{\rho}_A)}{\overline{\rho}} \frac{\partial \overline{\rho}_A}{\partial \rho_B} + \overline{w} \Delta \frac{\overline{\rho}_A (\overline{\rho}_A - \overline{\rho}_B)}{\overline{\rho}} \frac{\partial \overline{\rho}_B}{\partial \rho_B} + \overline{\rho}_A \overline{\rho}_B \Delta \frac{\partial \overline{w}}{\partial \overline{\rho}} \frac{\partial \overline{\rho}}{\partial \rho_B}
\]

(6-8)

with \( \frac{\partial \overline{w}}{\partial \rho_a} = \frac{\partial \overline{w}}{\partial \eta} \frac{\partial \eta}{\partial \rho_a} = \overline{w} \frac{\rho}{6} \).

We begin the calculations by specifying the bulk densities of each component. This fixes the individual chemical potentials, which at equilibrium remain constant throughout the fluid. The bulk chemical potential can be calculated as,

\[
\mu_a = \mu_a^\text{ex,kr} + \mu_a^\text{ex,MIX1} + kT \ln(x_a \rho_{\text{bulk}}),
\]

(6-9)
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 [63]. The non-additive part can be calculated as,

$$\mu_a^{\text{ex,MX1}} = \Delta k T \left[ \rho_{\text{bulk}} w' x_A x_B + w(1 - x_a)^2 \right] \quad (6-10)$$

where

$$w' = \frac{dw}{d\eta} = \frac{12\eta(2 + 2\eta - \eta^2)}{(1-\eta)^4} \quad (6-11)$$

These equations with the Tarazona weighting functions are solved for the equilibrium density profile.

We obtained results for symmetric systems where two components are at 50-50 mixing and non-symmetric system with other mixing ratio. Both cases were calculated for equal-sized spheres for both species. For 50-50 mixing, we start the calculation with a bias with one species having a slightly higher concentration at one side of the pore while the other species having a slightly higher concentration at the other side of the pore. At densities lower than critical density, the two components will mix and form one
uniform phase in the system, they show basically the behavior of hard spheres against a hard wall. At densities higher than the critical density, the two component quickly separate into two phases, with each species dominant at one side of the pore.

Critical densities at which phase separation starts at certain pore size are obtained by starting from a low density at which no phase demixing occurs and gradually increasing density in the pore until fluid-fluid phase separation start to occur. We found that phase separation is very sensitive to this critical density, which allows us to increment density at very small step (reduced $\Delta \rho = 0.01$) from both sides of the phase diagram to get a relatively accurate critical value.

6.3 Mean Field Theory proposed by Duda et.al.

Duda developed mean field model for NAHS using a potential model like,

$$
U_{aa}(R) = \begin{cases} 
\infty, & \text{if } R < \sigma_a \\
0, & \text{if } R > \sigma_a 
\end{cases}, \quad U_{AB}(R) = \begin{cases} 
\infty, & \text{if } R < \sigma_{AB} \\
0, & \text{if } R > \sigma_{AB} 
\end{cases}
$$

(6-12)

where the subscript $a=A,B$ and $R$ measures the particle separation.

This fluid is adsorbed in a slit-like pore, the simplest example of the confinement.

The interaction of fluid species A (or B) with pore walls is assumed to be of a hard sphere type, that is
\[
U^a_{hw}(z) = \begin{cases} 
\infty, & \text{if } \frac{1}{2} \sigma_a > z, \text{ or } z < \frac{1}{2} \sigma_a \\
0, & \text{if } \frac{1}{2} \sigma_a < z < \frac{1}{2} \sigma_a 
\end{cases} \quad (6-13)
\]

where \( z \) is the distance along the normal of a fluid particle to the pore walls. The mean field theory also uses MIX1 approximation for the reference part. The theory shows a stabilizing role of the pore, i.e. that the critical density varies with the pore width and the non-additivity parameter, reaching its bulk value when the pore becomes infinitely wide.

6.4 Computer Simulations

Monte Carlo simulations were carried out by Duda et.al. to test the theories. In order to determine the coexistence curve of the two fluid phases of NAHS system, the semi-grand canonical ensemble (SGC) simulations were carried out. For binary symmetric mixtures there is no need to simulating two phases simultaneously [90,98], as is done in conventional Gibbs ensemble simulations. Fluid-fluid phase equilibria can be obtained by simulating one system in the semi-grand canonical ensemble. In order to investigate the adsorption equilibrium between a bulk fluid phase and the interior of a slit, the Gibbs ensemble was applied. The equilibrium constraints are that chemical potentials of all components in the bulk and in the interior of pore should be the same. For density profiles and fluid-fluid interface, the usual NVT ensemble has been used similar to what we performed in chapter 5.
6.5 Results and discussion

First of all, in figure 6-1, we present the coexistence curves for the NAHS fluid mixture confined in a slit pore whose parallel walls are separated by a distance H. As can be seen, the critical density is lowest for the bulk mixture. This suggests that confinement stabilize the system, preventing its phase separation up to high densities.

Analysis of Figure 6-2 shows that stability of the confined mixture is non-linear function of the non-additivity and increasing of $\Delta$ leads to the low density critical point. Moreover, the influence of pore width on phase diagram is more pronounced for small non-additivity.

Figure 6-3 represents the adsorbate composition as a function of bulk composition. These results show the dependence of stability conditions on the non-additivity parameter $\Delta$ as well as on the pore width H. As can be seen the two-phase bulk fluid can be in equilibrium with one phase of confined fluid. For example, bulk 1.5:10 composition corresponds approximately to 3:10 composition inside the H=6 pore for $\Delta = 0.2$. Meanwhile, for $\Delta = 0.4$ at the same bulk composition there is one phase fluid mixture inside the same pore. With decreasing pore width, the separation of confined fluids takes place when the difference of bulk fluid concentrations $|c_A - c_B|$ increases.

The critical density is plotted as a function of non-additivity in Figure 6-4, where we compare the theory (mean-field and DF) to the simulation results. As is evident from
Fig. 6-1. Density-composition coexistence curves for the fluid-fluid equilibria of a NAHS binary mixture with $\Delta = 0.2$. Dash and dash-dotted lines represent fluid confined in the pore with $H = 4$ and 8, respectively. The solid line corresponds to the bulk fluid, $H \to \infty$.

Fig. 6-2. Density-composition coexistence curves for the fluid-fluid equilibria of a NAHS binary mixture in the slit pores with $H = 4$ (dash-dotted lines) and $H = 8$ (solid lines). From the bottom to the top the pairs of curves correspond to $\Delta = 0.6, 0.4$ and 0.2. Diamonds note the critical points approximated from the SGC MC simulation and the accuracy of approximation does not extend the size of symbols. Circles correspond to the critical densities calculated from mean field theory.
Fig. 6-3. Adsorbed composition vs. bulk composition for NAHS mixture. The symbols correspond to the following parameters: square ($H = 6$ and $\Delta = 0.2$), triangle ($H = 8$ and $\Delta = 0.2$), cross ($H = 6$ and $\Delta = 0.4$) and circle ($H = 4$ and $\Delta = 0.4$).

Figure 6-4. The critical fluid density $\rho^c$ as a function of $\Delta$ at different pore width $H$. $H = 2$ (short dash), $H = 4$ (dash-dotted) and $H = 8$ (solid curve). Lines represent the mean field theoretical predictions. Circles and crosses correspond to the simulation and DFT results, respectively, at $H = 4$ and $H = 8$ pores.
Fig. 6-6. Total density profiles $\rho_f(x)$ (part a), each species density profiles $\rho_s(x)$ (part b), and concentration profiles, $c_s(x)$ (part c) of NAHS fluid, in the slit like pore with $H = 10$. The NVT simulation results are presented by symbols. The curves are obtained from DF T.

Figure 6-7. Local density profiles, $\rho_s(x)$, of NAHS fluids ($\Delta = 0.4$) in the slit like pore with $H = 6$. The NVT simulation results are presented by symbols. The curves are obtained from DF T.
Figure 6-5. Local density profiles, $\rho_s(x)$, of NAHS fluid, $\Delta = 0.2$, in the slit like pore with $H = 6$. The NVT simulation results are presented by symbols. The curves are obtained from DFT.
the previous discussion, $\rho^c$ falls off with increasing $\Delta$. This decrease is slower for more narrow slits. It is seen a qualitative agreement between two approaches, especially for large $\Delta$.

DFT calculations are carried out with $\Delta=0.2$, 0.4 and 0.6 for various density combinations. We have confirmed the existence of a phase separation for both symmetric ($c_A = c_B = 0.5$) and non-symmetric binary systems. The critical densities for phase separation for fluid confined in a certain sized slit are obtained by gradually increasing the densities until a phase separation is observed. The co-existence density mole fraction is obtained by averaging the densities of the two components in a “bulk” like region in the density profile. The results show good to excellent agreement of density profiles for small $\Delta$ (0.2) and good agreement for coexistence curves for all $\Delta(0.2, 0.4, 0.6)$ values. The trend that the critical density decreases as both the non-additivity and pore width increase is also shown. One interesting feature we see is the trace amount of a lean component near the wall, as predicted by simulation. The good agreement for $\Delta=0.2$ is especially appealing because in real systems, only small non-additivities ($\Delta<0.1$) are usually present [97]. For larger $\Delta$, the density profile shows qualitative agreement with the simulation results. The discrepancy is significant at the interfacial region, with the DFT results showing a density peak. This occurs because the phase rich in the other component looks more and more like a wall as $\Delta$ increases. While this effect is the correct limiting behavior for large $\Delta$, the DFT appears to over-predict the effect for $\Delta = 0.4, 0.6$. 
Despite the discrepancy in the large $\Delta$ cases, the DFT is appealing because it offers a quick calculation for critical density for all $\Delta$ values (0.2, 0.4, 0.6) and density profile and coexistence curves for small $\Delta$ (0.2). For large $\Delta$, the poor agreement in density profile may be due to the breakdown of the perturbation density functional theory because of the weighting functions we chose were optimized for additive hard spheres.

6.6 Conclusions

We have applied the density function theory for binary mixtures to equal-sized non-additive hard sphere system. It has successfully shown fluid-fluid phase separation and compared favorably with simulation of critical density at all non-additivity ($\Delta=0.2, 0.4, 0.6$). It also gave excellent agreement for density profiles for small non-additivity ($\Delta=0.2$). The pore stabilizing effect as predicted by the mean-field theory was also correctly shown by our density functional theory. However, at higher non-additivity ($\Delta=0.4, 0.6$), the density profile predicted by DFT does not agree well with simulation.
Table 6-1. Simulation results: the number fluid density $\rho_f(x)$, and the concentration of component A, $c_A$ for different pores and non-additivities. Number of particles in the box, $N_{part} = 1000$.

<table>
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<th>$\Delta$</th>
<th>$\rho_f$</th>
<th>$c_A$</th>
<th>$\rho_f$</th>
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<td></td>
<td>$H = 8$</td>
<td></td>
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### Table 6-2. Critical fluid densities, $\rho^c$, calculated from SGC MC simulations, mean-field and density functional theories.

<table>
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</tr>
<tr>
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<td>4</td>
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Chapter 7 Associating Fluids against an Active Surface

7.1 Introduction

Prediction of the interaction of complex fluids (e.g. hydrogen bonding fluids, hydrocarbons, proteins, and polymers) with active solid surfaces is essential for the control of many processes of current industrial and scientific interest. Potential applications are diverse, including wettability as related to oil recovery and environmental remediation, biochemical separation, bio-compatibility of materials, adsorption in porous solids, micro- or nano-manufacturing of thin films, adhesion and lubrication, and the properties of composites involving polymers. For example, the adsorption of strongly associating fluids, e.g. water, alkanols, onto active carbon is affected strongly by the presence, type and density of active sites on the carbon surfaces with which the adsorbate molecules can bond. A fundamental understanding at molecular level of such phenomena would be extremely helpful to prepare improved adhesives and composites. Advances in these areas requires a fundamental understanding of how hydrogen-bonding, molecular size and shape, the chemical composition of the surfaces and other molecular and surface interactions affect the properties and structure of fluids in the interfacial region. Of special interest is the ability to modify and control the adsorption of associating molecules through doping or activating surfaces, which can find wide application in mixture separation processes and nano-manufacturing.

However, efforts to model these systems have been hindered by the lack of accurate theories, even though many simulations of simple or chain molecules near
surfaces other than the hard wall have been performed [3]. Muller et al. [33] have reported a molecular simulation study of water adsorption on activated carbons, where water molecules have been modeled as Lennard-Jones spheres with four square-well sites. It has been shown that the effect of wall fluid association can strongly influence the adsorption characteristics of water, in cases changing the slit pore from desorption to adsorption. McCallum et al. also used a similar water model and molecular simulation to study the adsorption isotherm of water onto activated carbons at low pressures. Erich, et al. studied the adsorption isotherms of associating Lennard-Jones (LJ) chain molecules against an LJ surface with active sites using Monte Carlo simulations. This study gave some interesting results for the consequence of competition between the tendency of the individual spheres forming a chain to place themselves in the center of the pore and the strongly favorable bonding of a molecule onto the wall. Lee and Rossky [36] investigated, using 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 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.

Chmiel et al. [37] used the Tarazona density functional theory to study a Lennard-Jones fluid against a wall formed of parallel strips possessing different adsorbing energies. Most other theoretical work on associating fluids used integral equation (IE) theory to study dimmerizing spheres near crystalline and other associatively
attractive walls [38, 86-90]. In the last several years, there has been an intense effort to study polyatomic molecules (flexible, linear chains) in the interfacial region using molecular simulation and interaction site theories [110, 111]. Less work has considered hydrogen bonding and chemical strength association within the fluid and between the fluid and surface [108, 109].

Three groups (Henderson and co-workers [108, 109], Holovko and co-workers [49, 93] and our group [40, 69, 81]) have developed new theories to predict the structure of association fluid in the surface region. While Henderson's group has primarily considered a spherically symmetric model, we have studied molecules with directional association sites. We consider our model to be more realistic and to have greater potential for applications. Holovlko's model is similar to ours; however, recent comparisons have shown that our density functional theory is more accurate in most cases studied [49, 93], especially at regions within one molecular diameter of the wall. Moreover, since their IE theory uses Perkus-Yevick equation of state, it has error at wall contact. Since the fluid wall bonding happens at very close vicinity of the wall, we would prefer to use our DFT, which correctly reproduce the wall theorem at contact. In more recent work, Henderson's group has adopted our approach in a study of associating fluids near a permeable membrane [108].

In our earlier work and chapter 5, we have developed a new density functional theory which has been applied to a model fluid that mimics the hydrogen bonding in dimmering (one site), chain forming (two sites) and networking (four sites) molecules,
The latter can be regarded as mimicking the topology of hydrogen bonding in water or ammonia. In comparison with molecular simulation results, our density functional theory accurately predicts the adsorption and hydrogen bonding of pure fluids and mixtures as a function of distance from a hydrophobic or hydrophilic surface. In chapter 5, we have successfully extended this theory to mixtures of associating fluids, and the comparison with simulation data is generally good.

In this and following chapters, we will consider an associating surface where directional hydrogen bonding sites or polar sites are present. These sites are modeled as OH group, which can associate with a O or H site on a fluid molecule if it is sufficiently close and in the correct orientation. This approach is more realistic than modeling the effect of active sites on surfaces as an averaged potential imposed by the wall, as used in many IE theory studies. The first order Wertheim’s theory for association assumes that a site allows only one other molecule to approach sufficiently close and in the correct orientation to form a bond. When a site is occupied, it is no longer available for bonding to other fluid molecules. The averaged potential approach, however, would allow further interactions between a wall site and fluid even if this site occupied.

By positioning wall sites close to one another, steric hindrance between fluid molecules bonded to surface sites and cooperative bonding may become important. This cooperative bonding effect, such as molecules forming bridges between wall sites, is thought to occur for water adsorbing on activated carbon. We will extend our density function theory to model these complex systems. Molecular simulations are performed
as a test of the theory and to provide insight into thermodynamic properties and structure of this model. Since the same molecular force model is used in the simulation and theory, no adjustable parameters are needed, and a comparison between the results of the simulation and theory provides a rigorous test of the approximations made in the theory. Furthermore, since direct experimental investigations are complicated greatly by the difficulty of separating the effects of the many different variables, and because the materials used are often poorly characterized, molecular simulations can provide very valuable information about the behavior of model systems.

We first consider a system where only the bonding between surface sites and sites on fluid molecules are allowed. This model would allow us to separate the effects of wall-fluid and fluid-fluid bonding, such as determining when the steric hindrance caused by molecules bonded to surfaces becomes important, and thus posing a limit to our first order perturbation theory. Comparison with simulation data would provide a rigorous test of the approach we take to include wall-fluid interactions. This wall-fluid-bonding-only system is important in understanding the biochemical interactions near membranes, where molecules can only bond with the surface. We will introduce fluid-fluid bonding, and competition between the wall-fluid and fluid-fluid associations for four sites molecules in next chapter, and study one- and two- sited molecules near active surfaces in chapter 9. The study of one-, two-, and four-sited molecules will cover a large set of nonpolar groups including dimmers, linear and branched chains, and networked molecules.
7.2 Molecular Simulations

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

\[ \phi(\mathbf{r}, \omega_1, \omega_2) = \phi_R(r) + \sum_A \sum_C \phi_{AC}(\mathbf{r}, \omega_1, \omega_2), \quad (7-1) \]

where \( r \) is the magnitude of the vector \( \mathbf{r} \) 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 \( \mathbf{r} \) and the double sum is over all association sites on each molecule. In the case of interaction between a fluid molecule and a wall site, then \( r \) is the vector connecting a fluid molecule and a "site center", visualized as the center of a "molecule" positioned 1.0\( \sigma \) from the wall, as in figure 7-1, and the double sum reduces to a single sum over all the sites on the fluid molecule. \( \phi_R \) is the reference potential; the reference hard sphere potential is defined by

\[ \phi_R(r) = \begin{cases} \infty & \text{if } r < \sigma, \\ 0 & \text{if } r > \sigma, \end{cases} \quad (7-2) \]

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

\[ \phi_{AC}(\mathbf{r}, \omega_1, \omega_2) = \begin{cases} -\varepsilon_{AC} & \text{if } r < r_C; \ \theta_{A1} < \theta_C; \ \theta_{C2} < \theta_C, \\ 0, & \text{otherwise}, \end{cases} \quad (7-3) \]

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 \( C \) on
Figure 7-1, Schematic drawing of the interaction between a wall site and fluid molecules near the wall.

Figure 7-2a Sketch showing distribution of wall sites, and wall spacing, a is distance between molecules.

Figure 7-2b, Steric hindrance between sites on the wall, the site pointed by arrow is blocked by molecule A.
molecule 2. For wall sites, molecule 2 is the pseudo-molecule in the wall which "owns" the site.

The associating fluid in the model selected in this work has four bonding sites, A, B, C, D, placed in tetrahedral symmetry around a spherical core, similar to the Bol [79] model. When in the vicinity of the wall, all four sites A,B,C,D can bond with a wall site. The bonding energies between wall and fluid were set to the same value \(-\varepsilon_{site}\). In the simulations and in our theoretical calculations, the radial limits of the square-well association between wall site and a site on a fluid molecule was set to \(r_c=1.05 \sigma\) and the angular limit was set to \(\Theta = 27^\circ\).

The simulation cell consists of active walls at \(z = 0\) and \(z = H\) with association sites on the walls, as show in figure 7-2. The sites were placed at spacing "a" on a plane parallel to a (100) plane of a face-centered cubic lattice. The wall site density is given by \(\sigma^2/a^2\). For our simulation runs, the spacing ‘a’ is chosen to be greater than 1.3 \(\sigma\), as steric hindrance becomes important at a smaller spacing, as shown later. A spacing between 1.4 ~ 1.6 \(\sigma\) is used to compare simulation data with density functional theory results. This spacing is of the same order of magnitude as that in silica if our four-sited fluid is water. We choose the site energies much higher than silica to test our theory at relatively high association energy. The simulations were run in a similar manner to those in chapter 5 and earlier works [69], but require more displacement configurations than hard wall cases to get a good convergence. The values of maximum displacement and orientation are much smaller compared to values used for hard wall system to obtain suitable
acceptance rates. A total of 500 million to 1 billion displacements are generally needed for a typical run, and it takes about five to ten hours on an Intel 900 MHz Pentium III processor.

Periodic boundary conditions with box length $L$ were imposed in the other two directions. To ensure that the density oscillations died away in the central region, $H = \alpha \times L$; where $\alpha > 1$. With this choice of $\alpha$, the two walls did not interfere with each other and there was a bulk region in the middle of the cell. Due to adsorption at the walls, the average density in the cell is different from the bulk density in the center of the cell. The density and monomer profiles were calculated by averaging the properties of each point on one side of the cell midpoint with its geometrically symmetrical twin on the other side of the midpoint. Hence, the results appear as a function of distance from one wall in the $z$ direction. In addition to the pair potential on the particles and between a fluid site and a wall site, the walls also exerted an external potential,

$$\phi_w(z) = \begin{cases} \infty & \text{if } r \leq 0 \text{ or } z \geq H, \\ 0 & \text{otherwise.} \end{cases}$$  \hspace{1cm} (7-4)

Systems were first equilibrated. Each equilibrated configuration was used as the starting configuration of a series of further runs. Each series consisted of 10 to 20 runs. The sub-averages of properties from each run of a series were used to calculate averages and errors. Generally, more configurations were needed at the highest amount of association, a requirement that becomes more necessary at higher densities.
Criteria used for determining if equilibration had been reached at the end of a series of simulations include those listed in [40]. In addition, the fraction of monomers should be symmetrical on either side of the cell to within 5%. Densities and fractions of monomers were calculated as described in [40]. Fractions of monomers are reported for the associating fluid between walls. It is noteworthy that wall theorem for hard surfaces, which gives the exact result $P/kT = \rho_{\text{wall}}$ no longer holds in the active wall system, where $P$ is the pressure and $\rho_{\text{wall}}$ is the singlet density at the wall.

7.3 Wertheim's Theory for Associating Wall Sites

The most successful theory of bulk associating fluids is that of Wertheim [6]. Wertheim's theory is often written in the form of a perturbation theory that relates excess Helmholtz free energy to the fraction of unbonded molecules. Wertheim's first order perturbation theory assumes that the sites on associating molecules are independent of each other, and only one bond can be formed between molecules. For two bonding sites A and C on two associating molecules 1 and 2, Wertheim's theory gives,

$$\chi_A(1) = \frac{1}{1 + \sum_c \rho(2) \chi_c(2) g_{\text{ref}}(1,2) f_{AC}(1,2) d^2}$$  \hspace{1cm} (7.5)$$

where $\chi_A(1)$ and $\chi_c(2)$ are the fractions of molecules not bonded at site A (molecule 1) and C (molecule 2), respectively. $\rho(2)$ is the total singlet number density and $g_{\text{ref}}(1,2)$ is the reference fluid's (hard sphere) pair correction function. $f_{AC}(1,2) = \exp(\epsilon_{AC} / kT) - 1$ is the Mayer function for the short ranged square well potential for the associating
interaction. \( \varepsilon_{AC}(1,2) \) is the bonding energy between sites A and C. The sum is over all association sites on molecule 2, and \( d\vec{z} = d\omega_2 dr_2 / \int d\omega_2 \), denotes an unweighted angle average and a volume integral over particle 2.

The change in Helmholtz free energy due to association is given by

\[
A_{asso} = A - A_{ref} = M_{site} \left( \ln \chi_A - \frac{\chi_A}{2} + \frac{1}{2} \right) \tag{7-6}
\]

where \( M_{site} \) is the number of association sites on the molecule. To calculate \( A_{asso}, \chi_A \) the fraction of site a on a fluid molecule not bonded, and \( \chi_{wall} \), the fraction of wall sites not bonded, need to be determined.

### 7.3.1 Fraction of unbonded sites on fluid molecules

As a first attempt to form a theory describing the wall sites adsorption, we adopt a molecular model that contains only the essential physics. We start with a wall with homogeneous sites having the same wall-fluid bonding energy. It, however, should be straightforward to extend this model to a system where walls contain heterogeneous sites with different fluid-wall bonding energies. Following Wertheim’s first order theory, we assume that the wall sites are independent of each other, and only one molecule is allowed to bond to a wall site. We only allow fluid-wall bonding at the moment. This simplified model can be extended to include effects from fluid-fluid bonding in later chapters, and could be generalized to describe more realistic cases of adsorption of


mixtures or include cooperative bonding effects. Steric hindrance effect may be modeled by extending Wertheim’s perturbation theory to second order or including a factor for the bonding volume that is dependent on wall site density.

Similar to (7-5), we can construct a term in denominator to account for wall-fluid hydrogen bonding effect,

$$\chi_{A}(l) = \frac{1}{1 + \sum_c \int \rho(wall) \chi_{wall} g_{ref}(l, wall) f_{AC}(l, wall) d\bar{2}}$$  \quad (7-7)$$

where $\chi_{wall}$ is the fraction of wall sites not bonded and $\rho(wall)$ is the wall site number density, here $\rho(wall) = \delta(r - r_{wall})$, because the position of the wall sites are fixed on the wall. $f_{AC}(l, wall)$ is the Mayer $f$ function, describing the short-ranged squall wall interaction between wall sites and a site on fluid molecule. $g_{ref}(l, wall)$ is the pair correlation function between a wall site and fluid particle. Since wall sites are fixed in position, $g_{ref}(l, wall)$ is 1.0. $d_{wall} = d\omega / \int d\omega dr_{wall}$ denotes an unweighted average for fluid molecule orientation. The sum is over all the sites on the wall, and the sites are assumed independent of one another. The fraction of a site on fluid molecule not bonded is then given by,

$$\chi_{A}(l) = \frac{1}{1 + \sum_c \int \delta(r - r_{wall}) \chi_{wall} f_{AC}(l, wall) d\bar{2}}$$  \quad (7-8)$$
Follow the derivation in [69] for fluid-fluid bonding, we have

$$\chi_A(l) + \chi_A(l) \sum_C \int \delta(r - r_{wall}) \chi_{wall} F_{AC}(l, wall) d\tilde{z} = 1 \quad (7-9)$$

Since there are no association sites in the reference fluid (hard sphere), and therefore the only inhomogeneity is caused by wall potential in the z direction perpendicular to the wall. The only term in the integral that is dependent on the position of molecule 1 is $f_{AC}(l, wall)$. We integrate both sides of (7-9) over all possible orientations of molecule 1 and over the area of the wall ($\int dxdy$), assuming that $\chi_A(l)$ doesn't depend on orientation, (7-9) becomes

$$A\chi_A(l) + \chi_A(l) \sum_C A_{one-site} F_{AC}(l, wall) \frac{1 - \cos(\theta_C)}{2} = A \quad (7-10)$$

where $A$ is total wall area, $A_{one-site}$ is the surface area of one site available for bonding. The factor $(1 - \cos(\theta_C))/2$ is a fluid molecule's fraction of orientation available for bonding, given by

$$\frac{1}{4\pi} \int_0^{2\pi} \int_0^\theta \sin(\theta) d\theta d\phi = \frac{1 - \cos(\theta_C)}{2} \quad (7-11)$$
We have assumed that $\chi_A(l)$ can be averaged over the wall area. This would be true if the wall sites are fixed or can only move along the wall. 

$$F_{AC}(1, \text{wall}) = \exp(e_{site}/kT) - 1,$$ is the Mayer $f$ function.

For a wall site, A one-site, the area available for bonding, can be determined geometrically. As in figure 7.3, The radius $r$ of a circular area within which bonding can occur is $z \tan \theta$, and $\theta$ is given by 

$$\theta = \cos^{-1} \left( \frac{z}{r_c} \right)$$

and 

$$A_{one-site} = \pi r^2 = \pi z^2 \tan^2 \theta = \pi (r_c^2 - z^2) \quad (7-12)$$

(7-12) holds as long as $\theta < \theta_c$. In our case, we have $r_c = 1.05$, $\theta_c = 27^\circ$ and 

$$\theta_{max} = a \tan \left( \frac{1}{1.05} \right) = 17.75^\circ < 27^\circ,$$ which satisfies this condition.

Since the terms in the sum of (7-10) are the same for all wall sites, we replace it with the factor $N_{wall}$, the total number of sites on the surface, and have,

$$\chi_A(l) = \frac{1}{1 + \frac{N_{wall}}{A} F_{AC}(1, \text{wall}) \pi \frac{1 - \cos(\theta_c)}{2} (r_c^2 - z^2)} \quad (7-13)$$
Figure 7-3. Geometric Drawing showing the bonding volume of a wall site

Figure 7-4. A four site molecule near a wall always has one site oriented towards the wall
where \( N_{\text{wall}} / A \) is the so-called "wall site density", given by \( \sigma^2 / a^2 \), where \( a \) is the spacing between sites for evenly distributed surface sites, representing the site-site separation on the active surface.

### 7.3.2 Fraction of wall sites that are not bonded

To calculate \( \chi_{\text{wall}} \), the fraction of wall sites that are unbonded to fluid molecules, we may take two views of a fluid adsorbing at sites on a solid. In the first view, the fluid and solid belong to different phases and the system is inhomogeneous. Properties depend on the distance from the surface. In the second view, the surface can be thought of as a large particle in the fluid phase, as long as surfaces do not interact with each other, i.e., the wall particle is at infinite dilution. Wertheim's theory allows us to take each of these views of wall sites. An advantage of the second view is that we do not need to solve for equilibrium density profile to determine site occupancy. Both approaches can be extended to allow for steric hindrance at surface sites by extending the perturbation theory to second order, or by including a factor in the bond volume (or number of sites) that is dependent on coverage.

In general, fluid particles can associate with the wall particles and with each other. We will only consider in this chapter the case that only fluid-wall association is allowed. We shall extend this to include fluid-fluid association in next chapter.
Using first approach, analogously to equation (7-5), but from a wall site's "point of view",

\[
\chi_{\text{wall}} = \frac{1}{1 + \sum_c \int \rho(2) \chi_c(2) g_{\text{ref}}(2, \text{wall}) f_c(2, \text{wall}) d^2} \tag{7-14}
\]

where \( \rho(2) \) is the fluid's singlet number density, \( \chi_c(2) \) is the fraction of molecules not bonded at site \( C \) of fluid molecule 2, and \( f_c(2, \text{wall}) \), is the Mayer \( f \) function for the square well potential model of wall-fluid association. Since walls do not move in space, the pair correlation function between wall sites and fluid molecule, \( g_{\text{ref}}(2, \text{wall}) \), is 1.0. Follow the same derivation for fluid molecules, and again we assume \( \chi_c(2) \) does not depend on orientation. After doing an unweighted angle average, and integrating over \( \int dxdy \), we have,

\[
\chi_{\text{wall}} = \frac{1}{1 + M_{\text{site}} \frac{1 - \cos(\theta_c)}{2} \left[ \exp(e_{\text{wall-site}} / kT) - 1 \right] \int \rho(z) \chi(z) A_{\text{one-site}} dz} \tag{7-15}
\]

where \( A_{\text{one-site}} = \pi (r_c^2 - z^2) \), i.e. the area available for bonding for one wall site. It's noteworthy that wall site density does not enter the calculation of \( \chi_{\text{wall}} \). This is generally true when wall sites are independent of one another and the steric effect is small. This approach can be used when we have \( \rho(z) \) and \( \chi(z) \), e.g. from simulation. It has the
advantage of easily extendable to heterogeneous associating sites on the wall by summing
the effects from all wall site species.

There is a unique property of the four-sited model that we can exploit to simplify
(7-15) further. Near the wall, there is one site on a four-sited molecule that is always
oriented towards the wall, as shown in figure 7-4, i.e. one site is always available for
bonding with the wall. This property, as pointed out by Segura et.al. in earlier work from
this group, has been confirmed by simulation data for four-sited associating hard spheres
against a hard wall [40]. Simulation data show that near the hard wall, the fraction of
molecules with all four sites bonded is always zero. Thus, for four-sited fluid, \( M_{\text{site}} \) is 4
and \( \chi(z) \) in integral in (7-15) is approximately 1.0. (7-15) becomes,

\[
\chi_{\text{wall}} = \frac{1}{1 + 4\pi \frac{1 - \cos(\theta_C)}{2} \left[ \exp(\varepsilon_{\text{wall-site}} / kT) - 1 \right] \int \rho(z)(r_c^2 - z^2) dz}
\tag{7-16}
\]

On the other hand, consider an infinitely dilute, large sphere with any number
\( N_{\text{wall}} \) of association sites labeled A,B,C, etc. From the bulk form of Wertheim's theory
[6] we have,

\[
\chi_{\text{wall}} = \frac{1}{1 + \frac{1}{M_{\text{site}} \rho_{\text{bulk}} \chi_{\text{bulk}} A(1, \text{wall})}}
\tag{7-17}
\]

where
\[ \Delta(1, \text{wall}) = \int_{\text{bond volume}} f(1, \text{wall}) g_{HS}(1, \text{wall}) d(1, \text{wall}) \quad (7-18) \]

and \( \chi_{\text{bulk}} \) is the bulk fluid fraction of molecules that are not bonded at site A, and is given by

\[ \chi_{\text{bulk}} = \frac{1}{1 + M_{\text{site}} \rho_{\text{bulk}} \chi_{\text{bulk}} \Delta} \quad (7-19) \]

where \( \Delta \) is \( 4\pi K g_{HS}(\sigma) F_{AC} \), and \( g_{HS}(z) = \frac{\rho_{HS}(z)}{\rho_{\text{bulk}}} \).

After an integral on \( \int dx dy \) and orientation, (7-17) becomes,

\[ \chi_{\text{wall}} = \frac{1}{1 + M_{\text{site}} \pi \frac{1 - \cos \theta_c}{2} (\exp(\varepsilon_{\text{site}} / kT) - 1) \chi_{\text{bulk}} \int \rho_{HS}(z)(r_c^2 - z^2) dz} \quad (7-20) \]

Since reference fluid (hard sphere)'s density profile \( \rho_{HS}(z) \) only depends on chemical potential (or bulk density), the integral in (7-20) is a constant for a given bulk density. Combining (7-20) with (7-19), we see that \( \chi_{\text{wall}} \) is only a function of \( \varepsilon_{\text{site}} / kT \) and \( \rho_{\text{bulk}} \).

Of course, this is only true as long as Wertheim's first order perturbation theory's assumptions hold, i.e. wall sites are independent of one another.
Without fluid-fluid bonding, $\chi_{\text{bulk}}$ is approximately 1.0, since for a large volume, wall site number is far smaller than number of molecules in the bulk, therefore, for four site fluid, the fraction of wall sites not bonded is,

$$
\chi_{\text{wall}} = \frac{1}{1 + 4\pi \frac{1 - \cos \theta_C}{2} \exp(e_{\text{site}} / kT) \int \rho_{HZ}(z)(r_C^2 - z^2) dz}
$$  \hspace{1cm} (7-21)

### 7.3.3 Langmuir Adsorption Isotherm for Fluids

The familiar Langmuir adsorption isotherm treats the localized monolayer adsorption on active solid surfaces. As a molecule is attached to a wall site, no lateral interaction between neighboring sites is allowed. In Langmuir's adsorption, the attractive forces of the wall decays rapidly with distance, and only the molecules near the wall are affected. This is similar to our wall-fluid association model, where the association only extends to 5% of a molecular diameter and only wall-fluid bonding is allowed.

The surface coverage in of wall sites in Langmuir adsorption is defined as

$$
\theta = \frac{\text{Number of wall sites occupied}}{\text{Total number of wall sites}}
$$

which is $1 - \chi_{\text{wall}}$. Recall (7-17),
\[ \theta = 1 - \chi_{\text{wall}} = \frac{M_{\text{site}} \rho_{\text{bulk}} \chi_{\text{bulk}} \Delta_{\text{wall}}}{1 + M_{\text{site}} \rho_{\text{bulk}} \chi_{\text{bulk}} \Delta_{\text{wall}}} \]  

(7-22)

where

\[ \Delta_{\text{wall}} = \frac{1 - \cos(\theta_c)}{2} \pi \left( \exp\left(\frac{e_{\text{site}}}{kT}\right) - 1 \right) \int \frac{\rho_{\text{HS}}(z)}{\rho_{\text{bulk}}} (r_z^2 - z^2) dz \]  

(7-23)

The term in numerator of (7-22) is a function of temperature \( T \) and \( \rho_{\text{bulk}} \), because \( \rho_{\text{HS}}(z) \) is only a function of \( \rho_{\text{bulk}} \). We rewrite (7-22) as,

\[ \theta = \frac{c_f(T, \rho_{\text{bulk}})}{1 + c_f(T, \rho_{\text{bulk}})} \]  

(7-24)

where \( c_f(T, \rho_{\text{bulk}}) \) is a function of temperature \( T \) and bulk fluid density \( \rho_{\text{bulk}} \), and can be further broken down to

\[ c_f(T, \rho_{\text{bulk}}) = (\exp(e_{\text{site}}/kT) - 1)q_f(T, \rho_{\text{bulk}}) \]  

(7-25)

Langmuir's adsorption isotherm equation gives

\[ \theta = \frac{c(T)P}{1 + c(T)P} \]  

(7-26)
where \( P \) is pressure at the wall and \( c(T) \) is a constant that only depends on temperature. (7-26) was derived for ideal gas. For ideal gas, \( P = \rho k T \), (7-26) can be rewritten as,

\[
\theta = \frac{c(T)kT\rho}{1 + c(T)kT\rho} \quad (7-27)
\]

Recall that in the derivation of (7-26), for a simple model of zero or one occupancy at wall, we can write the grand partition function for Langmuir adsorption as

\[
Z = 1 + \lambda \exp(\varepsilon_{\text{site}} / kT) \quad (7-28)
\]

where \( \varepsilon_{\text{site}} \) is the bonding energy between wall sites and fluid molecule, and \( \lambda \) is the so-called absolute activity, and ideal gas, \( \lambda \) is \( \frac{P}{kT} N_q^3 \), where \( N_q \) is the so called quantum concentration [112], and is only dependent on \( T \). The wall coverage is then given as,

\[
\theta = \frac{\frac{P}{kT} N_q^3 \exp(\varepsilon / kT)}{1 + \frac{P}{kT} N_q^3 \exp(\varepsilon / kT)} \quad (7-29)
\]

and is the same as (7-26) and (7-27), and can be written generally as,

\[
\theta = \frac{c_0(T, \rho) \exp(\varepsilon / kT)}{1 + c_0(T, \rho) \exp(\varepsilon / kT)} \quad (7-30)
\]
(7-30) is similar to (7-24) and (7-25), except in our equation, we have factor \( \exp(\varepsilon_{site}) - 1 \) instead of \( \exp(\varepsilon_{site}) \), and this is due to our modeling of the association potential model as a directional square well, which is more realistic than treating association as an isotropic potential. We can also utilize the Perkis-Yevick or Carlanhan-Sterling relationship between pressure \( P \) and bulk density \( \rho \) for Hard Sphere fluid to rewrite (7-24) and (7-25) in terms of \( P \) rather than \( \rho \). At the limit of ideal gas, (7-25) reduces to (7-30) or (7-26). We have extended the Langmuir adsorption isotherm derived for ideal gas to (7-24) for non-ideal fluid, encompassing super critical conditions.

From (7-24), at a given bulk density and temperature,

\[
\frac{\theta}{1 - \theta} = \frac{q_f(T, \rho_{bulk}) \exp(\varepsilon_{site} / kT) - 1}{\varepsilon_{site} / kT} \quad (7-31)
\]

and

\[
\ln \frac{\theta}{1 - \theta} = \ln \frac{1 - \chi_{wall}}{\chi_{wall}} \approx C(T, \rho) \frac{\varepsilon_{site}}{kT} \quad (7-32)
\]

where \( C(T, \rho) \) is a constant at given temperature and bulk density, and \( \frac{\varepsilon_{site}}{kT} \) is the reduced bonding energy or the inverse reduced temperature.
7.4 Free Energy Functional for Associating Fluids Interacting with Wall Sites

There are two views that we can take to calculate the free energy functional for a fluid interacting with a surface that has association sites: the effective bulk fluid view and the full density functional approach. In the bulk form of Wertheim's theory, we take a Tarazona weighted density and calculate a bulk extent of hydrogen bonding and a bulk free energy. However, if the fluid element is close enough to the wall, the extent of hydrogen bonding will include a contribution from bonding to a wall site. The probability that a wall site is not bonded will depend on an integral of bonding from the fluid element near the wall, as in (7.13). This approach is the same as Method 2 in [40] of bulk form of Wertheim's theory we have developed for associating fluids in places other than very close to the wall.

When a fluid molecule is within the bonding volume of a wall site, for the association portion of the free energy, we use the bulk relations of Ghonasi and Chapman [40],

\[ f^{\text{asso}}[\bar{\rho}(z)] = M_{\text{site}} kT \left( \ln \bar{\chi}_A(z) - \bar{\chi}_A(z) + \frac{1}{2} \right) \]  

(7-33)

and

\[ \bar{\chi}_A(z) = \frac{1}{1 + M_{\text{site}} \bar{\rho}(z) \bar{\chi}_A(z) \Delta} \]  

(7-34)

If we add the wall fluid bonding effect at the vicinity of wall, (7-34) becomes
\[ \bar{\chi}_A(z) = \frac{1}{1 + \frac{N_{\text{wall}}}{A} F_{AC}(1, \text{wall}) \pi \frac{1-\cos(\theta_C)}{2} (r_C^2 - z^2) + M_{\text{free}} \bar{\rho}(z) \bar{\chi}_A(z) \Delta}, \quad z \leq r_C \] (7-35)

Without fluid-fluid bonding, \( \bar{\chi}_A(z) \) is 1.0 except when \( z < r_C \), then

\[ \bar{\chi}_A(z) = \frac{1}{1 + \frac{N_{\text{wall}}}{A} F_{AC}(1, \text{wall}) \pi \frac{1-\cos(\theta_C)}{2} (r_C^2 - z^2)} \] (7-36)

Other equations needed to calculate fluid density profile \( \rho(z) \) can be derived similarly to chapter 5, but using (7.36) instead for \( \bar{\chi}_A(z) \).

The second approach is to calculate the Wertheim association free energy functional directly. As noted by Chapman [9] and later Kierlik and Rosenberg [43], the first order perturbation solution to Wertheim's Associating Fluid Theory is general for inhomogeneous fluids. In this approach, only the fluid \( \chi_A(z) \) should be included since the wall is not part of the system. The equations for this approach are the same as those found in [40] for method 1, except when using iterative method to calculate \( \chi_A(z) \), an extra term for wall bonding needs to be included in the denominator.

As noted by Segura and Chapman [9], in the case of associating spheres against a hard wall, Method 2 gives more accurate contact densities and peak heights, but the positions of the peaks are slightly offset from the simulation results. Moreover, method 2 avoided solving two integral equations and is generally one orders of magnitude faster.
than method 1. Since we are here more concerned about the region near the wall, method 2 (bulk form) is an obvious choice than method 1 (inhomogeneous form). Our density functional theory results used to compare with simulation data are obtained using the bulk form of Wertheim's theory.

7.5 Results and Discussion

As noted earlier, our theory for wall sites is an extension of Wertheim’s first order perturbation theory, which assumes that association sites on a molecule are independent of one another, not accounting for steric hindrance effect. However, in molecular simulation, overlap of molecules is not allowed. When wall sites are closely distributed, a molecule bonded with one wall site may block a nearby site, making it unavailable to bond to an approaching molecule in fluid, as shown schematically in Figure 7-2. From (7-21), for a system of four-sited molecules which can only bond to wall, the fraction of unbonded wall sites is not a function of wall site density. However, this may not be true for closely packed wall sites. Several simulation runs were performed using the same wall site bonding energy and bulk fluid density, but with different wall site density. The results for \( \chi_{\text{wall}} \) is listed in table 7-1, and the total adsorption is plotted versus wall site density in figure 7-5. Total adsorption generally goes up as wall site density increases, until when site spacing approaches the fluid molecular diameter, when adsorption levels out, indicating the tightest possible packing of fluid molecules on the wall is reached. The data for \( \chi_{\text{wall}} \) also show that when wall site spacing is smaller than about 1.3 \( \sigma \), \( \chi_{\text{wall}} \) starts to go down when more sites are placed on the wall, because the number of bonded sites has reached a maximum. Since our first order density functional theory works only
Figure 7-5. Total adsorption at different wall site density, at simulation average density of 0.5 and wall site energy of 5.0
when the steric hindrance effect is negligible, we choose wall site spacing above this
limit to compare the simulation data with our DFT results.

Table 7-1. At simulation average density of 0.5 and wall site energy of 5.0, Xwall
and adsorption vs. wall site spacing

<table>
<thead>
<tr>
<th>NO. wall site</th>
<th>Avg density</th>
<th>Wall site density</th>
<th>Site spacing</th>
<th>Xwall</th>
<th>Adsorption</th>
</tr>
</thead>
<tbody>
<tr>
<td>18</td>
<td>0.5</td>
<td>0.143</td>
<td>2.646</td>
<td>0.731067</td>
<td>0.1756</td>
</tr>
<tr>
<td>32</td>
<td>0.5</td>
<td>0.254</td>
<td>1.984</td>
<td>0.738028</td>
<td>0.1918</td>
</tr>
<tr>
<td>50</td>
<td>0.5</td>
<td>0.397</td>
<td>1.587</td>
<td>0.73368</td>
<td>0.2203</td>
</tr>
<tr>
<td>72</td>
<td>0.5</td>
<td>0.571</td>
<td>1.323</td>
<td>0.726389</td>
<td>0.2709</td>
</tr>
<tr>
<td>98</td>
<td>0.5</td>
<td>0.778</td>
<td>1.134</td>
<td>0.742429</td>
<td>0.3016</td>
</tr>
<tr>
<td>128</td>
<td>0.5</td>
<td>1.016</td>
<td>0.992</td>
<td>0.771797</td>
<td>0.3316</td>
</tr>
<tr>
<td>162</td>
<td>0.5</td>
<td>1.286</td>
<td>0.882</td>
<td>0.81179</td>
<td>0.3327</td>
</tr>
</tbody>
</table>

Table 7-2 summaries the results for this study. \( \rho_{\text{bulk}} \) is the average bulk singlet
number densities from simulation, and is used as input to density functional theory. \( \chi_{\text{wall}} \)
is the fraction of wall sites that are not bonded. \( \rho_{\text{wall}} \) is the singlet number density of fluid
at the wall. \( \Gamma \sigma^2 \) is adsorption in reduced units. The uncertainties stand for one standard
deviation. The fluid contact numbers for simulations are extrapolated from the properties
close to wall. The uncertainties 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. Theoretical adsorption was calculated numerically using

\[
\int_0^{\text{bulk}} (\rho(z)\sigma^3 - \rho(\text{bulk})\sigma^3)dz , \quad \rho(z)\sigma^3 \text{is the singlet reduced number density and}
\]

where \( \rho(\text{bulk})\sigma^3 \) is the reduced number density in the bulk region. For simulation,
Table 7.2 Density Functional Theory versus Simulation for Four-sited Hard Spheres against Active Surfaces
(Only bonding between fluid and wall sites is allowed)

<table>
<thead>
<tr>
<th>Bulk Density $\rho_{\text{bulk}} \sigma^3$</th>
<th>Wall Site energy, $\epsilon_{\text{site}}/kT$</th>
<th>Wall Site density $N_{\text{site}}/A$</th>
<th>Wall Density $\rho_{\text{wall}}$</th>
<th>$\chi_{\text{wall}}$</th>
<th>$\chi_{\text{0,fluid}}$</th>
<th>Adsorption $\Gamma/\sigma^3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$0.4831 \pm 0.0002$</td>
<td>3</td>
<td>0.396</td>
<td>1.896 2.0522±0.0511</td>
<td>0.9814</td>
<td>0.6187</td>
<td>0.1303</td>
</tr>
<tr>
<td>$0.4800 \pm 0.0001$</td>
<td>5</td>
<td>0.396</td>
<td>4.900 4.836±0.1511</td>
<td>0.7224</td>
<td>0.7238±0.0120</td>
<td>0.1072</td>
</tr>
<tr>
<td>$0.4742 \pm 0.0002$</td>
<td>7</td>
<td>0.396</td>
<td>7.969 7.76±0.2921</td>
<td>0.2648</td>
<td>0.2566±0.0180</td>
<td>0.01223</td>
</tr>
<tr>
<td>$0.4702 \pm 0.0004$</td>
<td>9</td>
<td>0.396</td>
<td>15.69 17.41±0.3653</td>
<td>0.0461</td>
<td>0.0484±0.0150</td>
<td>0.0057</td>
</tr>
<tr>
<td>$0.7151 \pm 0.0015$</td>
<td>0</td>
<td>0.52</td>
<td>8.3022 10.38±0.0271</td>
<td>1.0</td>
<td>0.9994±0.0002</td>
<td>1.0</td>
</tr>
<tr>
<td>$0.7149 \pm 0.0018$</td>
<td>1</td>
<td>0.52</td>
<td>8.413 8.718±0.0356</td>
<td>0.9873</td>
<td>0.9821±0.0048</td>
<td>0.9404</td>
</tr>
<tr>
<td>$0.7148 \pm 0.0014$</td>
<td>3</td>
<td>0.52</td>
<td>10.497 10.886±0.0923</td>
<td>0.8749</td>
<td>0.8758±0.0240</td>
<td>0.5670</td>
</tr>
<tr>
<td>$0.7096 \pm 0.0012$</td>
<td>5</td>
<td>0.52</td>
<td>14.560 14.133±0.330</td>
<td>0.4752</td>
<td>0.4760±0.0160</td>
<td>0.1385</td>
</tr>
<tr>
<td>$0.7086 \pm 0.0016$</td>
<td>6</td>
<td>0.52</td>
<td>16.046 15.633±0.393</td>
<td>0.2491</td>
<td>0.245±0.0132</td>
<td>0.0744</td>
</tr>
<tr>
<td>$0.7064 \pm 0.0019$</td>
<td>7</td>
<td>0.52</td>
<td>18.265 18.056±0.655</td>
<td>0.1086</td>
<td>0.1090±0.0012</td>
<td>0.0529</td>
</tr>
</tbody>
</table>
adsorption is calculated using \((\rho_{\text{average}}\sigma^3 - \rho_{\text{bulk}}\sigma^3) \times h\), where \(h\) is half of the simulation cell length in \(z\) direction.

In the limit of zero bonding energy between fluid molecules and wall sites, the system becomes Tarazona hard spheres against hard wall, which have been studied extensively by earlier works from our group [7,9,40,69] and others. The results from this study show consistency with the hard sphere hard wall (HSHW) system, and we provide the results from HSHW as a limit of our system.

In the wall-fluid interfacial region, there are two kinds of adsorption. One is the adsorption of hard spheres on a hard wall, due to the effect of "excluded volume" and the external potential exerted by the wall. This HSHW adsorption is responsible for the multi-layered structure near the wall and a high contact value of fluid density. Another adsorption is the so-called Langmuir monolayer adsorption, as discussed earlier. This effect greatly enhances the adsorption at the vicinity of the wall as shown in table 7-2: at a given bulk density, the contact value of fluid density and adsorption grows rapidly as the bonding energy between wall site and fluid is increased. Note also in table 7-2 that the averaged bulk density, in general, goes down slightly with wall site bonding energy as a result of more molecules bond with wall sites, and therefore fewer molecules were found in the bulk. However, because the wall fluid association is limited to a small region very close to the wall, and because the system is generally very large, the bulk density does not vary much. The change of adsorption characteristics is expected, as the attractive wall has a greater tendency to adsorb fluid molecules. The bulk fluid, which is composed
of hard spheres, is purely repulsive and cannot pull the adsorbate away from the active wall.

Table 7-2 shows that the $\chi_{\text{wall}}$ calculated using (7-22) agrees remarkably well with the simulation result, even at high bonding energies and high densities. The theoretical and simulation values for adsorption compare well except for the highest association at a high bulk density of 0.71. The fraction of monomers at the wall predicted from the density functional theory is in good to excellent agreement with the simulation results. The contact fluid densities calculated from theory are in good agreement with simulation results at low to medium density and bonding energy. At higher density (0.71), the comparison is good for low bonding energy and as bonding energy increases, DFT results tend to slightly underestimate the contact density. For the case of bonding energy of 7 and 9, the theory contact density is about 10% smaller than simulation results. However, this is a severe test to our theory. At very high fluid density and wall bonding energy, the contact density was greatly enhanced, for a bulk density of 0.71 and bonding energy of 7, the contact density was 18.2, more than 20 times the bulk density. Because of the short-range association between fluid and wall, we have only a few data points near the wall which are directly affected by fluid wall bonding. Thus the extrapolated wall density is very sensitive to how the fitting is done. It is also noted that the standard deviation for wall contact density is much larger than our earlier results for hard wall system. Table 3 shows the standard error for contact density at different simulation average density and wall site energy.
Figure 7-6 to figure 7-10 compare theory against simulation results for reduced density versus distance from the wall for the simulation average reduced number densities equal to 0.2, 0.5 and 0.75 and 0.9. At each density, results are given at several wall site bonding energies. The plot at right gives a close up look at interfacial region for the same profile from the left. The DFT results for the region near the wall follows well with the simulation data, especially for lower to medium densities (0.2-0.5). At higher density (0.75), as in figure 7-9 and 7-10, DFT predicts lower contact density, but higher value at region just outside the bonding cutoff. Further away from the wall, the density profile matches the simulation remarkably well, except in fig 7-6 for region from 0.1σ to 1 σ, DFT over predicted the density. This may seem obvious, since outside wall bonding cutoff, the fluid is essentially hard sphere, and should reproduce Tarazona's hard sphere behavior. However, in fig 7-11, a comparison of density profiles for fluid that bonds with wall to density profile for hard sphere at same bulk density shows density profiles are modified far beyond the wall region, extending to as far as 3-4σ, when bonding with wall is introduced to the system. Fig 7-11 shows this change in density profile is most profound for higher bonding energy and within a molecular diameter away from the wall. As bonding energy increases, the position of the oscillation peaks are shifted towards the wall, density values beyond the wall cutoff but before the first trough are lowered, and between the first trough and first peak are raised. Both simulation and DFT results confirm this trend, with DFT predicts a slightly higher peak for high bonding energy.

The change in density profile is also fairly "long-range", extending to about 3-4 σ, considering wall bonding volume only extends to about 0.05 σ from the wall. This is,
Figure 7-6. Density profiles as a function of distance from wall at simulation average density of 0.75, the right plot is a close up of the same one on the left. Reduced wall site energies are (a) 0.0 (b) 3.0.
Figure 7.7. Same as 7.6, with reduced wall site energies of (a) 5.0 and (b) 7.0.
Figure 7-8. Same as 7-6, but at simulation average density of 0.5, wall site energy of 3.0.
Figure 7.9. Same as 7.8, at simulation average density of 0.5, wall site energies of (a) 5.0, (b) 7.0.
Figure 7.10. Same as 7.6, at simulation average density of 0.2, with wall site energies of (a) 3.0 and (b) 5.0.
Figure 7-11. Density profiles for the same simulation average density of 0.75 but at different wall site energies, showing the influence of wall site bonding on fluid structure near wall, (a) Simulation, (b) DFT
Figure 7-12. Plot of $\ln \left( \frac{(1 - X_{\text{wall}})}{X_{\text{wall}}} \right)$ versus reduced wall site energy, showing Langmuir behavior of four site fluid for simulation average density of (a) 0.75 (b) 0.50. Line is from DFT and symbols are simulation data.
however, consistent with the hard sphere hard wall system, when an inhomogeneity introduced by hard wall also extends to several molecular diameters away from the wall. As temperature decreases, and association at wall increases rapidly, more molecules pile up near the wall, the "volume exclusion" effect is more pronounced, as shown by further depressed trough near the wall. The change to density profile caused by wall-fluid bonding is important in changing the nature of disjoining pressure and interaction between two walls when they are brought closer.

Finally, following (7-32), we plot the DFT and simulation results for \( \ln \frac{1 - \chi_{\text{wall}}}{\chi_{\text{wall}}} \) versus inverse reduced temperature in fig. 7-12. They clearly show the Langmuir type adsorption behavior for the system which only allows wall-fluid bonding.

7.6. Conclusions

We have extended first order Wertheim's theory for association to solid wall with single layer of active sites. Combined with our density functional theory for associating fluids, we were able to correctly predict density profile, adsorption, wall coverage, fluid fraction of monomer for a broad range of density and inverse reduced temperature. We tested this theory with a four site model fluid like water. Comparison with simulation data was good to excellent at low to medium bonding energy, and fair at high bonding energy. Based on this theory, we also extended Langmuir adsorption isotherm from ideal gas to fluid of associating hard spheres.
Chapter 8 Competition between Fluid-fluid and Wall-Fluid bonding, a Four-Site Model

8.1 Introduction

In chapter 7, we studied the system where a four site water-like molecule is only permitted to bond with a wall site. The adsorption occurs via the formation of a fluid mono-layer on the surface, showing a Langmuir type behavior. This model provides a good approximation at low pressure at which the wall-fluid bonding is dominant and when the bonding energies between wall sites and fluid are much stronger than that between fluid molecules. We have constructed a perturbational density functional theory for this model, and it has shown in good agreement with simulation results at broad density and wall site energy. When bonding between fluid molecules is allowed, chain or cluster molecules may form in the fluid. These polymers avoid a drop in configurational entropy by avoiding the wall, an effect favoring desorption. The formation of cluster and chain molecules in the fluid poses a competition to fluids bonding to wall sites, which favors adsorption. On the other hand, when fluid-fluid bonding is allowed, the adsorbed fluid molecules could act as nuclei for the formation of larger clusters, and these clusters may connect, either along the surface or across the slit pore, forming multi-layered adsorption. When wall site density increases, this cooperative adsorption effects becomes more important, with cluster molecules forming in regions near the wall when two or more wall sites are placed at a separation suitable for both wall-fluid and fluid-fluid bonding. Such cooperative effect was believed to be important in water. As shown
in last chapter, wall site enhanced adsorption results in a steep increase in density near the wall. However, when the wall site density reaches certain value, a fluid molecule bonded at one wall site may "block" a nearby wall site, making it unavailable to bond to other fluid molecules. This steric hindrance effect, as shown in last chapter, poses a limit to our first order density functional theory, which considers all wall sites to be independent of one another.

Erich, et al studied the adsorption isotherms of associating Lennard-Jones (LJ) chain molecules against an LJ surface with active sites using Monte Carlo simulations. This study gave some interesting results for the consequence of competition between the tendency of the individual spheres forming a chain to place themselves in the center of the pore and the strongly favorable bonding of a molecule onto the wall. However, this system is too complex for early theoretical study. 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 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.

In this chapter, we will extend our density functional theory (DFT) for active surfaces derived in chapter 7 to include fluid- fluid bonding effects. We continue using a
four sited model like the one in Bol [79] configuration. This model is qualitative for water against a hydrophilic wall, although we have omitted the long range attraction forces between fluid molecules. We present here results from simulation and DFT on adsorption, density structure in fluid, wall coverage at different level of reduced density and reduced bonding energy (inverse reduced temperature).

8.2 Molecular Simulations

The associating fluid in the model selected in this work has four bonding sites, A, B, C, 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 $\varepsilon_{AC} = \varepsilon_{AD} = \varepsilon_{BC} = \varepsilon_{BD} = \varepsilon_{\text{site}}$, and $\varepsilon_{AA} = \varepsilon_{BB} = \varepsilon_{CC} = \varepsilon_{DD} = 0$. In effect, if two eligible bonding sites are close enough and oriented correctly, then a bond is formed. When in the vicinity of the wall, all four sites A, B, C and D can bonding with a wall site. In general the bonding energy between a wall site and fluid particle $\varepsilon_{\text{wall}}$ and the bonding energy between fluid molecules $\varepsilon_{\text{site}}$ are different. In the simulations and in our theoretical calculations, the radial limits of the square-well association were set to $r_c=1.05 \sigma$ and the angular limit was set to $\theta = 27^\circ$.

With fluid-fluid bonding, the simulation acceptance rate is greatly reduced. We have to use smaller maximum displacement and orientation step to obtain reasonable acceptance rate. The acceptance criterion was set to $\sim 10\%$ to $20\%$, which was enforced within several collections of slices, especially and including the collection of slices within 0.25 of either wall. More configurations were needed to get a statistically
meaningful results than the case only wall-fluid bonding is allowed. Typically, one billion displacements were needed for higher densities and higher bonding energies. The density profile and adsorption were obtained in a way similar to that in Chapter 7. In addition, we will keep track of the fraction of monomers and cluster size distribution of fluid as functions of distance from wall.

8.3 Wertheim's theory for associating fluid against active wall, including fluid-fluid and fluid-wall bonding

We follow the same derivation as in last chapter by extending Wertheim's first order perturbation theory for association to including both fluid-fluid and fluid-wall bonding. Generally, bonding energy between a wall site and a site on fluid molecule $\varepsilon_{f_w}$ and bonding energy between sites on fluid molecules, $\varepsilon_{f_f}$, are different. Wertheim's first order theory assumes all wall sites and sites on one molecule are independent of one another, and only one site between a wall site and a molecule, or between two molecules are allowed.

8.3.1 Fraction of a site on fluid molecules that is unbonded

Similar to (7-7), but include the bonding between fluid molecules, the fraction of site As on molecule 1 that are not bonded is given by

$$\chi_A(1) = \frac{1}{1 + \sum_c \int \rho(wall) \chi_{wall} \varepsilon_{ref}(1,wall) f_{AC}(1,wall) dwall + \sum_b \int \rho(2) \chi_{b}(2) \varepsilon_{ref}(1,2) f_{AB}(1,2) d^2}$$

(8-1)
Following the derivation in chapter 7, we integrate over wall area and the bonding volume of a wall site,

$$\chi_A(1) = \frac{1}{1 + \frac{N_{\text{wall}}}{A} F_{AC}(1, \text{wall}) \pi \frac{1 - \cos(\theta_c)}{2} (r_c^2 - z^2) + \sum_b \int \rho(2) \chi_b(2) g_{\text{ref}}(1,2) f_{AB}(1,2) d\tilde{z}}$$

(8-2)

If we assume $\chi_A(1)$ is only a function of $z$ and is not a strong function of orientation, and $g_{\text{ref}}(1,2)$ is independent of position and direction and can be approximated by $g_{\text{ref}}(\sigma)$, the contact value, we can follow the same procedure in [9] to get the iterative equation for $\chi_A(z)$,

$$\chi_A^{z+1}(z) = \frac{1}{1 + \frac{N_{\text{wall}}}{A} F_{AC}(1, \text{wall}) \pi \frac{1 - \cos(\theta_c)}{2} (r_c^2 - z^2) + 2n \pi K g_{\text{HS}}(\sigma) F_{AB} \int_{-1+z}^{1+z} \chi_A(z_1) \rho(z_1) dz_1}$$

(8-3)

where $K$ is a constant that measures the volume available for bonding of the two sites on molecules 1 and 2, which is $\frac{(1 - \cos(\theta_c))^2 (r_c - \sigma)}{4}$, and $F_{AB}$ is the Mayer $f$ function $\exp(\varepsilon_{\text{sike}} / kT) - 1$, and $g_{\text{HS}}(\sigma; \rho_{\text{bulk}})$ is the hard sphere pair correlation function at contact a the bulk density, $n$ is the number of sites on molecules 2 that a site on molecule 1 can bond.
8.3.2 Fraction of wall sites that are not bonded

Using the first approach in 7.3.2, the fraction of wall sites that are not bonded is,

\[ \chi_{\text{wall}} = \frac{1}{1 + \sum_c \int \rho(2) \chi_c(2) g_{\text{ref}}(2, \text{wall}) f_c(2, \text{wall}) d2} \]  

where \( \rho(2) \) is the fluid's singlet number density, \( \chi_c(2) \) is the fraction of molecules not bonded at site C of fluid molecule 2, given by (8-3), and \( f_{\text{ac}}(2, \text{wall}) \), is the Mayer \( f \) function for the square well potential model of wall-fluid association. Since walls do not move in space, the pair correlation function between wall sites and fluid molecule, \( g_{\text{ref}}(2, \text{wall}) \), is 1.0. Assuming \( \chi_c(2) \) does not depend on orientation. After doing an unweighted angle average, and integrating over \( \int dx dy \), we have,

\[ \chi_{\text{wall}} = \frac{1}{1 + M_{\text{site}} \frac{1 - \cos(\theta_c)}{2} \left[ \exp(e_{\text{wall-site}} / kT) - 1 \right] \int \rho(z) \chi(z) A_{\text{one-site}} dz} \]  

where \( A_{\text{one-site}} = \pi (r_c^2 - z^2) \), i.e. the area available for bonding for one wall site.

For four-sited fluid, there is one site on the molecule that is always oriented towards the wall, so \( \chi(z) \) in integral in (7-15) is approximately 1.0. (8-5) becomes,
\[
\chi_{\text{wall}} = \frac{1}{1 + 4\pi \frac{1 - \cos(\theta_c)}{2} \left[ \exp \left( \frac{\varepsilon_{\text{wall-site}}}{kT} \right) - 1 \right] \int \rho(z)(r_c^2 - z^2) \, dz} \tag{8-6}
\]

On the other hand, using the bulk form of Wertheim's theory [6], we have,

\[
\chi_{\text{wall}} = \frac{1}{1 + M_{\text{site}} \rho_{\text{bulk}} \chi_{\text{bulk}} \Delta(1, \text{wall})} \tag{8-7}
\]

where

\[
\Delta(1, \text{wall}) = \int_{\text{bond volume}} f(1, \text{wall}) g_{\text{HS}}(1, \text{wall}) d(1, \text{wall}) \tag{8-8}
\]

and \( \chi_{\text{bulk}} \) is the bulk fluid fraction of molecules that are not bonded at site A, and is given by

\[
\chi_{\text{bulk}} = \frac{1}{1 + M_{\text{site}} \rho_{\text{bulk}} \chi_{\text{bulk}} \Delta} \tag{8-9}
\]

where \( \Delta = 4\pi K g_{\text{HS}}(\sigma) F_{AC} \), and \( g_{\text{HS}}(z) = \frac{\rho_{\text{HS}}(z)}{\rho_{\text{bulk}}} \).

After an integral on \( \int dx dy \) and orientation, (8-9) becomes,
\[
\chi_{\text{wall}} = \frac{1}{1 + M_{\text{site}} \pi \frac{1 - \cos \theta}{2} \left( \exp(\varepsilon_{\text{site}} / kT) \chi_{\text{bulk}} \right) \int \rho_{\text{HS}}(z) (r_c^2 - z^2) \, dz}
\]

(8-10)

With fluid-fluid bonding, \( \chi_{\text{bulk}} \) is not 1.0. However, only the fraction of fluid not bonded very near the wall is of the concern of a wall site. So for four site fluid, one site is always oriented towards the wall, and "\( \chi_{\text{bulk}} \)" at the vicinity of wall can be approximated to be 1.0. The fraction of wall sites not bonded is then,

\[
\chi_{\text{wall}} = \frac{1}{1 + 4 \pi \frac{1 - \cos \theta}{2} \left( \exp(\varepsilon_{\text{site}} / kT) \int \rho_{\text{HS}}(z) (r_c^2 - z^2) \, dz \right)}
\]

(8-11)

It is noteworthy that the equations (8-6) and (8-11) are the same as the equations in (7-20) and (7-21) for calculating the fraction of wall sites that are not bonded. This is due to the steric property of four-sited molecules and is not generally true for other molecular configurations, such as one- and two-sited molecules which we will study in next chapter. Because of this unique property of four-sited model, the adsorption at wall demonstrates Langmuir behavior even if when fluid-fluid bonding is present, and multilayer adsorption occurs. Generally, (8-10) implies that with fluid-fluid bonding, \( \chi_{\text{bulk}} \) is reduced, and \( \chi_{\text{wall}} \) will increase, meaning fewer wall sites are occupied.
8.4 Free Energy Functional for Associating Fluids Interacting with Wall Sites

Because of the reasons cited in chapter 7, we only utilize the bulk form of Wertheim's theory, and take a Tarazona weighted density and calculate a bulk extent of hydrogen bonding and a bulk free energy. However, if the fluid element is close enough to the wall, the extent of hydrogen bonding will include a contribution from bonding to a wall site. The probability that a wall site is not bonded will depend on an integral of bonding from the fluid element near the wall. Equations (7-32) to (7-34) holds for the fluid-wall and fluid-fluid case, but the equation for weighted fraction of site A on a fluid molecule needs to add a term for fluid-fluid bonding, i.e.,

\[
\bar{\chi}_A(z) = \frac{1}{1 + \frac{N_{\text{wall}}}{A} F_{AC}(1, \text{wall}) \pi \frac{1 - \cos(\theta_c)}{2} \left( r_c^2 - z^2 \right) + M_{\text{site}} \bar{\rho}(z) \overline{\chi}_A(z) \Delta}, \quad z \leq r_c
\]

Other equations needed to calculate fluid density profile \( \rho(z) \) can be derived similarly to chapter 5, but using (8-12) instead for \( \bar{\chi}_A(z) \).

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, Ghonasgi and Chapman [5] have derived the following equations for \( \chi_n(z) \), the fraction of molecules bonded at \( n \) sites at distance \( z \) from the wall,

\[
\chi_0(z) = \chi_1^A(z)
\]
\[ \chi_1(z) = 4 \chi_A^3(z)(1 - \chi_A(z)) \]
\[ \chi_2(z) = 6 \chi_A^3(z)(1 - \chi_A(z))^2 \]
\[ \chi_3(z) = 4 \chi_A(z)(1 - \chi_A(z))^3 \]
\[ \chi_4(z) = (1 - \chi_A(z))^4 \]

8.5 Results and discussion

As noted in chapter 7, our theory for wall sites is an extension of Wertheim's first order perturbation theory, which assumes that association sites on a molecule are independent of one another, not accounting for steric hindrance effect. Since our first order density functional theory works only when the steric hindrance effect is negligible, we choose wall site spacing greater than 1.3\( \sigma \) to compare the simulation data with our DFT results.

Table 8-1 summarizes the results for this study. \( \rho_{\text{bulk}} \) is the average bulk singlet number densities from simulation, and is used as input to density functional theory. \( \chi_{\text{wall}} \) is the fraction of wall sites that are not bonded. \( \rho_{\text{wall}} \) is the singlet number density of fluid at the wall. \( \Gamma \sigma^2 \) is adsorption in reduced units. The uncertainties stand for one standard deviation. The fluid contact numbers for simulations are extrapolated from the properties close to wall. The uncertainties 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. Theoretical adsorption was calculated numerically using

\[ \int_{0}^{\text{bulk}} (\rho(z)\sigma^3 - \rho(\text{bulk})\sigma^3) dz \]
\( \rho(z)\sigma^3 \) is the singlet reduced number density and
### Table 8.2 Density Functional Theory versus Simulation for Four-sited Hard Spheres against Active Surfaces

<table>
<thead>
<tr>
<th>Bulk Density $\rho_{\text{bulk}} , \sigma^3$</th>
<th>Bonding energetic Site/Wall $\varepsilon_{\text{sim}}/kT$</th>
<th>Wall Site Density $N_{\text{wall}}/\sigma^2$</th>
<th>Wall Density $\rho_{\text{wall}}/\sigma^3$</th>
<th>$\chi_{\text{wall}}$</th>
<th>$\chi_{\text{wall,thd}}$</th>
<th>Adsorption $\Gamma/\sigma^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$0.7154 \pm 0.0038$</td>
<td>3/3</td>
<td>0.52</td>
<td>4.696</td>
<td>5.6023 $\pm$ 0.1822</td>
<td>0.8772</td>
<td>0.8798 $\pm$ 0.0006</td>
</tr>
<tr>
<td>$0.7103 \pm 0.0022$</td>
<td>3/5</td>
<td>0.52</td>
<td>8.928</td>
<td>11.623 $\pm$ 0.4122</td>
<td>0.4806</td>
<td>0.486 $\pm$ 0.020</td>
</tr>
<tr>
<td>$0.7073 \pm 0.0034$</td>
<td>3/7</td>
<td>0.52</td>
<td>13.89</td>
<td>18.127 $\pm$ 0.483</td>
<td>0.1107</td>
<td>0.112 $\pm$ 0.010</td>
</tr>
<tr>
<td>$0.7224 \pm 0.0004$</td>
<td>5/3</td>
<td>0.52</td>
<td>3.56</td>
<td>4.707 $\pm$ 0.1635</td>
<td>0.8772</td>
<td>0.877 $\pm$ 0.003</td>
</tr>
<tr>
<td>$0.7166 \pm 0.005$</td>
<td>5/5</td>
<td>0.52</td>
<td>5.406</td>
<td>10.85 $\pm$ 0.436</td>
<td>0.4806</td>
<td>0.4902 $\pm$ 0.006</td>
</tr>
<tr>
<td>$0.7086 \pm 0.005$</td>
<td>5/7</td>
<td>0.52</td>
<td>8.21</td>
<td>17.29 $\pm$ 0.9215</td>
<td>0.1113</td>
<td>0.1104 $\pm$ 0.010</td>
</tr>
<tr>
<td>$0.7106 \pm 0.0031$</td>
<td>7/7</td>
<td>0.52</td>
<td>3.25</td>
<td>17.08 $\pm$ 0.8354</td>
<td>0.1105</td>
<td>0.1108 $\pm$ 0.006</td>
</tr>
<tr>
<td>$0.4822 \pm 0.0023$</td>
<td>3/5</td>
<td>0.396</td>
<td>4.446</td>
<td>4.677 $\pm$ 0.2322</td>
<td>0.7205</td>
<td>0.7236 $\pm$ 0.0012</td>
</tr>
<tr>
<td>$0.4865 \pm 0.0034$</td>
<td>5/5</td>
<td>0.396</td>
<td>2.8755</td>
<td>3.9803 $\pm$ 0.1768</td>
<td>0.7162</td>
<td>0.7280 $\pm$ 0.0014</td>
</tr>
<tr>
<td>$0.4744 \pm 0.0032$</td>
<td>3/7</td>
<td>0.396</td>
<td>13.57</td>
<td>13.415 $\pm$ 0.0422</td>
<td>0.2575</td>
<td>0.2750 $\pm$ 0.010</td>
</tr>
</tbody>
</table>
where \( \rho(bulk) \sigma^3 \) is the reduced number density in the bulk region. For simulation, adsorption is calculated using \( (\rho_{\text{average}} \sigma^3 - \rho_{\text{bulk}} \sigma^3) \cdot h \), where \( h \) is half of the simulation cell length in \( z \) direction.

In the limit of zero bonding energy between fluid molecules and wall sites, the system becomes Tarazona hard spheres against hard wall, and when fluid-fluid bonding energy is zero, the system is the same as the one studied in chapter 7. We included the results of this limit for different wall site energy and simulation average density for comparison.

We can see from Table 8-1 that \( \chi_{\text{wall}} \), the fraction of wall sites that are not bonded, does not vary much with different fluid-fluid bonding energy, while keeping the same fluid-wall bonding energy. This confirms our assumption that four site water-like molecules always have one site available to bond with wall. The wall coverage calculated using (8-11) is remarkably accurate at all combination of bonding energies and densities.

Table 8-1 shows that the bulk density, generally goes up with fluid site bonding energy if the wall site energy stays the same. This trend was also shown in chapter 7 for system with only fluid-wall bonding. Hydrogen bonding tends to cluster the molecules together and away from the wall, so more molecules are found in the bulk. When the fluid-fluid bonding energy stays the same, but wall energy increases, fluid molecules are more attracted to the wall, and bulk density decreases. For the same wall site density,
Figure 8.1: Density profiles as a function of distance from wall at simulation average density of 0.5. The plots at right is a close up look of the same one on the left. Reduced fluid and wall site energies are (a) 3.0/0.0 and (b) 3.0/3.0.
Figure 8.2. Same as 8.1, at simulation average density of 0.5, with fluid/wall energies of (a) 3.0/5.0 and 3.0/7.0.
Figure 8.3. Same as 8.1, but with fluid/wall bonding energies of (a) 3.0/5.0 and (b) 5.0/5.0.
Figure 8.4. Same as 8.1, but as simulation average density of 0.75, with fluid/wall site energies of (a) 0.0/0.0 and (b) 3.0/3.0.
Figure 8.5. Same as 8.4, but with fluid/wall site energies of (a) 5/0.5 and (b) 7/0/7.0.
Figure 8-6. Fraction of monomers as a function of distance from wall, at simulation average density of 0.5, with fluid/wall site energies of (a) 3.0/3.0 and (b) 5.0/5.0, lines are DFT results and symbols are simulation data.
when both the wall and fluid site energies increase at the same rate, the wall contact
density increases rapidly, and the bulk density decreases.

The total adsorption shows similar trend. As fluid-fluid and fluid-wall bonding
ergies goes up at the same rate, total adsorption increases. This is in direct contract
with the system of associating fluid near a hard wall [69], where as fluid energy goes up,
bulk density goes up because cluster tends to pile up in the bulk, and total adsorption
goes down. The effect of wall sites have changed the adsorption characteristics of the
pore, and seem to overcome the decrease in entropy suffered by large clusters near the
wall. Therefore, the wall site energy dominates the fluid energy in the system. However,
it is noteworthy that the total adsorption predicted is only accurate at lower wall bonding
energies and the accuracy suffers as both wall bonding energy and total density goes up.
This result from the fact that our theory does not accurately predict the contact density at
such conditions, and it is the densities (inhomogeneity) near wall that accounts more for
total adsorption.

Figure 8-1 to figure 8-5 compare theory against simulation results for reduced
density versus distance from the wall for simulation average densities equal of 0.2, 0.5
and 0.75. At each density, results are given at several wall/fluid bonding energies
combinations. The plot at right gives a close up look at interfacial region for the same
profile at the left. The DFT results for the region near the wall follows well with the
simulation data, for low to medium densities (0.2-0.5) and low to medium bonding
energies (3.0-5.0). The contact density from theory also matches well with simulation
results, with error increases as fluid-fluid bonding energy increases. Figure 8-1 and 8-2 show the density profile for density of 0.50 and fixed fluid/fluid bonding energy of 3.0, wall site bonding energy goes from 0.0 (hard wall) to 7.0. The theory is in excellent agreement with simulation, except at wall site energy of 7.0, the theory gives lower contact density. This is similar to what we got in last chapter for only fluid wall bonding is allowed.

Figure 8-3 shows that for the same wall site energy, higher fluid-fluid bonding energy increase bonding in fluid and pull molecules away from the wall, lowering wall contact density. It's also noteworthy that for fixed wall site energy, our theory works well at lower fluid bonding energy, and the errors increases substantially with stronger competition from fluid. Figures 8-4 and 8-5 present a comparison between DFT and simulation at a rather high density of 0.75 and with wall site and fluid bonding energies goes up at the same rate, from 0.0/0.0 to 7.0/7.0. We see at this density, DFT gives excellent agreement at 3.0/3.0, and accuracy start to deteriorate at 5.0/5.0, predicting a contact value of slightly more than half of simulation results, but giving the correct trend of increasing wall density. At the extreme case of 7.0/7.0, the comparison if poor, our theory predicted a contact value of only 25% of simulation results, and it also failed to show the trend that contact density goes up when both wall and fluid bonding increase. However, this may not be a total failure for our wall site DFT at this condition, as we recall that in the case of associating fluid against a hard wall, the DFT compares poorly with simulation results and gives a lower contact value [40]. Nevertheless, our theory
accurately predicted $\chi_{\text{wall}}$, the fraction of wall sites unbonded, and $\chi_{0,\text{fluid}}$, the fraction of monomers of fluid at contact at all conditions.

Our theory seems to work remarkably well at low to medium density and low to medium bonding energy. Nonetheless, it works poorly at high bonding energy, especially when the fluid bonding is strong, when the theory overpredicts competition from fluid. One of the assumptions we made in deriving our theory may have contributed to this underprediction of fluid density near the wall. When we calculate $\chi_{\text{wall}}$, we made use of the fact that $\chi_{A}$, the fraction of site A on fluid molecule that are unbonded, is dependent on orientation. However, when calculating $\chi_{A}$, we assume that it is independent of orientation. This is not true close to the wall. By assuming that $\chi_{A}$ is orientation independent, we have allowed all four sites on a molecule close to the wall to be available to bond to other molecules. This is in direct competition to bonding to wall sites. For high fluid-fluid bonding energy, the theory may over predict bonding in fluid near the wall, and under predict wall site bonding.

We plot in figure 8-6, the fraction of monomers versus distance from wall at the range of density and bonding energy where our theory works well. At density of 0.5, and fluid/wall bonding energy of 3.0/3.0 and 5.0/5.0, theoretical results compare remarkably well with simulation data, for both the region close to wall and bulk region. For theory, the cusp in the fraction of monomers curve at $z = \sigma$ is due to the nature of integral in equation (8-3) and an approximation of bonding only at hard sphere contact. If molecule 1 is within a molecular diameter of the wall, the integrand is zero for some positions of
molecule 2 due to the excluded volume of the wall. The theory also slightly overpredicts the fraction of monomers in the bulk for bonding energies of 5.0/5.0, as found earlier [9] due in part to the different definition of a monomer in the theory and in the simulation. As in direct contrast to the case of associating hard spheres against a hard wall, where fraction of monomer near the wall is higher than in bulk, we see with the presence of wall sites, fraction of monomers are greatly reduced because of bonding between fluid and wall. The agreement within the wall bonding cutoff is excellent. This high accuracy of fraction of monomers between theory and simulation suggests that even with some discrepancy of wall contact density and density profile near the wall, and the theory misses some structural details, but it is still accurate for fraction of monomers and thus free energy.

![Figure 8-7. Plot of ln((1-Xwall)/Xwall) versus reduced wall site energy. The fluid/fluid bonding energy is 3.0, simulation average density is 0.75. line is DFT and symbols are from simulation.](image)
Finally, we show Langmuir behavior of four site molecule even with fluid-fluid bonding by plotting in figure (8-7) \( \ln \left( \frac{1 - \chi_{\text{wall}}}{\chi_{\text{wall}}} \right) \) versus wall site bonding energy. This rather unique behavior of four site molecule is due to its steric property that at the vicinity of wall, there is always one site oriented towards the wall, and available to bond to wall sites.

8.6 Conclusions

We continued our study of chapter 7 by extending our theory of associating fluids near active surfaces to include fluid-fluid bonding. Our theory has shown good agreement with simulation data at low to medium density and low to medium bonding energy. We have shown with the presence of both fluid/wall and fluid/fluid bonding, wall site energy dominates fluid energy and determines the adsorption characteristics of the confined system. Although our theory deviates from simulation as density and bonding energy increases, it is still an attractive tool for predicting fluid structure and thermodynamic properties, given its simplicity and much shorter computing time compared to simulations at same conditions, sometimes more than three orders of magnitude faster.
Chapter 9 One- and Two-Site Associating Fluids near Active Surfaces

9.1 Introduction

We continue our work in chapter 8 to study one- and two-sited associating molecules near an active wall. The behavior of chain molecules at solid surfaces is of scientific interest and of particular importance in chemical process. Chain molecules that can bond to sites on the solid surfaces are of particular interest, since their behavior controls numerous processes, including adhesion, lubrication, the properties of composites involving polymers and mixture separation. For example, it is now possible to attach active sites to the solid surface that bond to suitable sites in the polymer chain in a controlled manner, but there is little understanding of the molecular behavior to the underlying molecular and surface characteristics. It would be helpful to have a fundamental understanding of how the structure, molecular configuration and bonding of the associating chains varies with the chemical nature of the solid surfaces, the density and type of active sites on the surface, and temperature and pressure. With a detailed molecular understanding, it should be possible to prepare improved adhesives and composites, and even "grow" nano-scale structures such as polymer brushes attached to a surface.

For two site model, linear chains can be formed in the fluid. As observed in [40], chains have bigger tendency to avoid the drop in entropy by concentrating in the bulk region. However, unlike the one-site model, when a two-site molecule is bonded to wall,
the remaining site generally orient away from the wall and is readily available for bonding with other fluid molecules. This molecule may act as a nuclei to attract other molecules, and grow into linear chains that are attached to wall.

For one-sited model, only dimers can be formed in the fluid, and when the only site on a molecule is bonded with another molecule, the molecule cannot bond with wall site. The formed dimer would avoid a drop in entropy by avoiding the wall. On the other hand, when enough one-site molecules are bonded to the wall, they effectively change the active surface to a repulsive hard wall. Moreover, the cooperative bonding effect that is important in a four site model system does not exist in a one-site fluid system.

In this chapter, we will extend our density functional theory (DFT) for active surfaces to one- and four-site associating fluids. The two site molecule has one O site and one H site on opposite side of the molecule. Between molecules, only unlike sites can bond. The one site molecule has only one active site and can bond with the site on another molecule. We present here results from simulation and DFT on adsorption, density structure in fluid, wall coverage at different level of reduced density and reduced bonding energy (inverse reduced temperature).

### 9.2 Molecular Simulations

The associating fluids in this study one or two bonding sites. The one-site molecular model used in these simulations has one bonding site labeled A placed on a spherical core. The square well depth for association bonding is $\epsilon_{AA} = \epsilon_{ff}$. For two-site
model, two sites labeled A and B are placed on opposite sides of each sphere; unlike-labeled sites on different molecules are eligible for bonding, so our square well depth in this case is $\epsilon_{AA} = \epsilon_{BB} = 0$; $\epsilon_{AB} = \epsilon_{BA} = \epsilon_{ff}$. In effect, if two eligible bonding sites on two different molecules are close enough and oriented correctly, then a bond is formed. When in the vicinity of the wall, all sites on a molecule can bond with a wall site. In general the bonding energy between a wall site and fluid particle $\epsilon_{fw}$ and the bonding energy between fluid molecules $\epsilon_{ff}$ are different. In the simulations and in our theoretical calculations, the radial limits of the square-well association were set to $r_c=1.05 \sigma$ and the angular limit was set to $\theta = 27^\circ$.

The simulation acceptance rate is lower than the case without fluid-fluid bonding but higher than the four site model in chapter 8. In general, two-site model has a lower acceptance than one-site model. Maximum displacement and orientation steps are adjusted for different conditions to obtain reasonable acceptance rate. The acceptance criterion was set to $\sim10\%$ to $20\%$, which was enforced within several collections of slices, especially and including the collection of slices within 0.25 of either wall. Typically, more displacements were needed for higher densities and higher bonding energies. The density profile and adsorption were obtained similar to Chapter 7. In addition, we will keep track of the fraction of monomers and cluster size distribution of fluid as functions of distance from wall.
9.3 Wertheim's theory for associating fluid against active wall, one- and two-site model

We follow the same derivation as in last chapter by extending Wertheim's first order perturbation theory for associating fluids to including both fluid-fluid and fluid-wall bonding. Generally, the bonding energy between a wall site and a site on fluid molecule \( \varepsilon_{fu} \) and bonding energy between sites on fluid molecules, \( \varepsilon_{ff} \), are different. Wertheim's first order theory assumes all wall sites and sites on one molecule are independent of one another, and only one site between a wall site and a molecule, or between two molecules are allowed.

9.3.1 Fraction of a site on fluid molecules that is unbonded

The fraction of site A not bonded is given the same way as (8-2),

\[
\chi_A(1) = \frac{1}{1 + \frac{N_{wall}}{A} F_{AC}(1, wall) \pi \frac{1 - \cos(\theta_c)}{2} (r_c^2 - z^2) + \sum_B \int \rho(2) \chi_B(2) g_{mf}(1,2) f_{AB}(1,2) d\tilde{2}}
\]

(9-1)

and

\[
\chi_A^{(1)}(z) = \frac{1}{1 + \frac{N_{wall}}{A} F_{AC}(1, wall) \pi \frac{1 - \cos(\theta_c)}{2} (r_c^2 - z^2) + 2n \pi K g_{HS}(\sigma) F_{AB} \int_{-\infty}^{\infty} \chi_A(z_1) \rho(z_1) dz_1}
\]

(9-2)
where $K$, $F_{ab}$ and $g_{hs}(\sigma; \rho_{bulk})$ are defined the same way as in chapter 7 and 8, $n$ is the number of sites on molecule 2 that a site on molecule can bond. For one- and two-site model, $n$ is one, and for four-site model, $n$ is 2.

9.3.2 Fraction of wall sites that are not bonded

The equation for fraction of wall site not bonded is the same as (8-5)

$$\chi_{wall} = \frac{1}{1 + M_{site} \frac{1 - \cos(\theta_c)}{2} \left[ \exp(\varepsilon_{wall-site} / kT) - 1 \right] \int \rho(z) \chi(z)(r_c^2 - z^2) dz} \quad (9-3)$$

but for one- and two-site model, $\chi(z)$ is now a function of distance from wall. And generally, $\chi(z)$ and $\rho(z)$ are known beforehand, (9-3) has to solved iteratively.

Using the bulk form of Wertheim's theory, we have,

$$\chi_{wall} = \frac{1}{1 + M_{site} \pi \frac{1 - \cos(\theta_c)}{2} (\exp(\varepsilon_{site} / kT) \chi_{bulk} \int \rho_{hs}(z)(r_c^2 - z^2) dz} \quad (9-4)$$

Unlike the case of four-site model, $\chi_{bulk}$ has to solved using bulk form of Wertheim's theory,

$$\chi_{bulk} = \frac{1}{1 + n \chi_{bulk} \rho_{bulk} \Delta} \quad (9-5)$$
where $\Delta$ is defined the same way as in chapter 7, and $n$ is the number of sites on molecule 2 that a site on molecule 1 is eligible to bond. For our one- and two-site model, $n$ is 1.

Without fluid-fluid bonding, $\chi_{\text{bulk}}$ is 1.0, the wall coverage shows Langmuir behavior. However, with fluid-fluid bonding, because of the competition from fluid bonding, as temperature reduces and association increases, wall coverage will decrease, deviating from Langmuir behavior.

9.4 Free Energy Functional for Associating Fluids Interacting with Wall Sites

Because of the reasons cited in chapter 7, we only utilize the bulk form of Wertheim's theory, and take a Tarazona weighted density and calculate a bulk extent of hydrogen bonding and a bulk free energy. However, if the fluid element is close enough to the wall, the extent of hydrogen bonding will include a contribution from bonding to a wall site. The probability that a wall site is not bonded will depend on an integral of bonding from the fluid element near the wall. Equations (7-32) to (7-34) holds for the fluid-wall and fluid-fluid case, but the equation for weighed fraction of site $A$ on a fluid molecule needs to add a term for fluid-fluid bonding, i.e.,

$$
\bar{\chi}_A(z) = \frac{1}{1 + \frac{N_{\text{wall}}}{A} F_{\Delta C}(1, \text{wall}) \pi \frac{1 - \cos(\theta_C)}{2} (r_C^2 - z^2) + n\rho(z)\bar{\chi}_A(z)\Delta}, \quad z \leq r_C \quad (9-6)
$$
Other equations needed to calculate fluid density profile $\rho(z)$ can be derived similarly to chapter 5, but using (9-6) instead for $\bar{L}_A(z)$.

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, the fraction of monomers is

$$\chi_0(z) = \chi_A^{M_{\infty}}(z) \quad (9-7)$$

### 9.5 Results and discussion

We choose a wall site spacing greater than $1.3\sigma$ to compare the simulation data with our DFT results for the same reason cited in chapter 7 and 8.

Table 9-1 lists some of the major results for one-site dimerizing fluid and table 9-2 lists similar results for two-site linear chain forming molecules. $\rho_{\text{bulk}}$ is the average bulk singlet number densities from simulation, and is used as input to density functional theory. $\chi_{\text{wall}}$ is the fraction of wall sites that are not bonded. $\rho_{\text{wall}}$ is the singlet number density of fluid at the wall. $\Gamma\sigma^2$ is adsorption in reduced units. The uncertainties stand for one standard deviation. The fluid contact numbers for simulations are extrapolated from the properties close to wall. The uncertainties 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. Theoretical adsorption was calculated numerically.
<table>
<thead>
<tr>
<th>Bulk Density $\rho_{bulk} \sigma^3$</th>
<th>Bonding energies, Site/Wall $\epsilon_{site}/kT$</th>
<th>Wall Site Density $N_{wall}/A$</th>
<th>Wall Density $\rho_{wall} \sigma^3$</th>
<th>$X_{wall}$</th>
<th>$X_{0,fluid}$</th>
<th>Adsorption $\Gamma \sigma^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>DFT</td>
<td>Simulation</td>
<td>DFT</td>
<td>Simulation</td>
</tr>
<tr>
<td>0.4840 ± 0.0029</td>
<td>0/0</td>
<td>0.396</td>
<td>1.5172</td>
<td>1.4822 ± 0.0153</td>
<td>1.0</td>
<td>0.9994 ± 0.0001</td>
</tr>
<tr>
<td>0.4839 ± 0.0024</td>
<td>0/3</td>
<td>0.396</td>
<td>1.6660</td>
<td>1.6253 ± 0.0342</td>
<td>0.9874</td>
<td>0.9876 ± 0.0012</td>
</tr>
<tr>
<td>0.4815 ± 0.0037</td>
<td>0/5</td>
<td>0.396</td>
<td>2.568</td>
<td>2.5342 ± 0.0932</td>
<td>0.9104</td>
<td>0.9108 ± 0.0068</td>
</tr>
<tr>
<td>0.4780 ± 0.0031</td>
<td>0/7</td>
<td>0.396</td>
<td>5.7039</td>
<td>6.6224 ± 0.2329</td>
<td>0.5777</td>
<td>0.5748 ± 0.0110</td>
</tr>
<tr>
<td>0.4775 ± 0.0029</td>
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<td>0.396</td>
<td>5.628</td>
<td>6.4501 ± 0.2140</td>
<td>0.5861</td>
<td>0.5902 ± 0.015</td>
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<tr>
<td>0.4780 ± 0.0021</td>
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<td>0.396</td>
<td>5.245</td>
<td>6.2845 ± 0.2436</td>
<td>0.6317</td>
<td>0.622 ± 0.020</td>
</tr>
<tr>
<td>0.4837 ± 0.0043</td>
<td>7/7</td>
<td>0.396</td>
<td>4.399</td>
<td>4.6459 ± 0.3448</td>
<td>0.7383</td>
<td>0.730 ± 0.023</td>
</tr>
<tr>
<td>0.7088 ± 0.0015</td>
<td>3/7</td>
<td>0.52</td>
<td>9.6828</td>
<td>14.192 ± 0.448</td>
<td>0.3491</td>
<td>0.350 ± 0.014</td>
</tr>
<tr>
<td>0.7113 ± 0.0022</td>
<td>5/7</td>
<td>0.52</td>
<td>9.2897</td>
<td>13.118 ± 0.635</td>
<td>0.4183</td>
<td>0.4162 ± 0.018</td>
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<tr>
<td>0.4843 ± 0.0025</td>
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<td>0.396</td>
<td>1.617</td>
<td>1.6081 ± 0.0352</td>
<td>0.9879</td>
<td>0.9878 ± 0.0014</td>
</tr>
<tr>
<td>0.4832 ± 0.0028</td>
<td>5/5</td>
<td>0.396</td>
<td>2.2611</td>
<td>2.2721 ± 0.0440</td>
<td>0.9264</td>
<td>0.9279 ± 0.0016</td>
</tr>
<tr>
<td>Bulk Density $\rho_{\text{bulk}}$</td>
<td>Bonding energies, Site/Wall $\epsilon_{\text{site}}/kT$</td>
<td>Wall Site Density $N_{\text{wall}}/A$</td>
<td>Wall Density $p_{\text{wall}}/\Omega$</td>
<td>$z$</td>
<td>$\chi_{\text{wall}}$</td>
<td>$\chi_{\text{fluid}}$</td>
</tr>
<tr>
<td>---</td>
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<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>0.4844±0.0022</td>
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<td>1.503</td>
<td>1.475±0.0182</td>
<td>1.0</td>
<td>0.9984±0.0011</td>
</tr>
<tr>
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<td>1.773±0.0336</td>
<td>0.9753</td>
<td>0.974±0.0012</td>
</tr>
<tr>
<td>0.4819±0.0031</td>
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<td>0.396</td>
<td>3.5520</td>
<td>3.515±0.0854</td>
<td>0.8369</td>
<td>0.833±0.0030</td>
</tr>
<tr>
<td>0.4759±0.0028</td>
<td>0/7</td>
<td>0.396</td>
<td>7.9902</td>
<td>8.087±0.3104</td>
<td>0.4084</td>
<td>0.409±0.0210</td>
</tr>
<tr>
<td>0.4763±0.0034</td>
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<td>0.396</td>
<td>7.8081</td>
<td>8.473±0.2620</td>
<td>0.4167</td>
<td>0.414±0.0011</td>
</tr>
<tr>
<td>0.4779±0.0038</td>
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<td>0.396</td>
<td>6.9232</td>
<td>8.260±0.2523</td>
<td>0.4586</td>
<td>0.453±0.0036</td>
</tr>
<tr>
<td>0.4836±0.0041</td>
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<td>0.396</td>
<td>4.6154</td>
<td>6.997±0.3126</td>
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<tr>
<td>0.7125±0.0016</td>
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<td>0.52</td>
<td>7.3106</td>
<td>8.42±0.228</td>
<td>0.6659</td>
<td>0.666±0.0022</td>
</tr>
<tr>
<td>0.7130±0.0024</td>
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<td>0.52</td>
<td>5.896</td>
<td>7.1±0.316</td>
<td>0.7263</td>
<td>0.710±0.0087</td>
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<tr>
<td>0.7104±0.0019</td>
<td>5/7</td>
<td>0.52</td>
<td>12.338</td>
<td>16.07±0.794</td>
<td>0.2631</td>
<td>0.235±0.0340</td>
</tr>
<tr>
<td>0.4840±0.0022</td>
<td>3/3</td>
<td>0.396</td>
<td>1.663</td>
<td>1.7±0.037</td>
<td>0.9760</td>
<td>0.972±0.0014</td>
</tr>
<tr>
<td>0.4831±0.0019</td>
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<td>0.396</td>
<td>2.806</td>
<td>3.06±0.051</td>
<td>0.8625</td>
<td>0.860±0.0016</td>
</tr>
</tbody>
</table>
using \( \int_0^{\text{bulk}} (\rho(z)\sigma^3 - \rho(\text{bulk})\sigma^3) \, dz \), \( \rho(z)\sigma^3 \) is the singlet reduced number density and where \( \rho(\text{bulk})\sigma^3 \) is the reduced number density in the bulk region. For simulation, adsorption is calculated using \( (\rho_{\text{average}}\sigma^3 - \rho_{\text{bulk}}\sigma^3) \star h \), where \( h \) is half of the simulation cell length in \( z \) direction.

From table 9-1 and 9-2, we find that the \( \chi_{\text{wall}} \), the fraction of wall sites that are not bonded, calculated using (9-4) agrees remarkably well with simulation results at all combination of bonding energies and densities, and works well for one- and two-sited molecular fluids. Unlike the case for four site fluid, the presence of fluid-fluid bonding now poses direct competition to the number of sites on a fluid molecule available to bond with wall sites. For one-site fluid, molecules adsorped onto wall form a single molecular layer, but it does not exhibit Langmuir behavior, due to competition from fluid-fluid bonding.

Table 9-1 and 9-2 show that for both one- and two-site molecules, the bulk density generally goes up with fluid site bonding energy if the wall site energy stays the same. Hydrogen bonding between molecules forms dimers for one-site fluid and chains for two-site molecules, which prefer to stay in bulk to avoid entropy drop. This effect is more pronounced for chains than for dimers. When fluid-fluid bonding energy stays the same, but wall energy increases, fluid molecules are more attracted to the wall, and bulk density decreases. For the same wall site density, when both the wall and fluid site energies increase at the same rate, the wall contact density increases rapidly, and the bulk
density decreases. However, because of the large volume of the system, the change in bulk density due to wall bonding is small.

The total adsorption shows similar trend as bulk density. As fluid-fluid and fluid-wall bonding energies goes up at the same rate, total adsorption increases. This is in direct contract with the system of associating fluid near a hard wall [40], where as fluid energy goes up, bulk density goes up because cluster tends to pile up in the bulk, and total adsorption goes down. The effect of wall sites has changed the adsorption characteristics of the pore, and seem to overcome the decrease in entropy suffered by large clusters near the wall. It has for one extreme case changed the wall from desorption to adsorption by placing bonding sites on the hard wall. It is noted the total adsorption given by theory only compares favorably with simulation results at low wall bonding energy and low density. This may due to the fact that our theory does not accurately predict contact density at high wall site energy and high density, and it is the density near the wall, where inhomogeneity is most pronounced, that determines the total adsorption of the system.

Figure 9-1 to figure 9-10 compare theory against simulation results for reduced density versus distance from the wall at simulation average densities equal of 0.5 and 0.75. At each density, results are given at several wall/fluid bonding energies combinations. The plot at right gives a close up look at interfacial region for the same profile at the left. The DFT results for the region near the wall follows well with the simulation data, for medium density (0.5) and low to medium bonding
Figure 9.1: Density profiles as a function of distance from wall at simulation average density of 0.5. Reduced fluid and wall site energies are (a) 0.0/0.0, (b) 0.0/3.0, (c) 0.0/5.0, (d) 0.0/7.0, one site fluid.
Figure 9-2. Same as 9-1, with reduced fluid and wall site energies of (a) 0.0/7.0, (b) 3.0/7.0, one site fluid.
Figure 9.3. Same as 9.1 at simulation average density of 0.5, with fluid and wall site energies of (a) 5.0/7.0 (b) 7.0/7.0, one site fluid.
Figure 9-4. Same as 9-1 at simulation average density of 0.75, with fluid and wall site energies of (a) 0.0/7.0 (b) 3.0/7.0, one site fluid.
Figure 9-6. Density profiles as a function of distance from wall at simulation average density of 0.5. Reduced fluid and wall site energies are (a) 0.0/0.0, (b) 0.0/3.0, (c) 0.0/5.0, (d) 0.0/7.0, two site fluid.
Figure 9.7. Same as 9.4, with reduced fluid and wall site energies of (a) 0.0/7.0, (b) 3.0/7.0, two site fluid.
Figure 9-8. Same as 9-1 at simulation average density of 0.5, with fluid and wall site energies of (a) 5.0/7.0 (b) 7.0/7.0, two site fluid.
Figure 9-9. Same as 9-1 at simulation average density of 0.75, with fluid and wall site energies of (a) 0.0/7.0 (b) 3.0/7.0, two site fluid.
Figure 9.10. Same as 9.4, at simulation average density of 0.75, with fluid and wall site energies of 0.5, 0.7, 0.7, 0.7. Two site fluid.
Figure 9.11. Fraction of monomers as a function of distance from wall, at simulation average density of 0.5 and fluid and wall bonding energies of (a) 3.0/3.0, (b) 5.0/5.0, one site fluid.
Figure 9-12. Fraction of monomers as a function of distance from wall, at simulation average density of 0.5 and fluid and wall bonding energies of (a) 3.0/3.0, (b) 5.0/5.0, two site fluid.
Figure 9-13. Plot of $\ln((1-X_{\text{wall}})/X_{\text{wall}})$ versus reduced wall site energy. (a) 1 site model (b) 2 site model.
energies (3.0-5.0). The contact density from theory also matches well with simulation results, with error increases as fluid-fluid bonding energy increases. Figure 9-1 and 9-2 show the density profile for density of 0.50 and fixed fluid/fluid bonding energy of 3.0, wall site bonding energy goes from 0.0 (hard wall) to 7.0. The theory is in excellent agreement with simulation, except at wall site energy of 7.0, the theory gives lower contact density. This is similar to what we got in last chapter for only fluid wall bonding is allowed.

The rest of the figures of density profiles show similar trend as that for four site model in last chapter. Our theory seems to work remarkably well at low to medium density and low to medium bonding energy. Nonetheless, it works poorly at high bonding energy, especially when the fluid bonding is strong, and the theory overpredicts competition from fluid. One of the assumption we made in deriving our theory may have contributed to this under prediction of fluid density near the wall. When we calculate $\chi_{\text{wall}}$, we made use of the fact that $\chi_A$, the fraction of site A on fluid molecule that are unbonded, is dependent on orientation. However, when calculating $\chi_A$, we assume that it is independent of orientation. This is not true close to the wall. By assuming that $\chi_A$ is orientation independent, we have allowed all four sites on a molecule close to the wall to be available to bond to other molecules. This is in direct competition to bonding to wall sites. For high fluid-fluid bonding energy, the theory may over predict bonding in fluid near the wall, and thus over predicting fluid-fluid competition.
We plot in figure 9-11 and 9-12 the fraction of monomers versus distance from wall at the range of density and bonding energy where our theory works well. At density of 0.5, and fluid/wall bonding energy of 3.0/3.0 and 5.0/5.0, theoretical results compare remarkably well with simulation data, for both the region close to wall and bulk region. The theory slightly overpredicts the fraction of monomers in the bulk for bonding energies of 5.0/5.0, as found earlier [5] due in part to the different definition of a monomer in the theory and in the simulation. As in direct contrast to the case of associating hard spheres against a hard wall, where fraction of monomer near the wall is higher than in bulk, we see with the presence of wall sites, fraction of monomers are greatly reduced because of bonding between fluid and wall. The agreement within the wall bonding cutoff is excellent. This high accuracy of fraction of monomers between theory and simulation suggests that even with some discrepancy of wall contact density and density profile near the wall, and the theory misses some structural details, but still be accurate for fraction of monomers and thus free energy.

One of the features that is unique to two-site model, as shown in figure 9-8, is that at certain wall site energy, the peak amplitudes at $z = \sigma, 2\sigma$ are enhanced as fluid bonding energy increases. The peak at $z = \sigma$ at fluid bonding energy of 7.0 is almost twice as high as that for fluid bonding energy of 3.0. This feature was not observed for four-site model or one-site model. For two-site model, at high wall site energy, most wall sites are occupied. Molecules bonded to wall have to have one site oriented towards the wall. Due to site geometry of a two-site molecule, the remaining sites of these molecules are now oriented toward fluid, effectively making another "active wall" at $z = \sigma$, and
similarly at distance of multiple \( \sigma \) away from wall, albeit at less degree. As has been demonstrated, "active wall" tends to greatly enhance the contact density, thus enhancing peak amplitude for two site molecules. For one-site molecule, high wall coverage "creates" a hard wall at \( z = \sigma \), which pulls dimers away. For four-site molecule, because of the complex and large clusters formed in the system at high fluid bonding energy, it fails to show ordered enhancement for peak amplitude as what two-site molecule does. This enhancement of peak amplitude is also shown in 9-8, the fraction of monomers was reduced heavily at distances of \( \sigma, 2\sigma \) from wall, and is more so at higher fluid bonding energy. Again, our theory fails to pick up this feature. This may due the bulk nature of the method 2 that is used in this study. As shown in [10], the inhomogeneous form of Wertheim's theory for association seems to give better peak amplitude and position, albeit less accurate contact density at wall than bulk form of Wertheim's theory. It would be an interesting to see whether inhomogeneous form of Wertheim's theory could predict this unique properties of two site molecular fluid.

Finally, we show that one- and two-site molecules demonstrate Langmuir behavior when no fluid-fluid bonding presents, as in figure 9-13, and deviate from Langmuir behavior when fluid-fluid bonding competes with fluid/wall bonding. Multilayer adsorption no longer observe Langmuir isotherm, expect for four-site model, as shown in last chapter.

9.6 Conclusions
We continued our study of chapter 7 and 8 by extending our theory of associating fluids near active surfaces to dimerizing and chain-forming fluids. Our theory has shown good agreement with simulation data at low to medium density and low to medium bonding energy. We have shown that fluid/wall bonding dominates the adsorption characteristics of the confined system. Our theory is accurate in predicting wall coverage for a broad range of density and bonding energy, and fraction of monomers as a function of distance from wall, showing good behavior in estimating free energy of the system. However, our theory misses some fine structural features predicted by simulation, and tend to underpredict wall contact density at high bonding energy. Nonetheless, as a first step in constructing a density functional theory to describe the complex system of associating fluids near active wall, our theory has shown success in predicting thermodynamic properties at low to medium density and medium bonding energy. It can serve as a good reference system for studying more complex fluids confined by active walls.
Chapter 10  Summary and Future Work

In this work, we extended our Density Functional Theory to binary mixtures of hard spheres and associating fluids, and applied the mixture theory to non-additive hard spheres. We have accurately predicted phase separation, critical temperature and structural properties for this model. We were able to extend this theory to describe the properties of associating fluids near active surfaces.

In chapter 5, we studied a binary mixture of non-associating hard spheres and associating hard-spheres. Our theoretical results are in good agreement with simulation data. In chapter 6, we developed a density functional theory for non-additive hard sphere mixtures, and this theory correctly predicted phase separation and gave reasonable results for critical density and density profile for small non-additivity. In chapter 7, 8 and 9, we further extended our theory to describe the interaction between fluid and active walls, and studied fluids with one-, two-, four-bonding sites. We found that bonding energy, fluid density and fluid molecule’s geometric configuration have strong influence on interfacial phenomena. Comparison with simulation data showed good agreement for low to medium density and low to medium bonding energy cases.

Some immediate follow up work would include using different weighting function from that of Tarazona, such as Meister-Kroll weighting to test our DF theory, and applying our DF theory for wall sites to describe disjoining pressure and salvation force in a slit/pore system filled with liquids. There is also great need to improve the computer simulation algorithm. Also of importance is to apply our density functional
theory to industrial applications. Our theory is about 2 to 3 orders of magnitude faster than comparable computer simulation calculations, and should find readily applications in real-time systems.
References


6. (a) WERTHEIM, M. S., 1984, J. Statist. Phys., 35, 19; (b) ibid., 1984, 35,35; (c) ibid., 1986, 42, 459; (d) ibid., 1986, 42, 477


27. Rickayzen, G., Molec. Phys. 80, 1093.


42. Tarazona, P., 1985, Phys. Rev. A., 31, 2672; ibid, Erratum, 32, 3148


54. Ball, P. C, and Evans, R., 1988, Molec. Phys., 63, 159
75. Haymet, A. D. J., in [3].
78. Heffelfinger, G. S., Tan, Z., Gubbins, K. E., Marini, B. M. U., and van Sowl, F.,
1989, Molec. Simul., 2, 393.


