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Thermodynamic Modeling of Associating Fluids: Theory and Application

by

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ABSTRACT

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The association interaction plays a significant role in self-assembly and determining the properties of associating fluids. The patch-patch attraction in patchy colloids, and hydrogen bonding are two examples of association. Due to the strength, range, and directionality of association, an accurate theory including information at the level of the structure of self-assembling species is required for a precise prediction of the behavior of these fluids. Wertheim's thermodynamic perturbation theory, which uses density expansion method, has presented a promising performance in capturing the thermo-physical properties of both hydrogen bonding and patchy colloidal fluids through prediction of all possible states of the bonding of associating species. While most of the previous studies were focused on utilizing the first order limit of Wertheim's theory, recent simulation and theoretical studies have shown that the simplifying assumptions included in the first order make it not capable of modeling complex self-assembling species.

In this thesis, we develop Wertheim's theory beyond its first order to include accurate information about the structure of associating species like the size of association sites and their relative positions (in case of fluids with multiple sites), and possible self-assembled clusters of associated species. The theory developments are applied for both hydrogen bonding in molecular fluids and patchy colloids and verified with Monte Carlo simulations and previous experimental measurements results, where the agreements were excellent.

Beyond the introduction and conclusion chapters, the scope of this thesis can be summarized into the followings:

Chapter 2: the prediction of the self-assembly of a binary mixture of patchy colloids with two similar patches and small bond angle.

Chapter 3: modeling the effect of hydrogen bond cooperativity and bond angle dependent ring formation for associating hard spheres and Lennard Jones spheres. Applying the final equations to predict the thermodynamic properties of hydrogen fluoride.

Chapter 4: developing an asymmetric model for water including the effect of hydrogen bond cooperativity and multiple bonding at an association site.

Chapter 5: the extension of Wertheim's theory for fluids of patchy colloids with two divalent patches confined between two planar hard walls in a classical density functional theory formalism.

Chapter 6: investigating the effect steric hindrance for association between an associating fluid and a planar hard wall with discrete divalent active sites.

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Chapter 1

Introduction

1.1 Motivation

Prediction of fluid properties is significantly important in many industries. Production, separations, storage, and transmission processes in the chemical, petroleum, food, pharmaceutical, advanced materials, and other industries require knowledge of fluid properties and phase behavior. Calculating the thermo-physical properties of fluids is a primary application of statistical mechanics. For many decades researchers have attempted to propose mathematical models (equations of state) that can accurately predict the thermodynamic properties based on knowledge of molecular interactions, but to a limited success. The complex nature and broad diversity of the inter- and intra-molecular interactions are the main reason that achieving this goal has still remained as a challenge.

In statistical mechanics, non-ionic fluids are mainly described by five types of interactions: ideal gas [16], short range repulsion, long range dispersion, multipolar, and hydrogen bonding. Depending on the characteristics of the molecules, only some of these interactions might be significant. Van der Waals' [17] equation of state (EOS) was one of the first models that included some of the physical characteristics of the molecules into its final equation. In his model the interactions between two molecules is divided into two separate parts: a short range repulsion that corresponds to the rigid core of the molecule followed by a long range attraction. Following this approach other models like Peng-Robinson [18] and Soave-Redlich-Kwong [19], which are known as Cubic EOS's, were developed that found extensive industrial applications. Despite their simplicities, the incapabilities shown by Cubic equations in modeling complex fluids left the field open for more accurate theories such as thermodynamic perturbation theories, mainly developed for liquids, which are based on the similar idea of separating the interactions into short and long range [16]. Barker and Henderson (BH) [20, 21] developed a successful second order perturbation theory for Lennard-Jones (LJ) liquids by choosing a hard sphere reference fluid, and later it was followed by Weeks, Chandler, and Anderson (WCA) [22, 23] with the choice of an effective hard sphere diameter. In addition to LJ liquids, perturbation theories were extended for multipolar fluids. Good examples are the models developed by Pople [24], Barker [25], Gubbins and Gray [26] that predict the properties of weak polar spherical molecules with good accuracy.

The last and the strongest interaction among these five types is the hydrogen bonding which is considered responsible for anomalous properties of fluids such as water [27] and hydrogen fluoride [28]. Hydrogen bonds are short range directional attractions which in statistical mechanics are considered as association. The complex nature of this interaction makes it very hard to be mathematically modeled and that's why it attracted the attention of researchers for many decades. The attempt to model association was started by chemical equilibrium theories in which the formation of hydrogen bonds is described as a chemical reaction and the characteristics of the bonds are lumped and presented by the equilibrium constant [29, 30]. Chemical equilibrium approaches were incorporated into equations of states such as Van der Waals [31], perturbed anisotropic chain theory [32], and the Sanchez-Lacombe [33]. Lattice theories were another approach proposed to model hydrogen bonding that follow Veystman [34] method and were even applied to model hydrogen bond cooperativity [35] and intera-molecular hydrogen bonding [36]. The simplistic assumptions in both approaches make them incapable of handling the complications in hydrogen bonding thus causing inaccuracy in final predictions of the theories.

Unlike the other methods, cluster expansion theories, first introduced by Mayer [37], had the potential of extensions toward including a detailed description of association interactions [38, 39, 40]. Among all cluster expansion methods for modeling association there are two significant works: Anderson [41, 42] and Wertheim [43, 44, 45, 46]. And erson used renormalization and cancellation theorem in order to derive a convergent theory, and Wertheim developed his theory using multiple densities. While both methods have similarities, Wertheim's theory is simpler to develop for complex systems. Soon after it was developed, Wertheim's multi-density approach [45, 46] received lots of attention from researchers in statistical mechanics. In the limit of complete association, Chapman developed his statistical associating fluid theory equation of state [47] based on Wertheim's first order perturbation theory that could account for molecular size and shape as well as multiple hydrogen bonding sites. Further, not only could bulk fluid properties be described, but the behavior of associating polymeric fluids at hydrophobic and hydrophilic interfaces could be modeled by use of classical density functional theory [48]. Over a period of less than 15 years, the field completely changed from being able to model bulk thermodynamic properties of spherical, slightly polar molecules to predicting the bulk, interfacial, and confined fluid properties [49, 48] and self-assembly of branched polymers [50, 51] made of linear and cyclic structures in associating polyatomic solvents [52, 53].

Despite all the applicabilities that Wertheim's first order thermodynamic perturbation theory (TPT1) has shown in modeling polyatomic and associating fluids, there are simplifying assumptions that recent studies have found important to be relaxed in order to accurately capture the properties of complex fluids. Here we briefly explain some these assumptions: Wertheim's theory limits each association site to form only one bond and any additional possible bonds is rejected due to steric hindrance effect. In this theory every bond is assigned with the same energy and there is no considerations for effects like bond cooperativity. Also, with any number of association sites and geometry, associating species can only form linear and branched (open) clusters, while the formation of closed loop structures is not predicted.

Extensions beyond Wertheim's TPT by removing such restrictions and developing a theory applicable for complex hydrogen boning fluids and colloidal systems in homogeneous systems or close to the interfaces is the main motivation for this thesis. In next sections of this chapter, each of these limitations and the importance of their removal is explained in detail.

1.2 Association Interactions

Association is defined as a short range directional attractive interaction between fluid species which reduces the energy of the system by a certain amount. By short range it means there exists a maximum distance (between two species centers) beyond which association does not happen. In addition to distance, associating species, which are normally modeled as spheres, must orient in such a way that their association sites, which are the sources of attraction, are not separated by more than a critical angle, which explains the directionality of this interaction.

Associating fluid species are normally be considered as spheres with diameter d, and conical associating sites on their surfaces. The association potential of interaction for a fluid with an association site A is written by a square well potential as:

$$\phi_{AB}(12) = \begin{cases} -\varepsilon_{AA}, & r_{12} \le r_c, \ \theta_{A(1)} \le \beta_c, \ \theta_{A(2)} \le \beta_c \\ 0, & otherwise \end{cases}$$
(1.1)

Figure 1.1 depicts the association between two spheres of this fluid where the notation $(i) = \{\overrightarrow{r_i}, \Omega_i\}$ represents the vectors of position $\overrightarrow{r_i}$ and orientation Ω_i of the sphere at i. r_{12} is the distance between the centers of species 1 and 2, and r_c is the critical distance between the centers of two species beyond which they cannot associate. $\theta_{A(1)}$ is the angle between r_{12} and the vector which connects the center of the sphere at (1) to the center of its associating site A ($\theta_{A(2)}$ is defined in a similar way). β_c is the maximum value for $\theta_{A(1)}$ and $\theta_{A(2)}$ at which association can occur. Once the association bond forms the energy of the system reduces by ε_{AA} .

Many researchers attempted to propose a mathematical model for association interactions and among them Wertheim [43, 44, 45, 46] developed a thermodynamic perturbation theory using density expansion that can accurately predict thermo-physical properties of an associating fluid. Using Wertheims framework one can model fluids with any number of association sites. Wertheim obtained the Helmholtz free energy due to association using density expansion method where the total density of a fluid is defined as the sum of density factors that describe all possible state of bondings of associating species. Each density factor is an infinite sum over all possible irreducible graphs of species connected by Mayer f-functions. For further details on Wertheim's density expansion the reader is encouraged to study Marshall's paper which explains thermodynamic perturbation theory of association beyond its first order [54], and Wertheim's papers [43, 44, 45, 46].

In Wertheim's density expansion, two types of density factors are used. In one form the total density of the fluid is the sum of monomer density (density of species



Figure 1.1 : A scheme view of a pair of associating species. r_{12} is the distance between spheres at 1 and 2, $\theta_{A(i)}$ is the angle between r_{12} and the vector connecting the center of the sphere at i to its association site A.

that are not bonded) and density of bonded species. In the other form the total density is the sum of monomer density and the densities that exactly describe which association site or set of sites are bonded. The former type is called two-density formalism and the latter one called multi-density formalism. Wertheim used the twodensity method for fluids with one association site and multi-density approach for fluids with more than one association site. In the following section the features and the scopes of applicability of each formalism are introduced.

1.3 Multi-density and Two-density formalism

An associating fluid with any number of association sites can be modeled by Wertheim's thermodynamic perturbation theory using multi-density approach. In this approach the Helmholtz free energy due to association (A^{assoc}) is a function of density and temperature of the system. The effect of temperature is embedded into Mayer *f*-function, and the density effect is presented using total ρ , monomer ρ_o and site densities $\sigma_{\Gamma-\alpha}$

(Γ is the set of all association sites on a species and α is a subset of Γ). The site densities describe the state of the bonding of the species at that specific set of sites. The bonding happens once a pair of species are appropriately (as explained in the previous section) positioned and oriented with respect to each other, and they have their required bonding sites available (not bonded). This situation is mathematically presented in Wertheim's TPT1. TPT1 only focuses on availability of a pair of species, which corresponds to the availability of a pair of association sites on them. Therefore, if we limit the theory to only its first order (which mainly specifies formation of a dimer), for a fluid with more than one site, any linear or branched structure can be formed as reducible graphs because only dimer bonds exist in those graphs. This makes the theory very powerful because using the simplest form (TPT1), a wide range of structural formations can be predicted in an associating fluid. Chapman developed his statistical associating fluid theory (SAFT) [47] based on Wertheims TPT1 in a multi-density formalism framework. This formalism gives the capability to SAFT to model a fluid with any number of associating sites, which makes it capable for a broad range of fluids and applications. Within TPT1 frame, first a dimer forms directly by a first order irreducible graph; then if the fluid has more than one association site, the un-bonded sites on different species can form similar bonds. To elaborate more on what we mean by these explanations on density factors and TPT1, relevant equations are mentioned briefly. According to Wertheim the Helmholtz free energy due to association is written as:

$$\frac{A^{assoc}}{Vk_BT} = \rho \ln\left(\frac{\rho_o}{\rho}\right) + \rho + Q - \frac{\Delta c^{(o)}}{V}$$
(1.2)

where ρ is the total number density, ρ_o is the number density of monomers, k_B is the Boltzmann constant, T is the temperature and V is the volume of the system. The term Q is defined as:

$$Q = -\sigma_{\Gamma} + \sum_{\alpha \subset \Gamma} \sigma_{\Gamma-\alpha} c_{\alpha}$$
(1.3)
$$\alpha \neq 0$$

where Γ is the set of all types of association sites on a species. The density parameter σ_{α} is defined as:

$$\sigma_{\alpha} = \sum_{\gamma \subset \alpha} \rho_{\gamma} \tag{1.4}$$

where ρ_{γ} is the density of a segment that is bonded at all sites included in the set γ , the improper set of ρ_o is included in this sum, and c_{α} by Wertheim is defined as

$$c_{\alpha} = \frac{\partial \Delta c^{(o)} / V}{\partial \sigma_{\Gamma - \alpha}} \tag{1.5}$$

 $\Delta c^{(o)}$ is the sum of all irreducible graphs with a single path of association Mayer f-function bonds between each pair of bonded species. The first order limit (TPT1) of this infinite sum which corresponds to a single bond between two association sites labeled as A and B of two separate species is:

$$\Delta c^{(o)} = \int \sigma_{\Gamma-A}(1)\sigma_{\Gamma-B}(2)f_{AB}(12)g_R(12)d(1)d(2)$$
(1.6)

The graph in figure 1.2 represents equation 1.6.

In equation 1.6, $\sigma_{\Gamma-A}$ is the density of associating species with site A not bonded $(\sigma_{\Gamma-B} \text{ is defined similarly})$, $g_R(12)$ is the correlation function of the reference fluid, $f_{AB}(12) = exp(-\phi_{AB}(12)/k_BT) - 1$ is the Mayer *f*-function of association, and $d(1) = \{d\vec{r_1}, d\Omega_1\}$ is the position and orientation vector of particle 1 (*d*(2) is defined similarly). According to equation 1.3; in order to form a bond, only availability of a pair of A and B sites is required, regardless of the states of bonding of other sites on the species. For the case of an associating fluid with two association sites the form of the reducible graph presenting a linear chain is presented in figure 1.3.



Figure 1.2 : A graphical representation of TPT1 in multi-density formalism. The solid line and dash line represent the Mayer *f*-function $(f_{AB}(12))$ and exponential of reference fluid potential of interaction $e_R(12) = exp(-\phi_{AB}(12)/k_BT)$, respectively. A and B represent the association sites of the species at (1) and (2) which are bonding through f_{AB} .



Figure 1.3 : A reducible graph of a linear chain of associated species, where each adjacent pair of species are connected by a Mayer f-function and exponential of reference fluid potential of interaction.

Unlike multi-density, in two-density formalism framework, density factors describe only whether species are bonded or not, and no reducible graph can be formed. Because according to its graph presentation; any species that wants to join a graph/ or any graph that wants to form, could only form through connecting monomer species. In a physical sense it means all members of an associated cluster must be monomers before joining that cluster. Here two-density formalism in TPT1 limit is shown in order to bring a comparison with the equations mentioned earlier in this section. According to Wertheim, in a two-density formalism A^{assoc} is written as:

$$\frac{A^{assoc}}{Vk_BT} = \rho ln \frac{\rho_o}{\rho} - \rho_o + \rho - \frac{\Delta c^{(o)}}{V}$$
(1.7)

The first order contribution from association between sites A and B of species at (1)



Figure 1.4 : A graphical representation of TPT1 association in two-density formalism. The solid line and dash line represent the Mayer f-function and exponential of reference fluid potential, respectively.

and (2) is written as:

$$\Delta c^{(o)} = \int \rho_o(1)\rho_o(2)f_{AB}(12)g_R(12)d(1)d(2)$$
(1.8)

which corresponds to the graph in figure 1.4.

While building the associated clusters from dimers (TPT1) is considered as an advantage of multi-density formalism (to build reducible graphs of linear and branched structures), it makes any extension beyond first order (TPT1) complicated. Because building anything except rings will involve a double counting of irreducible graphs over reducible graphs of the lower orders. For this reason, Wertheim proposed a re-summation approach that keeps track of replacing reducible graphs by irreducible ones at any order of TPT. This approach adds complications to the theory since it requires an add-and-subtract procedure that includes correlation functions of the size of any order which is involved in the re-summation, while except two-body and three-body correlation functions in first and second order TPT, usually higher order correlation functions will still exist, there is no need for re-summation when a twodensity formalism is used in beyond TPT1. Since no reducible graph is built in this framework, two-density formalism is considered as a more transparent and straight forward approach compared with multi-density formalism for beyond TPT1 develop-



Figure 1.5 : A scheme of bond angle (α_{AB}) , and critical angle of the sites (β_c) for a fluid with two association sites, labeled as A and B.

ments. Two-density formalism for fluids with two association sites and its application for a binary mixture of patchy colloid with small bond angle, and the effect of ring formation and hydrogen bond cooperativity in hydrogen fluoride is studied in this thesis. The rest of the chapter introduces each topic studied in chapters of the thesis.

1.4 Binary Mixture of Patchy Colloids

In chapter 2, modeling of a binary mixture of patchy colloids is studied. The patchpatch interaction in patchy colloidal fluids is a short range directional attraction which is considered as association. These colloids are synthesized through glancing angle deposition [55, 56], polymer swelling methods [57], and stamping DNA to their surfaces [58] etc.. During the synthesis process, the shape, size and the number of patches are all under control, and depending on the design, these colloids can self-assemble to various types of clusters (linear, branched chains, and closed loop structures) [59] which provides them the opportunity to be used for a wide range of applications in microelectronics [60], self-healing materials [61], solar panels [62], empty liquid [63], etc.. Wertheims TPT1 is the primary theory for modeling the thermo-physical properties and phase behavior of these colloidal fluids. Depending on the architecture of the colloid (e.g. patch size and shape, and relative position of the patches) the fluid shows different physical properties. The simplifying assumptions in TPT1 makes it not accurate for every architecture and design of these colloids. For example, a patch can be large enough to bond with more than one colloid, or the positions of the patches on one colloid can be very close that bonding at one patch limits the available space of bonding for another patch (the relative position of the patches can be indicated by bond angle which is the angle between the vectors connecting the center of the colloid to the center of the patches and it is illustrated in Figure 1.5). This makes the need for a theory that includes more information of patches obvious.

In higher orders of Wertheim TPT there is the potential for including more information on associating species because the contributions to association can be based on any number of associating species participating in a cluster. Marshall [54] and Kalyuzhni [64] were the first among the researchers who used higher order Wertheim TPT to develop thermodynamic models for various designs of patchy colloids. Marshall extended the theory to capture the effect of bond angle [14], formation of cyclic structures, and multiple bonding per patch[65]. Marshalls theory on bond angle (which is a re-summation in multi-density formalism framework) is very robust, and the final equation reduces to TPT1 for very large bond angles. However his theory can only be applied to pure fluids. For the case of a mixture of associating fluids, where the bond angle is important, a new theory needs to be developed since using multidensity formalism requires re-summation which will be inefficient and complicated. In such systems, going to higher orders of TPT will be more feasible in two-density formalism because no re-summation is required, and all possible clusters of associated species are presented in the theory as irreducible graphs.

In this thesis, a thermodynamic perturbation theory is developed in a two density formalism framework for a binary mixture of associating fluids with two identical association sites. We study the situation where the sites are small enough that they saturate after formation of one bond, and the bond angle is small enough that formation of one bond at a site affects the available space for bonding at the other site.

1.5 Hydrogen Bond Cooperativity and Application

In chapter 3 modeling of cooperative hydrogen bonding is studied. In TPT1, and correspondingly SAFT equation of state, every bond reduces the energy of the system by a constant amount regardless of the state of the bonding of other sites on a molecule. Also, as mentioned in the previous section, in a single chain of associated species, those who are not bonded, are not correlated. Using these simplifications SAFT has shown a good record of applicability for various systems. However, quantum studies have revealed that in some hydrogen bonding fluids (e.g. hydrogen fluoride), formation of more than one hydrogen bond at each species can cause an electron delocalization, and that makes the energy of the hydrogen bonds dependent on the number of the bonds formed by the species [28]. Therefore, the hydrogen bonding energy of associated hydrogen fluoride molecules in a cyclic cluster is different than their bonding energy in a dimer. According to this study [28], in hydrogen fluoride, the energy of a



Figure 1.6 : Bond cooperativity for a fluid with two association sites. $\varepsilon^{(HB1)}$ and $\varepsilon^{(HB2)}$ represent hydrogen boding energies that due to cooperativity effect can be different

dimer bond is weaker than other structures. This effect makes the molecules to form two bonds and reduce the energy of the system, and in the low density states , like vapor phase, ring formation dominates over linear structures. In a previous study by Galindo et al. [6] SAFT-VR EOS accompanied by ring formation contribution in the Helmholtz free energy was used to model hydrogen fluoride. However the results on the densities of liquid and vapor phase, and enthalpy of vaporization were not in a good agreement with experimental data. In their work, no geometry constraint was considered for ring formation.

Marshall [1] used an intuitive approach, which requires re-summation over the Mayer f-functions in a multi-density formalism, to distinguish between the energy of the first bond in a linear chain, and the rest of the bonds in the same chain, and rings (illustrated in Figure 1.6). Here we develop a thermodynamic perturbation theory in a two-density formalism framework, since its extension for mixtures is more convenient, that includes the effects of bond angle, hydrogen bond cooperativity,

and ring formation similar to Marshall's model [66], and show its application for calculating thermodynamic properties of hydrogen fluoride.

1.6 Mixture of Divalent and Monovalent Association Sites

In chapter 4, a model for mixtures of divalent and monovalent association sites is proposed. Marshall [65] was the first who extended Wertheim's TPT beyond first order to include the formation of two bonds at a single association site, relaxing a restriction by Wertheim due to steric hindrance. The density factors used to describe the species with multi-valent association sites in the corresponding graph is not different than the one used for a species with monovalent sites. The density factors just describe if a site is bonded or not, so bond formation can only happen when a site is not bonded at all. Therefore, reducible graphs cannot be built from an already bonded site. In this development every bond to the multivalent site is introduced with a specific Mayer *f*-function which can be similar or receive different values. Such associated cluster gives a flexibility to the bond formation at the multivalent site to form between one and any possible number of bonds that can be affected and controlled by temperature and density of the system.

While the primary application of such theory is considered for patchy colloidal fluids, the theory can be used for molecules with hydrogen bond acceptor atoms that have more than one lone pairs of electrons; for example two lone pairs of electrons on an oxygen atom of a water molecule can be considered as two association sites which are very close to each other and modeled as a single divalent site. The anomalous behavior of water such as the maximum in saturated liquid density at $4^{\circ}C$ [10], and the minimum in solubility of alkanes in water [67] which might be caused by the hydrophobic effect of water on alkanes, have attracted the attention of researchers in statistical mechanics to develop an equation of state which can accurately capture these phenomena. Previous SAFT studies [11] suggested that hydrogen bond cooperativity and cyclic cluster formation might be the key elements to be considered in water model (SAFT does not include any information about these effects). It was also shown by Kumar and Skinner [68] that hydrogen bonding energy between water molecules is dependent on their state of bonding, for example if a water molecule is a double acceptor there can be negative cooperativity effect and the energy of the bonding is less than the case where it is an acceptor and a donor at the same time that is called positive coperativity. Marshall [27] developed a second order TPT to include hydrogen bond cooperativity for the case where a water molecule is a donor and a acceptor, at the same time, he showed a positive cooperativity. In this thesis we incorporate bond cooperativity only for oxygen atom which corresponds to the state where a water molecule is a double acceptor. We consider this as a step forward to capture the anomalous behavior of water. A scheme view of what we refer to as a water model with a mixture of divalent and monovalent association sites is presented in figure 1.7.

1.7 Fluids in Confinement

In chapter 5 a confined fluid with two divalent association sites is studied. Chapman [7] proposed a density functional theory (DFT) framework to extend Wertheim's TPT1 to inhomogeneous fluids. To describe hard spheres with multiple association sites, the hard sphere contribution to the Helmholtz free energy is calculated either by Rosenfeld's Fundamental Measure Theory (FMT) [69], or Tarazona's weighted density approach [70]. Segura et al. [48] considered two different approaches to the association free energy functional. In the first method, the free energy functional



Figure 1.7 : Mixture of divalent and monovalent sites which is indicated by two bonds formed from small sites to the large site.

is derived within TPT1. In the second approach, the homogeneous form of TPT1 is used for inhomogeneous fluids using weighted densities. Both methods have presented promising results in DFT applications [48, 71, 72, 73, 74]. In addition to associating spherical molecules, both forms of the DFT proposed by Segura, et al. have been extended to model polymers and associating polyatomic molecules [48, 71, 73, 75, 76, 77, 78, 79, 80]. The works by Tripathi and Chapman [74, 76, 49] and Bymaster and Chapman [72] have shown the extensive application of the DFT in studying interfacial phenomena and phase behavior of associating polyatomic fluids in confined systems or close to interfaces. Further, using weighted densities or FMT with the bulk association free energy has found application for associating molecules in a variety of publications by Segura and Chapman [48, 81, 82, 83], Sokolowski et al. [84, 85, 86, 87, 88, 89, 90, 91, 92, 93, 94], Wu et al. [71, 80, 95].

Marshall introduced the concept of divalent association sites for both single site fluids in bulk [65] and close to the interfaces [96]. However, the behavior of a fluid with more than one divalent associating site becomes interesting since it will form a combination of linear, branched, and cyclic structures. Specifically in the systems of patchy colloids, having more than one site is very common and in the case of divalent sites it can even lead to formation of Kagome lattice [97]. Furthermore, confinement affects fluids'behavior which is accurately captured by a density functional theory formalism through proper modeling of the confinement as an external field. The interesting aspect of such systems is that hard sphere fluids species usually aggregate at a rigid surface, and it is called wetting effect. However, when association exists, packing at the surface is affected by formation of bonds between fluid species that leads to formation of large clusters of associated species, and packing them toward the hard wall restricts their formation; therefore, the situation is considered as a



Figure 1.8 : A scheme of an association fluid species confined between two parallel infinite hard walls.

competition between minimizing the energy of the system (bond formation) and aggregation at the surface. Normally when association gets stronger, species are moved away from the surface. Observing the behavior of the associating fluids when they are confined between two parallel hard walls, and walls are few orders of associating species diameter separated from each other is very interesting, since the formation of clusters will be controlled by minimizing the energy of the system and aggregation at the surface. Figure 1.8 shows a picture of associating colloids confined between two parallel hard walls.

In chapter 5, we extend Wertheims TPT for a patchy colloidal system with two divalent patches. The theory is developed in a density functional form to predict the fluid behavior between two planar rigid walls. Marshall and Chapman [65] developed
the theory for confined colloids with a single association site that could form two bonds; our work extends this model to allow two divalent sites. The association model allowing multiple bonds leads to a competition between chains and rings.

1.8 Wall-Fluid Association

In chapter 6 the effect association between fluid species and wall discrete active sites is studied. Due to the importance of adsorption phenomena in many industrial applications, describing the distribution of molecules at heterogeneous surfaces has been a long standing challenge. Chmiel et al modeled a Lennard Jones fluid near a wall with adsorbing strips by Tarazona DFT [98, 99, 100]. Tripathi [49, 101] developed a DFT to model associating fluids near to a rigid functionalized surface with discrete association sites. In addition to the theoretical studies, similar systems were investigated by molecular simulation methods. Muller et al performed MC simulation for adsorption of water over activated carbons [102, 103, 104].Lee and Rossky [105] investigated the structure and dynamics of water on hydrophobic and hydrophilic solid surfaces.

Previous studies modeled fluid-wall association for the case where there are discrete sites on the surface forming a single bond with fluid species [49]. The sites were assumed to be separate enough that bonding at one active site does not affect other sites. However, one question remains; how about the case where surface sites are close to each-other that bonding at one affects the available space for bonding at the other sites. The model for divalent association sites developed by Marshall [65] can be used for active sites on a surface where a site can form two bonds simultaneously. This can be easily shown for the case where the active group on the surface has two bond formation capacity. Using this approach the effect of steric hindrance and geometry is applied for wall association for the first time. The application of



Figure 1.9 : An exhibition of an association fluid with one association site close to a rigid surface with discrete divalent association sites.

such theory can be for wall with active sites of hydroxyl groups, carbon active and graphite. A representation of the system is depicted in figure 1.9.

In chapter 6, we extend Wertheim's TPT to model an associating fluid with a monovalent site near to a hard planar surface which is functionalized with discrete association sites. A DFT is developed, and the fluid behavior close to the wall is studied under different conditions of density, and temperature. Tripathi [49] developed his DFT model for fluids interacting with wall association sites that could form only one bond; however, in our work the wall sites are large enough that two bonds can form. Such theory can be applied for modeling the adsorption of molecular fluids on a rigid surface with divalent active sites, and association of patchy colloids to rigid surfaces with large patches.

Chapter 2

Modeling A Binary Mixture of Two-Associating Site Fluids with A Small Bond Angle Using A Two-Density Formalism

2.1 Introduction

The challenge of modeling a highly directional attraction interaction, called association, was solved when Wertheim developed his thermodynamic perturbation theory (TPT) using a density expansion methodology for fluid with single or multiple association sites [43, 44, 45, 46, 106]. He used a two-density formalism approach to model single site fluids [43, 44] where the mass action equation is composed of densities of bonded and non-bonded segments, and for fluids with more than one association site he extended his theory to a multi-density formalism[45, 46] in which the densities are defined based on the state of the bonding of association sites. One example of association interactions is hydrogen bonding, and Chapman *et al.* [107] was the first who applied the first order Wertheim's TPT (TPT1) for fluids with any number of hydrogen bonding sites, and also modeled associating polyatomic molecules with his statistical associating fluid theory (SAFT) [107, 47, 108, 109]. SAFT predicts the thermodynamic properties and phase behavior of a broad range of mixtures of polyatomic and associating molecules with great precision [110, 111, 8, 9, 112, 113, 114, 115, 116, 117, 118, 119, 120, 121].

The patch-patch attraction in patchy colloidal fluids, similar to hydrogen bonding,

are modeled using Wertheim's TPT. These colloids are synthesized through glancing angle deposition [97, 55, 56], polymer swelling methods[57], and stamping DNA to their surfaces[58] etc.. During the synthesis process, the shape, size and the number of patches are all under control, and depending on the design, these colloids can self-assemble to various types of clusters (linear, branched chains, and closed loop structures)[59] which provides them the opportunity to be used for a wide range of applications in microelectronics[60], photonics[122], self-healing materials[61], solar panels[62], empty liquid[63], etc.. The primitive square well potential model proposed by Bol[123] was applied by Kern and Frankel[124] to model association between patchy particles. A good theory can turn such potential model into a predictive tool to predict system behavior, and accurately guide design processes.

The simplifications incorporated into Wertheim's TPT1, like no effect of steric hindrance between sites on a species, monovalent association sites, no bond cooperativity effect, etc. spawned an incentive for researchers to extend Wertheim's TPT beyond its first order to obtain a higher accuracy and more information about fluid's behavior. Sear and Jackson, Marshall and Chapman, Kalyuzhnyi *et al.*, and Ghonasgi *et al.* included formation of more than one bond at a site[96, 125, 15, 126, 127, 128, 129, 65], effect of bond angle[14, 130, 66], formation of cyclic structures [14, 130, 66, 131, 132], intermolecular association[133, 134, 135], and cooperative hydrogen bonding into the theory[66, 136, 137]. So far, all the theoretical works on bond angle dependency is limited to pure fluids, and extending the work to mixtures is an interesting problem which is the topic of the current work. Wang *et al.*[57] synthesized copolymer blocks using a binary mixture of two-patch colloidal particles. While in their work the patches were at a bond angle of 180 degrees relative to each other, an interesting question is what will happen if there is a small bond angle between the sites of a



Figure 2.1 : Schematic view of an associating species in the fluid; the sites are similar and no restriction is imposed on the association between sites.

colloid[57], and what type of structures will be formed. The answer to this question will be explained using the theory developed in this chapter.

In this manuscript, we develop an equation of state for a binary mixture of two fluids with two identical associating sites that have a small bond angle between their sites. We consider that the bond angle is similar for both types of species, and the sites are small enough that be considered saturated after forming one bond. We use a two-density formalism approach, and we include the chain and ring formation into the theory.

2.2 Theory

In this section, we develop an equation of state for a binary mixture of patchy colloids with two association sites. We consider two types of species (1 and 2), each type has two identical association sites, which are labeled as A_1 and A_2 for type 1, as depicted in Figure 1, B_1 and B_2 for type 2. For simplicity of notation, each colloid is assumed to have the same diameter d and it is set to 1.0. The angle between the vectors connecting the center of a colloid to the centers of the patches is α as presented in Figure 2.1. While the potential of interaction between similar species is given by the hard sphere potential $(\varphi^{(11)}(12) = \varphi^{(22)}(12) = \varphi_{HS}(r_{12}))$, the pair potential between two colloids of types 1 and 2 is written as

$$\varphi^{(12)}(12) = \varphi_{HS}(r_{12}) + \varphi^{(12)}_{assoc}(12)$$
(2.1)

We assume that a colloid of type 1 is at (1), and 2 at (2) where the notation $(1) = (\overrightarrow{r_1}, \Omega_1)$ represents the vectors of position $\overrightarrow{r_1}$ and orientation Ω_1 of species 1, and r_{12} is the distance between the centers of colloids 1 and 2. Bol[123] was the first who introduced a square well potential for modeling hydrogen bonding, and later Chapman *et al.*[107] re-developed and widely applied the potential due to its computational simplicity in molecular simulation and in SAFT. Kern and Frenkel[124] were the first to apply the potential to model the association interactions between patchy colloids. The potential of interaction for association between species 1 and 2 is given as

$$\varphi_{assoc}^{(12)}\left(12\right) = \sum_{A \in \Gamma(1)} \sum_{B \in \Gamma(2)} \varphi_{AB}\left(12\right)$$
(2.2)

where $\Gamma(1) = \{A_1, A_2\}$ is the set of association sites on colloid type 1 ($\Gamma(2)$) is defined in similar way), and the site-site association interaction is defined as:

$$\varphi_{AB}(12) = \begin{cases} -\varepsilon_{AB} & r_{12} < r_c, \ \theta_{A(1)} < \beta_c \ , \ \theta_{B(2)} < \beta_c \\ 0 & otherwise \end{cases}$$
(2.3)

 r_c is the critical distance between the centers of two patchy colloids beyond which they cannot associate. $\theta_{A(1)}$ is the angle between r_{12} and the vector from the center of colloid type 1 at (1) to its associating site A, which is A_1 or A_2 ($\theta_{B(2)}$) is defined in a similar way). β_c is the maximum value for θ_A and θ_B at which association can occur. According to equation 2.3 if two colloids are at the proper distance and orientation relative to each other, they will associate and the energy of the system will decrease



Figure 2.2 : Schematic view of the potential of interaction between two unlike fluid species.

by ε_{AB} . Figure 2.2 exhibits the potential of interaction between two unlike species, and figure 2.1 shows a pair of associated colloids. In this work association is limited to occur only between unlike species. To ensure that a site is not forming more than one bond, the angular and radial cutoffs for an association site are set to $\beta_c = 27^{\circ}$ and $r_c = 1.1$. Writing Wertheim's thermodynamic perturbation theory [43, 44, 45, 46] in a two-density formalism, the Helmholtz free energy due to association for a mixture is obtained as

$$\frac{A - A^{HS}}{Vk_BT} = \sum_{k} \left(\rho^{(k)} ln \frac{\rho_o^{(k)}}{\rho^{(k)}} - \rho_o^{(k)} + \rho^{(k)} \right) - \frac{\Delta c^{(o)}}{V}$$
(2.4)

where A is the total Helmholtz free energy, A^{HS} is the Helmholtz free energy of the hard sphere reference fluid. V is the total volume, k_B is the Boltzmann constant, T is the temperature, $\rho^{(k)}$ is the density of species k, and $\rho_o^{(k)}$ is the monomer density of species k. The term $\Delta c^{(o)}$ is the association contribution to the fundamental graph sum $c^{(o)}$ encoding intermolecular interactions, and it includes two major contributions



Figure 2.3 : Schematic view of the simplest chain contributions in $\Delta c^{(o)}$. **a**)first order dimer $\Delta c^{(1)}_{AB}$; **b**)second order chain $\Delta c^{(2)}_{BAB}$; **c**)second order chain $\Delta c^{(2)}_{ABA}$.

for chain and ring formation:

$$\Delta c^{(o)} = \Delta c_{chain} + \Delta c_{ring} \tag{2.5}$$

In equation 2.5, Δc_{ring} is the contribution from formation of rings of associated colloids, and Δc_{chain} represents the contribution from the formation of chains of bonded colloids. According to the constraint that similar species cannot form a bond, there are three possible ways of chain formation that must be considered into the graph sum $\Delta c^{(o)}$:

$$\Delta c_{chain} = \Delta c_{ABA} + \Delta c_{BAB} + \Delta c_{AB} \tag{2.6}$$

where the term Δc_{ABA} stands for the chains of any size that have colloid type 1 at each end, Δc_{BAB} accounts for the chains with type 2 at each end, and the chains with unlike species at each end are represented by Δc_{BA} . Here, to show our methodology in writing Δc_{chain} , we present the contributions for the shortest chains of each kind (diagrams of these chains are exhibited in Figure 2).

$$\Delta c_{ABA}^{(2)} = \frac{1}{2} \int \rho_o^{(1)}(1) \,\rho_o^{(2)}(2) \,\rho_o^{(1)}(3) \,f_{assoc}(12) \,f_{assoc}(23) \,g_{HS}(123) \,d(1) \,d(2) \,d(3)$$
(2.7)

$$\Delta c_{BAB}^{(2)} = \frac{1}{2} \int \rho_o^{(2)}(1) \,\rho_o^{(1)}(2) \,\rho_o^{(2)}(3) \,f_{assoc}(12) \,f_{assoc}(23) \,g_{HS}(123) \,d(1) \,d(2) \,d(3)$$
(2.8)

$$\Delta c_{AB}^{(1)} = \int \rho_o^{(1)}(1) \,\rho_o^{(2)}(2) \,f_{assoc}(12) \,g_{HS}(12) \,d(1) \,d(2) \tag{2.9}$$

 $\Delta c_{ABA}^{(2)}, \Delta c_{BAB}^{(2)}, \Delta c_{AB}^{(1)} \text{ and represent the three-body chains of kind ABA and BAB using second order graphs, and first order graph for a dimer, respectively. <math>g_{HS}(12)$ and $g_{HS}(123)$ are the two and three-body correlation functions of the hard sphere reference fluid, respectively. The Mayer *f*-function of association is defined as $f_{assoc}(12) = exp(-\varphi_{assoc}(12)/k_BT) - 1$. As mentioned in equation (2) the association pair potential is a sum over all sites of each pair of bonded species, and we need to elaborate on how that can affect $f_{assoc}(12)$. For the sake of brevity we define $exp\left(-\varphi_{assoc}^{(12)}(12)/k_BT\right) = e\left(\sum_{i}\sum_{j}A_iB_j\right)$ where A_i and B_j represent the sites on colloids of type 1 and 2, respectively, so

$$exp\left(-\varphi_{assoc}^{(AB)}(12)/k_{B}T\right) = e\left(A_{1}B_{1}\right)e\left(A_{1}B_{2}\right)e\left(A_{2}B_{1}\right)e\left(A_{2}B_{2}\right)$$
(2.10)

And according to the definition of Mayer f-function one can write $e(A_iB_j) = f_{A_iB_j}(12) +$ 1. In which $f_{A_iB_j}(12)$ is simply the Mayer f-function of association between site A_i of colloid of type 1 at (1) and site B_j of colloid of type 2 at (2) which we call a site-site Mayer f-function. Then, equation 2.10 is rewritten as

$$exp\left(-\varphi_{assoc}^{(AB)}(12)/k_{B}T\right) = (f_{A_{1}B_{1}}(12)+1)(f_{A_{1}B_{2}}(12)+1)...$$

$$(f_{A_{2}B_{1}}(12)+1)(f_{A_{2}B_{2}}(12)+1)$$
(2.11)

Expanding equation (11) we have:

$$exp\left(-\varphi_{assoc}^{(AB)}(12)/k_{B}T\right) = 1$$

$$1 + f_{A_{1}B_{1}}(12) + f_{A_{1}B_{2}}(12) + f_{A_{2}B_{1}}(12) + f_{A_{2}B_{2}}(12) + f_{A_{1}B_{1}}(12) f_{A_{1}B_{2}}(12)$$

$$+ f_{A_{2}B_{1}}(12) f_{A_{2}B_{2}}(12) + f_{A_{1}B_{1}}(12) f_{A_{2}B_{1}}(12) + f_{A_{1}B_{2}}(12) f_{A_{2}B_{2}}(12)$$

$$+ f_{A_{1}B_{1}}(12) f_{A_{2}B_{2}}(12) + f_{A_{1}B_{2}}(12) f_{A_{2}B_{1}}(12) + f_{A_{1}B_{1}}(12) f_{A_{1}B_{2}}(12) f_{A_{2}B_{1}}(12)$$

$$+ f_{A_{1}B_{1}}(12) f_{A_{1}B_{2}}(12) f_{A_{2}B_{2}}(12) + f_{A_{1}B_{2}}(12) f_{A_{2}B_{1}}(12) f_{A_{2}B_{2}}(12)$$

$$+ f_{A_{1}B_{1}}(12) f_{A_{1}B_{2}}(12) f_{A_{2}B_{1}}(12) f_{A_{2}B_{2}}(12)$$

$$(2.12)$$

Since in our system β_c and \aleph are chosen such that each pair of colloids can be considered associated with a maximum of one bond, all terms with more than one Mayer f-functions is eliminated and the equation above reduces to:

$$exp\left(-\varphi_{assoc}^{(AB)}\left(12\right)/k_{B}T\right) = 1 + f_{A_{1}B_{1}}\left(12\right) + f_{A_{1}B_{2}}\left(12\right) + f_{A_{2}B_{1}}\left(12\right) + f_{A_{2}B_{2}}\left(12\right) \quad (2.13)$$

Here, we come to the conclusion that the total Mayer f-function can be replaced by the sum over the site-site Mayer f-functions. Keeping this in mind, instead of f_{assoc} (12) f_{assoc} (23) in equation 2.7 we can put:

$$f_{assoc}(12) f_{assoc}(23) = \sum_{A \in \Gamma(1)} \sum_{B \in \Gamma(2)} \sum_{A \in \Gamma(1)} f_{A_i B_j}(12) f_{A_i B_j}(23)$$
(2.14)

where A_i and B_j correspond to the similar indices as in equations 2.11 and 2.12. Therefore, in contribution terms, we are taking all possible configurations in formation of *n*-body chains into account. For example, in equation 2.7 when colloid of type 1 at (1) wants to form a bond with colloid of type 2 at (2), there are four possible bonds. And when another colloid of type 1 at (3) wants to associate to the colloid of type 2, the non-bonded site on type 2 can form a bond with any of the sites of the colloid at (3). This results in a total of 8 possible configurations for a three body chain of kind ABA. The same concept rules over forming all other chains and rings. In this work, we simply consider that the sites on a colloid and the energy of their bonds are similar. This helps us to simplify the equations using the fact that all Mayer f-functions are similar ($f_{AB} = f_{A_iB_j}$); then, we can replace the sums over the Mayer f-functions with the total number of configurations:

$$\Delta c_{ABA}^{(2)} = \frac{8}{2} \int \rho_o^{(1)}(1) \,\rho_o^{(2)}(2) \,\rho_o^{(1)}(3) \,f_{AB}(12) \,f_{AB}(23) \,g_{HS}(123) \,d\,(1) \,d\,(2) \,d\,(3)$$
(2.15)

$$\Delta c_{BAB}^{(2)} = \frac{8}{2} \int \rho_o^{(2)}(1) \,\rho_o^{(1)}(2) \,\rho_o^{(2)}(3) \,f_{AB}(12) \,f_{AB}(23) \,g_{HS}(123) \,d\,(1) \,d\,(2) \,d\,(3)$$
(2.16)

$$\Delta c_{AB}^{(1)} = 4 \int \rho_o^{(1)}(1) \,\rho_o^{(2)}(2) \,f_{AB}(12) \,g_{HS}(12) \,d(1) \,d(2) \tag{2.17}$$

Now that the basic chain contributions are obtained, deriving the longer chain terms is straightforward and similar to the basic forms. Δc_{chain} is properly written only if we sum over all possible chain configurations, so the total chain contribution terms of each kind are approximated as:

$$\frac{\Delta c_{ABA}}{V} = \rho_o^{(1)} \sum_{n=2,4,\dots} \left(2 \left(\rho_o^{(1)} \rho_o^{(2)} \right)^{1/2} f_{AB} \right)^n I_n \tag{2.18}$$

$$\frac{\Delta c_{BAB}}{V} = \rho_o^{(2)} \sum_{n=2,4,\dots} \left(2 \left(\rho_o^{(1)} \rho_o^{(2)} \right)^{1/2} f_{AB} \right)^n I_n \tag{2.19}$$

$$\frac{\Delta c_{AB}}{V} = 2\left(\rho_o^{(1)}\rho_o^{(2)}\right)^{1/2} \sum_{n=1,3,\dots} \left(2\left(\rho_o^{(1)}\rho_o^{(2)}\right)^{1/2} f_{AB}\right)^n I_n \tag{2.20}$$

The term I_n is defined by:

$$I_{n} = \frac{1}{\Omega^{n}} \int \prod_{bonded \ pairs} O_{AB}(ij) g_{HS}(1 \dots n+1) d(2) \dots d(n+1)$$
(2.21)

 $\{ij\}$

 $\Omega = 8\pi^2$ is the total number of orientation that a colloid can occupy, and O_{AB} (12) checks whether two colloids are in proper orientation and distance relative to each

other to form a bond:

$$O_{AB}(12) = \begin{cases} 1 & r_{12} < r_c, \ \theta_{A(1)} < \beta_c \ , \ \theta_{B(2)} < \beta_c \\ 0 & otherwise \end{cases}$$
(2.22)

To calculate the multi-body correlation function, we follow the approximation used by Marshall and Chapman [14], where the n-body correlation function is replaced by a superposition of two-body correlation functions of all bonded colloids and exponentials of hard sphere potential between next nearest neighbors:

$$g_{HS}(1\dots n) = \prod_{i=1}^{n-1} g_{HS}(i,i+1) \prod_{j=1}^{n-2} e_{HS}(j,j+2)$$
(2.23)

where $e_{hs}(ij) = \exp(-\varphi_{HS}(ij)/k_BT)$ and using a superposition approximation of first order bonds, integral I_n is simplified to:

$$I_n = \kappa^n \zeta^n \psi^{n-1} \tag{2.24}$$

where $\kappa = (1 - \cos\beta_c)^2/4$ is the probability of finding two colloids in a proper orientation that allows them to form a bond, and $\zeta = 4\pi \int_{d}^{r_c} r^2 g_{HS}(r)$ is an approximation of the number of colloids existing within a distance of r_c of a colloid which is located at the center of coordinates when no patch exists. We use Marshall and Chapman's approximation [14] for the pair correlation function in ζ where $r^p g_{HS}(r) = d^p g_{HS}(d)$, $p = 17.866\eta^2 + 2.4709\eta$, and $\eta = \frac{\pi}{6}\rho d^3$ is the packing fraction. The term ψ is the steric hindrance which introduces the effect of bond angle into the chain contribution. ψ is the ratio of all the ways of building a three-body chain in which bonding at one site might limit the bonding volume of the other site over the case where bonding at one site has no effect on the other site's bond. For this term, we use the results obtained by Marshall and Chapman[14] for their steric hindrance term which is reported for specific bond angles (α) from 0 to 180 degrees.



Figure 2.4 : Schematic view of a four-mer ring of associated species.

By use of the results of equation 2.24; equations 2.18, 2.19, and 2.20 are written as:

$$\frac{\Delta c_{ABA}}{V} = \frac{4\rho_o^{(1)^2}\rho_o^{(2)}\Delta^2\psi}{1 - 4\rho_o^{(1)}\rho_o^{(2)}(\Delta\psi)^2}$$
(2.25)

$$\frac{\Delta c_{BAB}}{V} = \frac{4\rho_o^{(2)^2}\rho_o^{(1)}\Delta^2\psi}{1-4\rho_o^{(1)}\rho_o^{(2)}(\Delta\psi)^2}$$
(2.26)

$$\frac{\Delta c_{AB}}{V} = \frac{4\rho_o^{(2)}\rho_o^{(1)}\Delta}{1 - 4\rho_o^{(1)}\rho_o^{(2)}(\Delta\psi)^2}$$
(2.27)

where $\Delta = f_{AB}\kappa\zeta$. In our theory, rings are topologically distinct irreducible graphs, and for each ring size we need to sum over all possible configurations which is guided by the similar methodology we used for the Mayer *f*-functions in the chain terms. Due to the limitation we imposed on association, only rings of sizes 4, 6, etc. will be formed. However, Marshall and Chapman[14, 66] showed that small rings are most favored at small bond angle. Therefore, since α in our current model is small, we limit the ring formation to include only rings of size four. The contribution from forming a 4-mer ring is given by the following equation and it is exhibited in Figure 3 schematically:

$$\Delta c_{ring}^{(4)} = \frac{1}{2} \int \rho_o^{(1)}(1) \rho_o^{(2)}(2) \rho_o^{(1)}(3) \rho_o^{(2)}(4) \times \dots$$

$$\dots \sum_{A \in \Gamma(1)} \sum_{B \in \Gamma(2)} \sum_{A \in \Gamma(1)} \sum_{B \in \Gamma(2)} f_{A_i B_j}(12) f_{A_i B_j}(23) f_{A_i B_j}(34) f_{A_i B_j}(41) \times \dots$$

$$\dots g_{HS}(1234) d(1) d(2) d(3) d(4)$$

(2.28)

We follow Marshall and Chapman's approach[14] and estimate the n-body correlation function by a superposition of pair correlation functions of bonded pairs and exponentials of the hard sphere interactions between non-bonded pairs:

$$g_{HS}(1234) = g_{HS}(12) g_{HS}(23) g_{HS}(34) g_{HS}(41) e_{HS}(13) e_{HS}(24)$$
(2.29)

And using the assumption that all f-bonds are similar, the ring contribution term is simplified to:

$$\frac{\Delta c_{ring}^{(4)}}{V} = \frac{8\left(\left(\rho_{o}^{(A)}\rho_{o}^{(B)}\right)^{1/2}f_{AB}\right)^{4}}{\Omega^{3}} \times \dots$$

$$\dots \int \prod_{bonded \ pairs} g_{HS}\left(ij\right)O_{AB}\left(ij\right) \prod_{all \ pairs} e_{HS}\left(lk\right)d\left(2\right)d\left(3\right)d\left(4\right)$$

$$(ij) \qquad \qquad (lk)$$

$$(2.30)$$

Having 4-mer ring contribution derived, writing the contributions for larger rings is straightforward. The position and orientation ring integrals were solved by Marshall and Chapman's approach[14] in which they reported values for each specific ring size based on the bond angle. The reader is suggested to read the ring integrals section in reference [14] for the details of the method.

Using Wertheim's two-density formalism [43, 44] the mass action equations are:

$$\rho^{(1)} = \rho_o^{(1)} + \rho_b^{(1)} \tag{2.31}$$

$$\rho^{(2)} = \rho_o^{(2)} + \rho_b^{(2)} \tag{2.32}$$

In this framework, the density is categorized in bonded ρ_b and non-bonded ρ_o states. The non-bonded colloids are the monomers, and bonded ones are those which contribute into rings and chains. So we can write the density of the bonded species in specific form as follow:

$$\rho_b^{(1)} = \rho_{1c}^{(1)} + \rho_{2c}^{(1)} + \rho_{ring}^{(1)}$$
(2.33)

$$\rho_b^{(2)} = \rho_{1c}^{(2)} + \rho_{2c}^{(2)} + \rho_{ring}^{(2)}$$
(2.34)

where $\rho_{1c}^{(1)}$ is the density of colloids of type 1 that are bonded once (the colloids in a dimer or at the ends of a chain), $\rho_{2c}^{(1)}$ is the density of species 1 that are bonded at both sites in a chain, and $\rho_{ring}^{(1)}$ is the density of those colloids of type 1 that are bonded at both sites in a ring. Minimizing the free energy of the system with respect to the monomer densities, each density factor is obtained:

$$\frac{\rho_{1c}^{(1)}}{\rho_o^{(1)}} = \frac{\delta\Delta c_{ABA}}{\delta\rho_o^{(1)}} + \frac{\delta\Delta c_{AB}}{\delta\rho_o^{(1)}}$$
(2.35)

$$\frac{\rho_{1c}^{(2)}}{\rho_o^{(2)}} = \frac{\delta \Delta c_{BAB}}{\delta \rho_o^{(2)}} + \frac{\delta \Delta c_{AB}}{\delta \rho_o^{(2)}}$$
(2.36)

which leads to the following equations:

$$\frac{\rho_{1c}^{(1)}}{\rho_o^{(1)}} = \frac{8\rho_o^{(1)}\rho_o^{(2)}\Delta^2\psi}{1 - 4\rho_o^{(1)}\rho_o^{(2)}(\Delta\psi)^2} + \frac{4\rho_o^{(2)}\Delta}{1 - 4\rho_o^{(1)}\rho_o^{(2)}(\Delta\psi)^2}$$
(2.37)

$$\frac{\rho_{1c}^{(2)}}{\rho_o^{(2)}} = \frac{8\rho_o^{(1)}\rho_o^{(2)}\Delta^2\psi}{1 - 4\rho_o^{(1)}\rho_o^{(2)}(\Delta\psi)^2} + \frac{4\rho_o^{(1)}\Delta}{1 - 4\rho_o^{(1)}\rho_o^{(2)}(\Delta\psi)^2}$$
(2.38)

and,

$$\frac{\rho_{2c}^{(1)}}{\rho_o^{(1)}} = \frac{\delta\Delta c_{ABA}}{\delta\rho_o^{(1)}} + \frac{\delta\Delta c_{AB}}{\delta\rho_o^{(1)}} + \frac{\delta\Delta c_{BAB}}{\delta\rho_o^{(1)}}$$
(2.39)

$$\frac{\rho_{2c}^{(2)}}{\rho_o^{(2)}} = \frac{\delta\Delta c_{BAB}}{\delta\rho_o^{(2)}} + \frac{\delta\Delta c_{AB}}{\delta\rho_o^{(2)}} + \frac{\delta\Delta c_{ABA}}{\delta\rho_o^{(2)}}$$
(2.40)

which is:

$$\frac{\rho_{2c}^{(1)}}{\rho_o^{(1)}} = \frac{\left(2\left(\rho_o^{(1)}\rho_o^{(2)}\right)^{1/2}\Delta\right)^4\psi^3}{\left(1-4\rho_o^{(1)}\rho_o^{(2)}(\Delta\psi)^2\right)^2} + \frac{16\rho_o^{(2)^2}\rho_o^{(1)}\Delta^3\psi^2}{\left(1-4\rho_o^{(1)}\rho_o^{(2)}(\Delta\psi)^2\right)^2} + \frac{4\rho_o^{(2)^3/2}\rho_o^{(1)^{1/2}}\Delta^2\psi}{\left(1-4\rho_o^{(1)}\rho_o^{(2)}(\Delta\psi)^2\right)^2} + \frac{\rho_{2c}^{(2)}}{\left(1-4\rho_o^{(1)}\rho_o^{(2)}(\Delta\psi)^2\right)^2} + \frac{16\rho_o^{(1)^2}\rho_o^{(2)}\Delta^3\psi^2}{\left(1-4\rho_o^{(1)}\rho_o^{(2)}(\Delta\psi)^2\right)^2} + \frac{4\rho_o^{(1)^{3/2}}\rho_o^{(2)^{1/2}}\Delta^2\psi}{\left(1-4\rho_o^{(1)}\rho_o^{(2)}(\Delta\psi)^2\right)^2} + \frac{16\rho_o^{(1)^2}\rho_o^{(2)}\Delta^3\psi^2}{\left(1-4\rho_o^{(1)}\rho_o^{(2)}(\Delta\psi)^2\right)^2} + \frac{16\rho_o$$

and the ring densities are also calculated as:

$$\frac{\rho_{ring}^{(1)}}{\rho_o^{(1)}} = \frac{\partial \Delta c_{ring}^{(4)} / V}{\partial \rho_o^{(A)}}$$
(2.43)

$$\frac{\rho_{ring}^{(2)}}{\rho_o^{(2)}} = \frac{\partial \Delta c_{ring}^{(4)} / V}{\partial \rho_o^{(2)}}$$
(2.44)

where the derivatives are written as:

$$\frac{\partial \Delta e_{ring}^{(4)}/V}{\partial \rho_{o}^{(1)}} = \frac{16 \left(\left(\rho_{o}^{(1)} \rho_{o}^{(2)} \right)^{1/2} f_{AB} \right)^{4}}{\rho_{o}^{(1)} \Omega^{3}} \times \dots$$

$$\dots \int \prod_{\substack{m=1 \\ bonded \ pairs}} g_{HS} \left(ij \right) O_{AB} \left(ij \right) \prod_{\substack{m=1 \\ all \ pairs}} e_{HS} \left(lk \right) d\left(2 \right) d\left(3 \right) d\left(4 \right)$$

$$(14)$$

$$(14)$$

$$(2.45)$$

2.3 Results and Discussion

In this section we compare the predictions from theory with new Monte Carlo simulation results for thermodynamic and structural properties of a binary mixture of twopatch colloids as described in the previous section. We use standard methodology[138] to perform simulations. 500 particles are used in each simulation. The simulations were allowed to equilibrate for 500×10^6 trial moves, and averages were taken over another 500×10^6 trial moves. A trial move includes relocating and reorienting a particle. The cutoff distance and angle in simulations are consistent with that used in theory, $r_c = 1.1, \beta_c = 27^\circ$ that allows only one bond per association site.

The discussion begins with investigating the effect of density and bond angle over the fractions of k-times bonded colloids (X_k) . All of the results are at equimolar conditions, $\rho^{(1)} = \rho^{(2)}$, so we choose to report only fractions of colloids of type 1. In this work, we study three cases: case I with a total reduced number density ($\rho^* = \rho \sigma^3$) of $\rho^* = 0.2$, and a bond angle of $alpha = 60^\circ$; case II with $\rho^* = 0.6$ and $\alpha = 60^\circ$, and case III with $\rho^* = 0.2$ and $\alpha = 85^{\circ}$. In Figure 2.5, the fractions are plotted versus reduced association energy ($\varepsilon_{AB}^* = \varepsilon_{AB}/k_BT$). In all three cases, at very low association energies, almost no bond is formed; however, with increasing association energy, colloids form bonds with each other. According to all three cases in Figure 2.5, increasing ε_{AB}^* from zero, the fraction of colloids bonded once (X_1) increases until it reaches a maximum, where the concentration of dimers and short chains is at its highest value. After reaching the maximum point, at higher energies, the colloids will have the opportunity to form their second bonds, and that results in an increase in fraction of twice bonded species (X_2) . The reason behind such behavior is the competition between two effects: having a higher degree of freedom (DOF) and being at a lower energy. When a colloid is not bonded it has the highest DOF since it can occupy any position and orientation, but once it forms a bond it becomes restricted; therefore, the energy benefit from that bond must be large enough to offset the loss in DOF. Similarly, forming two bonds brings more restrictions. The theory accurately predicts the variations in X_k with respect to ε_{AB}^* .

The effect of density is shown in Figure 2.5 in cases I and II. According to this figure with an increase in ε_{AB}^* , the rate of the change in fractions in case II is greater



Figure 2.5 : The fraction of k-times bonded colloids (X_o : fraction of non-bonded colloids, X_1 : fraction of one-time bonded colloids, X_o : fraction of twice bonded colloids) versus the reduced association energy ($\varepsilon_{AB}^* = \varepsilon_{AB}/k_BT$). Solid line curves present theory results (Green: X_o , Red: X_1 , Blue: X_2) and symbols exhibit MC simulation results (Squares: X_o , Circles: X_1 , Triangles: X_2).



Figure 2.6 : The fraction of clusters of associated colloids $(X_{ring(4)})$: fraction of colloids in 4-mer rings, X_{chain} : fraction of twice bonded colloids in chains) versus the reduced association energy $(\varepsilon_{AB}^* = \varepsilon_{AB}/k_BT)$. Solid line curves present theory results (Blue: X_{chain} , Red: $X_{ring(4)}$) and symbols exhibit MC simulation results (Squares: X_{chain} , Triangles: $X_{ring(4)}$).

than case I because at higher densities particles are closer to each other, and the chances of finding particles in the bonding volume of one another is higher. Therefore an increase in association energy which enhances the tendency of particles to form a bond provides more association for a fluid with higher density.

Bond angle (α) refers to the angle between two vectors connecting the center of a colloid to the centers of its association sites. This angle plays a key role in determining the structure of clusters of associated colloids. Marshall and Chapman[14] were the first who showed a distribution of rings of various sizes over a wide range of bond angles. According to what they reported, at each bond angle there is a specific ring size which shows the major contribution among the rings. The peak for the smallest ring (3-mer ring) occurs at $\alpha = 60^{\circ}$, and for a 4-mer ring at $\alpha \approx 85^{\circ}$. In our work, only rings with even number of colloids are formed (4-mer, 6-mer, etc.). In Figure 2.5, the curves of case III show a higher amount of association compared with case I. This results because of the larger bond angle in case III that leads to more chain formation which is explained in Figure 2.6.

To better understanding the effects of association energy, density and geometry on fluid behavior, more information regarding the self-assembled structures is needed. Figure 2.6 elaborates on the fraction of twice bonded colloids to show whether a colloid is bonded twice in a chain (X_chain) or ring (X_ring) . Here, we limit the plots of rings to size four because the fraction of colloids in higher-mers is almost negligible. Comparing case I and II, increasing density raises X_chain , while $X_{(ring(4))}$ (fraction of colloids in rings of size four) is slightly reduced. This occurs because at low densities inter-particle interactions are less common, so depending on ε_{AB}^* short chains and small rings are the common structures in the fluid. At lower ε_{AB}^* the energy benefit of restricting colloids into rings is not high enough; therefore, the majority of structures



Figure 2.7 : The excess internal energy versus the reduced association energy at different bond angles (α) and reduced densities (ρ^*). Left panel compares $\rho^* = 0.6$ and $\rho^* = 0.2$ at fixed $\alpha = 60^\circ$, and right panel compares $\alpha = 60^\circ$ and $\alpha = 85^\circ$ at fixed $\rho^* = 0.2$. Solid line curves present theory results (on the left panel; Red: $\rho^* = 0.6$, Black: $\rho^* = 0.2$, and on the right panel: Red: $\alpha = 85^\circ$, Black: $\alpha = 60^\circ$) and symbols exhibit MC simulation results (on the left panel; Cross: $\rho^* = 0.6$, Star: $\rho^* = 0.2$, and on the right panel: Cross: $\alpha = 85^\circ$, Star: $\alpha = 60^\circ$).

are short chains. However, at greater ε_{AB}^* the system tends to maximize the energy benefit, so the colloids are pushed to form their maximum number of bonds (two bonds) that results in ring formation. As we explained earlier, at high densities colloids are closer to each other, so more chains are formed since less restriction is applied to a particle within a chain rather than a ring. Formation of more chains in the system maximizes the energy benefit while the limitations on DOF are lower compared with the situation where more rings are formed. Consequently, at higher densities long chains are the major structures inside the fluid as shown in Figure 2.6.

The fractions exhibited in Figure 2.6 of cases I and III introduce how the chain and ring formation is influenced by the bond angle. In case III, X_chain is always greater than $X_(ring(4))$, although $\alpha = 85^{\circ}$ is the angle at which 4-mers are the most probable rings[14]. The colloids prefer to stay in chain clusters in order to tolerate less constraint since at $\alpha = 85^{\circ}$ chains are more linear than $\alpha = 60^{\circ}$. Figure 2.7 supports our arguments on Figures 2.5 and 2.6 that increasing density enhances the extent of association corresponding to the reduction of the excess internal energy $(E/Nk_BT = E^*)$ of the system. Also, increasing the bond angle imposes less position/orientation restrictions by forming more long chains, so association increases slightly.

2.4 Summary and Conclusion

In this work a thermodynamic perturbation theory was developed for a binary mixture of fluids with two identical associating sites. According to the limitation we imposed on the association, the specific types of chains and rings with even number of colloids were formed. The impact of density, bond angle, and reduced association energy on association of colloids was investigated by theory. The theory results are in excellent agreement with Monte Carlo simulations.

In Wertheim's theory, fluids with more than one associating site are treated within a multi-density formalism[45, 46, 106] where each site is recognized with a density factor, separately. However, including the steric hindrance effect for such fluids is very difficult in that framework. Here we utilized a two-density formalism, a simpler and more transparent approach, through which the density terms do not include any site information, and every point inside a graph of associated species is represented by a monomer density term. The two-density formalism framework has shown promising results for single-site fluids[43, 44, 65]. In this work we extended this framework to an equimolar mixture of colloids with two association sites. Extensions of the current theory for bond cooperativity[66, 1], of two-site fluids, for the case where two species have different bond angles, and for a non-equimolar binary mixture will be the subjects of future publications.

Chapter 3

Bond Cooperativity and Ring Formation in Hydrogen Fluoride Thermodynamic Properties: A Two-Density Formalism Framework

3.1 Introduction

In spite of the wide range of applications that Wertheim's TPT1 has presented, it carries limited information about associating species. For example, in TPT1 association sites can form only one bond, for the case of species with more than one site, no steric hindrance between association sites is included, double bonding and ring formation are not counted, etc.. Kalyuzhnyi et al.[127, 128, 64], and Marshall and Chapman [65, 96, 126, 125, 15] developed Wertheim's graph sum beyond its first order to account for the graphs with more than one association bond at a site. Marshall and Chapman[14, 130, 66] also introduced the effect of steric hindrance for fluids with multiple association sites into the theory to predict formation of linear and closed loop structures.

TPT1 considers all of the association bonds formed in the fluid to be identical, and fluid molecules only form networks of linear and branched clusters of hydrogen bonds. However, quantum studies [28] have shown when a molecule forms more than one bond there can be a change in the energies of the bonds that is called cooperativity effect, especially when rings of associated molecules are formed. Examples of systems that present such phenomena include hydrogen fluoride[141], Alcohol[142], and Peptide[143] interactions. Sear and Jackson[131, 136] were the first to model these effects using TPT for a hard sphere fluid with two association sites. Later, Marshall and Chapman [14, 66, 1] used a multi-density formalism and developed a TPT to model the same effects where the relative position of the bonding sites on a species has an effective role in determining the structures formed at any condition.

A wide range of theoretical [144, 145, 146, 147, 148, 149, 150, 151], quantum and simulation [28, 152, 153, 154, 155] studies has been done to capture the thermodynamic properties of hydrogen fluoride. Galindo et al.[6] developed a SAFT-VR equation of state including ring formation to show the importance of the cyclic clusters in hydrogen fluoride. In their work, rings are allowed to form regardless of the position of the hydrogen bonding sites on the molecule. They predicted that among all ring sizes, tetramer rings are the most prevalent. However, this is an over-simplification compared to Marshall and Chapman theory [14] where they observe a direct relation between the bond angle of an associating species and the type of the ring it forms. For example, it is geometrically impossible to form a tetramer ring with a bond angle of 180°. Besides, experimental [141] investigations revealed the importance of forming hexamer rings (plus 5, 7, and 8-mer rings) in hydrogen fluoride. This is confirmed by a quantum study [28] which agrees with stability of cyclic clusters and in a study that uses association plus Peng-Robinson equation of states (AEOS) [145] that models this fluid as a mixture of monomers, hexamers, and octamers.

In this work, we develop a new two-density formalism for a pure fluid with two association sites. While the previous study [1] developed cooperativity in multi-density formalism, a two-density formalism is more straight forward and transparent, particularly for extensions to cooperative hydrogen bonding in mixtures, incorporating a distribution of bonding energies and tracking formation of specific clusters. We start with verifying our theory developments with reference fluids of hard spheres and Lennard Jones spheres with Monte Carlo simulation of corresponding fluids. Application of the theory for calculating the thermodynamic properties of hydrogen fluoride is demonstrated by adding on bond angle dependent cyclic structures, into the theory. The parameters of the model are obtained by fitting to experimental data [2, 3, 4, 5] for liquid and vapor density, and vapor pressure.

3.2 Theory

We develop a thermodynamic perturbation theory for the Helmholtz free energy of an associating fluid with two association sites. The theory includes the effect of bond angle and hydrogen bond cooperativity. Detailed derivation of the theory are presented below, for reference fluids of hard spheres and of Lennard Jones spheres. Having all required equations derived, we apply the theory for hydrogen fluoride in the following section.

3.2.1 Detailed Derivation of Theory Within Two Density Formalism

In this section a thermodynamic perturbation theory is developed for a fluid of diameter σ with two associating sites of type A and type B. In our system of interest, association is limited to happen only between sites A and B. The angular size of each association site is determined by the angular cutoff β_c which makes a solid angle of $2\pi (1 - \cos \beta_c)$, and the sites are separated by a bond angle of α_{AB} . A diagram of an associating species is shown in figure 3.1. To introduce the potential of interaction in our system we follow Sear and Jackson[136] approach where the total energy for a



Figure 3.1 : A scheme of an associating molecule and a pair interaction between two associating species

fluid of N species is defined as a sum of pairwise and triplet contributions:

$$U(1...N) = \frac{1}{2} \sum_{i,j} \left(\varphi_R(r_{ij}) + \varphi_{assoc}^{(2)}(ij) \right) + \frac{1}{6} \sum_{i,j,k} \left(\varphi_{assoc}^{(3)}(ijk) \right)$$
(3.1)

The notation $(1) = [\vec{r}_1, \Omega_1]$ represents the position \vec{r}_1 and orientation Ω_1 vectors of species 1. φ_R is the reference system potential, $\varphi_{assoc}^{(2)}(ij)$ and $\varphi_{assoc}^{(3)}(ijk)$ are the pairwise and triplet potentials of interaction, respectively, and are given by:

$$\varphi_{assoc}^{(2)}(ij) = -\varepsilon^{(HB1)} (O_{AB}(ij) + O_{BA}(ij))$$

$$\varphi_{assoc}^{(3)}(ijk) = -\left(\varepsilon^{(HB2)} - \varepsilon^{(HB1)}\right) ((O_{AB}(ij) O_{BA}(ik) + O_{BA}(ij) O_{AB}(ik)) + O_{AB}(ji) O_{BA}(jk) + O_{BA}(ji) O_{AB}(jk) + O_{AB}(ki) O_{BA}(kj) + O_{BA}(ki) O_{AB}(kj)) + O_{AB}(ji) O_{AB}(jk) + O_{AB}(jk) + O_{AB}(ki) O_{BA}(kj) + O_{BA}(ki) O_{AB}(kj))$$
(3.2)

where the $O_{AB}(ij)$ is the overlap function used to represent a square well associating site [7, 109, 123]:

$$O_{AB}(12) = \begin{cases} 1 & r_{12} < r_c, \ \theta_{A(1)} \le \beta_c, \ \theta_{B(2)} \le \beta_c \\ 0 & otherwise \end{cases}$$
(3.3)

According to this function, if the distance between centers of 1 and 2 (r_{12}) is less than a critical radius (r_c) and the angle $(\theta_{A(1)}, \theta_{B(2)})$ between the vector from the center of a sphere to a site on that sphere and the vector connecting the centers of the two spheres is less than a critical angle (β_c), the sites are considered bonded, and the energy of the system is reduced by ε_{AB} . Figure 3.1 exhibits the association between two species schematically. In this system we do not allow association of similar sites, $\varepsilon_{AA} = \varepsilon_{BB} = 0$. According to Wertheim's two-density formalism [43, 44, 45, 45, 46] the Helmholtz free energy of association is written as follow

$$\frac{A^{ASSOC}}{Vk_BT} = \rho ln \frac{\rho_o}{\rho} - \rho_o + \rho - \frac{\Delta c^{(o)}}{V}$$
(3.4)

Here, A^{ASSOC} is the association contribution to the Helmholtz free energy of the fluid, ρ is the total reduced number density, ρ_o is the monomer density, V is total volume, T is temperature, k_B Boltzmann's constant, and $\Delta c^{(o)}$ includes all association contributions in the form of a fundamental graph sum. Assuming monovalent association sites in our system, only clusters of linear chains and rings of associated species are expected to form, where the energy of the first bond ($\varepsilon^{(HB1)}$) in the chain is different than other bonds ($\varepsilon^{(HB2)}$), and all the bonds in a ring are considered $\varepsilon^{(HB2)}$. Figure 3.2 shows a diagram of a chain and a ring of associated species, and the contribution of association interactions is written as:

$$\Delta c^{(o)} = \Delta c_{chain} + \Delta c_{ring} \tag{3.5}$$

where Δc_{chain} , and Δc_{ring} are the chain and ring formation contributions, respectively. While the ring contribution is similar to Marshall and Chapman's approach [14, 66, 156], the chain contribution is an infinite sum over all orders of chains:

$$\Delta c_{chain} = \sum_{n=1}^{\infty} \Delta c_{(n)}^{ch} \tag{3.6}$$

For a specific chain of size n the contribution is written in the following way:

$$\frac{\Delta c_{(n)}^{ch}}{V} = \frac{\rho_o^{n+1}}{\Omega^n} \int f_1(12) f_2(23) \dots f_2(n, n+1) g_R(1 \dots n+1) d(2) d(3) \dots d(n+1)$$
(3.7)



Figure 3.2 : Diagram of the distribution of energies in a chain and a ring of bonded species

where $\Omega = 8\pi^2$ is the total number of orientations of a species, $g_R(1..n)$ is the n-body correlation function of the reference fluid, and we define the Mayer f-functions of association as $f_1(ij) = \left[\exp(\varepsilon^{(HB1)}/k_BT) - 1\right] O_{AB}(ij)$ and $f_2(lk) = \left[\exp(\varepsilon^{(HB2)}/k_BT) - 1\right] O_{AB}(lk)$. From here, 3.7 is simplified to:

$$\frac{\Delta c_{(n)}^{ch}}{V} = \frac{\rho_o^{n+1} f_1}{f_2} \frac{f_2^n}{\Omega^n} \int \prod_{i,j} O_{AB}(ij) g_R(1\dots n+1) d(2) d(3)\dots d(n+1)$$
(3.8)

where as $f_1 = \exp(\varepsilon^{(HB1)}/k_BT) - 1$ and $f_2 = \exp(\varepsilon^{(HB2)}/k_BT) - 1$ are constants. We will choose the bond angle (α_{AB}) in a range that its effect is negligible in chain formation [14], so the n-body correlation function is approximated as a superposition of pair correlation functions of the bonded species:

$$g_R(1\dots n+1) = g_R(12) g_R(23)\dots g_R(n, n+1)$$
(3.9)

Equation 3.8 can be simplified further in the following way:

$$\frac{\Delta c_{(n)}^{ch}}{V} = \rho_o^{n+1} f_1 f_2^{n-1} I_n \tag{3.10}$$

where

$$I_n = \frac{1}{\Omega^n} \int \prod_{i=1}^n O_{AB}(i, i+1) g_R(i, i+1) d(i)$$
(3.11)

 I_n calculates the probability of finding n + 1 species in proper orientations and positions through which they can association and form a linear chain. In our current work, we can approximate I_n by a superposition of first order integrals where a pair of species are connected by a single bond:

$$I_n = I_1^n \tag{3.12}$$

and

$$I_1 = \frac{1}{\Omega} \int O_{AB}(12) g_R(12) d(12)$$
(3.13)

where I_1 is determined according to the choice of reference system. Using equations 3.11, 3.12, and 3.13, equation 3.10 can be rewritten as:

$$\frac{\Delta c_{(n)}^{ch}}{V} = \frac{\rho_o f_1}{f_2} (\rho_o f_2 I_1)^n \tag{3.14}$$

and the total contribution is obtained:

$$\sum_{n=1}^{\infty} \frac{\Delta c_{(n)}^{ch}}{V} = \frac{\rho_o^2 f_1 I_1}{1 - \rho_o f_2 I_1}$$
(3.15)

Now that every term in the Helmholtz free energy of association is derived, the mass action equation, which is obtained by minimizing the free energy with respect to monomer density, is a closed equation that calculates the monomer density.

$$\rho = \rho_o + \rho_{1b} + \rho_{2b} \tag{3.16}$$

 ρ_{1b} is the density of species bonded at one site (the terminal group at either side of a chain $(\rho_{1b-chain})$), and ρ_{2b} is the density of species bonded at both sites (which

includes those bonded twice in a chain $(\rho_{2b-chain})$ or a ring of associated species). Each of these density factors are obtained via graphical derivatives [43, 44]:

$$\frac{\rho_{1b}}{\rho_o} = \left(\frac{f_1}{f_2}\right) \frac{2\lambda}{1-\lambda} \tag{3.17}$$

$$\frac{\rho_{2b}}{\rho_o} = \left(\frac{f_1}{f_2}\right) \left(\frac{\lambda^2}{(1-\lambda)^2}\right) + \frac{\rho_{ring}}{\rho_o}$$
(3.18)

where

$$\lambda = \rho_o f_2 I_1 \tag{3.19}$$

 ρ_{ring} which is the density of species bonded twice in a ring is determined similar to Marshall and Chapman's approach [14, 66], and the first term on the RHS of equation 3.18 is simply density of species bonded twice in a chain ($\rho_{2b-chain}$) divided by monomer density. In the following sections we calculate the λ term based on the choice of the reference system; also, we apply the theory to calculate the thermodynamic properties of hydrogen fluoride.

Hard Sphere Reference Fluid Model

For the choice of a hard sphere reference fluid, the pair potential of the reference fluid is defined in the following way:

$$\varphi_{HS}(12) = \begin{cases} \infty & r_{12} < \sigma \\ 0 & r_{12} \ge \sigma \end{cases}$$
(3.20)

and equation 3.13 is calculated as:

$$I_1 = \kappa \zeta \tag{3.21}$$

where $\kappa = (1 - \cos\beta_c)^2/4$ is the probability of finding two species properly oriented to associate, and ζ is the number of species that can be found within the bonding shell of species 1. We approximate the radial distribution function with the contact value through Marshall and Chapman's approach [14] within the association range $\sigma \leq r \leq r_c$. The correlation function is approximated as $r^p g(r) = \sigma^p g(\sigma)$ where $p = 18.87\eta^2 + 2.47\eta$. Using this approach ζ is evaluated as:

$$\zeta = 4\pi\sigma^3 g_{HS}\left(\sigma\right) \left[\frac{\left(r_c/\sigma\right)^{3-p} - 1}{3-p}\right]$$
(3.22)

and to avoid formation of more than one bond at a site we choose $r_c = 1.1\sigma$ and $\beta_c = 27^{\circ}$.

Lennard Jones Reference Fluid Model

With the Lennard Jones reference system, the pair potential of the reference fluid is written as:

$$\frac{\varphi_{LJ}\left(r_{12}\right)}{k_BT} = \frac{4}{T^*} \left[\left(\frac{\sigma}{r_{12}}\right)^{12} - \left(\frac{\sigma}{r_{12}}\right)^6 \right]$$
(3.23)

where $T^* = k_B T / \varepsilon_{LJ}$ is the reduced temperature, ε_{LJ} is the energy parameter of the Lennard Jones potential, and r_{12} is the distance between centers of two LJ spheres (shown in figure 3.3). Similar to the hard sphere section, we need to introduce a proper form of radial distribution function to calculate I_1 . This integral is approximated in an identical way to 3.21 with the same κ , but a different ζ :

$$\zeta = 4\pi \int_{0}^{r} g_{LJ}(r) r^{2} dr$$
(3.24)

We use the radial distribution function proposed by Tang [157] which is based on the first-order solution using the mean spherical approximation. This pair correlation function is a function of T^* , distance and density. We obtained the values of ζ as a function of density and T^* using Monte Carlo integration method[156]. The details of the Tang correlation function are clearly explained in the original paper [157]. Here, to avoid formation of more than one bond at a site we set $r_c = 1.05\sigma$ and $\beta_c = 27^{\circ}$.



Figure 3.3 : Schematic view of Lennard Jones interaction between a pair of fluid species.

3.2.2 Ring formation and Thermodynamic Properties

The ring contribution to the Helmholtz free energy due to association is written in following form:

$$\Delta c_{ring} = \sum_{n=3}^{10} \Delta c_{ring} \left(n \right) \tag{3.25}$$

where n is the number of fluid species in the ring. The term $\Delta c_{ring}(n)$ is the sum of all irreducible graphs of n associating species bonded to their nearest neighbours through a single path of Mayer f-functions of association. These contributions for an associating fluid with two association sites (with an angular cutoff $\beta_c = 27^{\circ}$) correlated by a bond angle of α_{AB} are already derived by Marshall et al [66] as the following form:

$$\frac{\Delta c_{ring}\left(n\right)}{V} = \frac{\left(\rho_o f_2 \kappa g_{HS}\left(\sigma\right)\right)^n}{n\sigma^3} \Gamma^{(n)}$$
(3.26)

 $\Gamma^{(n)}$ which is significantly bond angle dependent represents the probability of formation of a ring of n associated species, with respect to the defined potential of interaction, at isolated conditions where the final values are independent of the density and temperature. Marshall calculated this parameter, for n = 3..10 and $0^{\circ} < \alpha_{AB} < 180^{\circ}$, using monte carlo integration method and the numerical results are given in his paper [14]. While Marshall showed promising results for his model fluid, applying equation 3.26 for fluids with different β_c may not be as accurate. There are two solutions for this situation: one method is to repeat Marshall monte carlo integration for the new fluid (which requires the exact knowledge of β_c), in another method, which is more convenient, (especially for the sake of applying the theory for real molecular fluids), the effect of having a random β_c can be lumped into a parameter such as ϖ . This parameter, which can only possess real positive values, stands for the deviation into the final value of $\Gamma^{(n)}$ for a given α_{AB} due to a different β_c than 27°. ϖ can be obtained by fitting the theory predictions to available verified data for the fluid of target. Therefore, in our work we use the updated form of equation 3.26 as:

$$\frac{\Delta c_{ring}\left(n\right)}{V} = \frac{\left(\rho_o f_2 \kappa g_{HS}\left(\sigma\right)\right)^n}{n\sigma^3} \varpi \Gamma^{(n)}$$
(3.27)

The values of $\Gamma^{(n)}$, which will be used for each ring size ($\alpha_{AB} = 120^{\circ}$) in section 3.2.4 of this work, are reported in Table 3.3. According to Wertheim, the density of molecules bonded in rings of size n is written as:

$$\rho_{ring}\left(n\right) = \frac{\left(\rho_o f_2 \kappa g_{HS}\left(\sigma\right)\right)^n}{\sigma^3} \varpi \Gamma^{(n)}$$
(3.28)

which is the result of the graphical derivative of equation 3.27 with respect to monomer density and multiplying it by a factor of monomer density. The chemical potential due to association for an associating hard sphere fluid as in section 3.2.1, which is the derivative of the Helmholtz free energy with respect to the total density, is written as:

$$\frac{\mu^{ASSOC}}{k_B T} = \ln\left(\frac{\rho_o}{\rho}\right) - \frac{f_1 \rho_o^2 g_{HS}\left(\sigma\right) \kappa}{\left(1 - \rho_o g_{HS}\left(\sigma\right) \kappa f_2\right)^2} \left(\frac{\partial ln g_{HS}\left(\sigma\right)}{\partial \rho}\right) - \sum_{n=3}^{\infty} \frac{\partial \Delta c_{ring}\left(n\right)}{\partial \rho} \quad (3.29)$$

And the last term on RHS is written as:

$$\frac{\partial \left(\Delta c_{ring}\left(n\right)/V\right)}{\partial \rho} = \left(\rho_{o} f_{2} \kappa g_{HS}\left(\sigma\right)\right)^{n} \varpi \Gamma^{\left(n\right)} \frac{\partial ln g_{HS}\left(\sigma\right)}{\partial \rho} \tag{3.30}$$

The values for $\Gamma^{(n)}$ are reported in Table 3.3, also, pressure is calculated as:

$$P = \mu \rho - A/V \tag{3.31}$$

Once the pressure due to association is obtained, we can calculate the enthalpy using the following relation:

$$H = E + P \tag{3.32}$$

where the internal energy of the fluid from association E^{ASSOC} is written as:

$$\frac{E^{ASSOC}}{N} = \frac{\partial \left(A^{ASSOC}/Nk_BT\right)}{\partial \beta} \tag{3.33}$$

where

$$\frac{E^{ASSOC}}{N} = \frac{X'_o}{X_o} - X'_o - \Delta c'_{chain} - \Delta c'_{ring}$$
(3.34)

In equations 3.33 and 3.34, $\beta = 1/k_BT$ and $a' = \partial a/\partial \beta$, respectively.

$$\Delta c'_{chain} = \frac{\partial \left(\Delta c_{chain}/N\right)}{\partial \beta} = \frac{\Delta c_{chain}}{N} \left(\frac{2X'_o}{X_o} + \frac{f'_1}{f_1} + \left(\frac{\Delta c_{chain}}{N}\right) \left(\frac{f_1}{f_2}\right) \left(\frac{1}{X_o}\right) \left(\frac{X'_o}{X_o} + \frac{f'_2}{f_2}\right)\right)$$
(3.35)

$$\Delta c'_{ring} = \frac{\partial \left(\Delta c_{ring}/N\right)}{\partial \beta} = \sum_{n=3}^{10} n \frac{\Delta c_{ring}\left(n\right)}{N} \left(\frac{X'_o}{X_o} + \frac{f'_2}{f_2}\right)$$
(3.36)

To be able to calculate the internal energy we need to first obtain X'_o :

$$X'_{1ch} = X_{1ch} \left(\frac{2X'_o}{X_o} + \frac{f'_1}{f_1} \right) + X_{1ch}^2 \left(\frac{f_2}{f_1} \right) \left(\frac{1}{X_o} \right) \left(\frac{X'_o}{X_o} + \frac{f'_2}{f_2} \right)$$
(3.37)

$$X'_{2ch} = X_{2ch} \left(\frac{3X'_o}{X_o} + \frac{f'_1}{f_1} + \frac{f'_2}{f_2} \right) + X_{1ch} X_{2ch} \left(\frac{f_2}{f_1} \right) \left(\frac{1}{X_o} \right) \left(\frac{X'_o}{X_o} + \frac{f'_2}{f_2} \right)$$
(3.38)

$$X'_{ring}(n) = nX_{ring}(n)\Gamma(n)\left(\frac{X'_o}{X_o} + \frac{f'_2}{f_2}\right)$$
(3.39)

$$X'_{o} + X'_{1ch} + X'_{2ch} + \sum_{n=3}^{10} X'_{ring}(n) = 0$$
(3.40)

3.2.3 Theory Comparison with Molecular Simulation

In this section we show the effect of bond cooperativity on extent of association for both hard sphere and Lennard Jones reference fluids with only chain formation $\alpha_{AB} = 180^{\circ}$. For fluids with hard sphere reference we compare the results from the theory with Marshall and Chapman's monte carlo simulation results in reference [1]. For a Lennard Jones reference, the theory predictions are compared with new Monte Carlo simulation results, where we use standard methodology[138] to perform simulations. 864 particles are used at each simulation, and averages are taken after reaching equilibrium, for each 10⁹ trial moves. A trial move includes relocating and reorienting a particle. The cutoff distance and angle in simulations are set to the same values in our theory.

Hard Sphere Reference

Figure 3.4 exhibits the results for the fraction of molecules bonded k-times for a hard sphere fluid with two associating sites, with $\alpha_{AB} = 180^{\circ}$. The predictions from our theory for the extent of association are compared with Marshall and Chapman 's [1] simulation results where they reported an excellent agreement between their theory predictions and their monte carlo simulation results. Therefore, the two-density theory here agrees with the multi-density theory of Marshall et al [66]. Two cases of bond cooperativity are studied in this figure. In case I, the energy of the

first bond in a chain $(\varepsilon^{(HB1)}/k_BT = 7)$ is fixed, and $\varepsilon^{(HB2)}/k_BT$ is increased from 0 to 10, and in case II, $\varepsilon^{(HB2)}/k_BT = 7$ and $\varepsilon^{(HB1)}/k_BT$ is changing. According to case I, when $\varepsilon^{(HB1)}/k_BT = 0$ only dimers and monomers exist in the fluid, and once $\varepsilon^{(HB2)}/k_BT$ increases, some molecules associate at their both sites, so the fraction of molecules with only one site bonded decreases. Following this trend, when $\varepsilon^{(HB2)}/k_BT$ is very high (around 10), most of the molecules are bonded twice, and the fluid is composed of very long chains. In case II, increasing $\varepsilon^{(HB1)}/k_BT$ while $\varepsilon^{(HB2)}/k_BT$ is very low, almost all of the molecules in the fluid are either bonded twice or not bonded at all, corresponding to all the molecules associated in very long chains. Apparently, increasing $\varepsilon^{(HB1)}/k_BT$ decreases the monomer fraction X_o and the fraction of bonded twice X_2 since the energy benefit of being in the state of only one time bonded becomes considerable. In higher values of $\varepsilon^{(HB1)}/k_BT$, especially around 10, the fraction of bonded once X_1 is the largest fraction. This corresponds to the self-assembly of most of the species in the form of short chains in the fluid.

Lennard Jones Reference

Figures 3.5 and 3.6 present the predictions from theory with a Lennard Jones reference fluid, compared with Monte Carlo simulations. The interesting difference between working with a hard sphere and a Lennard Jones reference fluid is that additional attraction exists in Lennard Jones potential. The fact that the association cutoff $r_c = 1.05\sigma$ is smaller than $r_{min-LJ} \approx 1.12\sigma$ (maximum Lennard Jones attraction) causes a competition between association and Lennard Jones attraction. In figure 3.5, case III with $\varepsilon^{(HB1)}/k_BT = 7$ and $\varepsilon_{LJ}/k_BT = 1$, and case IV with $\varepsilon^{(HB2)}/k_BT = 7$ and $\varepsilon_{LJ}/k_BT = 1$ are studied. In case III, $\varepsilon^{(HB2)}/k_BT$ increases from 0 to 10, and a


Figure 3.4 : Fractions of species bonded k-times in hard sphere reference fluid at $\rho\sigma^3 = 0.6$. Solid lines: our theory results(Red: X_o , Green: X_1 , Blue: X_2); Symbols: Marshall and Chapman's [1] simulation results (Circles: X_o , Triangles: X_1 , Squares: X_2).

similar behavior to the case I of the hard sphere system is observed; however, a higher X_o is observed for III compared with I because the Lennard Jones potential decreases the number of molecules in the range of the association potential. Case IV shows a similar difference with case II. Using a similar logic the behavior in case IV can be explained. Agreement of the theory with molecular simulation results is excellent.

Variations in bonding states of molecules under the influence from bond cooperativity and Lennard Jones interactions are investigated in case V with $\varepsilon^{(HB1)}/k_BT = 7$ and $\varepsilon^{(HB2)}/k_BT = 5$, and case VI with $\varepsilon^{(HB1)}/k_BT = 5$ and $\varepsilon^{(HB2)}/k_BT = 7$ in figure 3.6 where ε_{LJ}/k_BT increases from 0.1 to 1. In case V, since the energy of the first bond is lower than other bonds, the fluid starts with a higher X_2 than X_1 ; however, increasing ε_{LJ}/k_BT results in a reduction in X_2 while X_1 shows a small increase. This is understood by considering that increasing the Lennard Jones energy parameter motivates the molecules to locate beyond association range and feel Lennard Jones attractions. An identical behavior is observed in case VI for X_2 and X_1 while X_2 is smaller than X_1 since $\varepsilon^{(HB2)}/k_BT < \varepsilon^{(HB1)}/k_BT$.

3.2.4 Application to Hydrogen Fluoride

In this section we show the applicability of our theory with hard sphere reference fluid to calculate the thermodynamic properties of hydrogen fluoride. The total Helmholtz free energy is composed of the following contributions:

$$\frac{A}{Nk_BT} = \frac{A^{ID}}{Nk_BT} + \frac{A^{HS}}{Nk_BT} + \frac{A^{DISP}}{Nk_BT} + \frac{A^{ASSOC}}{Nk_BT}$$
(3.41)

where A^{ID} , A^{HS} , A^{DISP} , and A^{ASSOC} are the ideal gas, hard sphere, dispersion and association contribution to the free energy, respectively. The ideal term is exactly known from statistical mechanics, we use the hard sphere term by Boublik [158],



Figure 3.5 : Fractions of species bonded k-times in Lennard Jones reference fluid at $\rho\sigma^3 = 0.6$. Solid lines: our theory results(Red: X_o , Green: X_1 , Blue: X_2); Symbols: Monte Carlo simulation results (Circles: X_o , Triangles: X_1 , Squares: X_2).

and Mansoori et al [159] and dispersion term by Gross and Sadowski[8, 9]. For the association contribution we simply use the two-density formalism we already developed in equation 3.4. Reported in previous studies[6, 28], hydrogen fluoride



Figure 3.6 : Fractions of species bonded k-times in Lennard Jones reference fluid at $\rho\sigma^3 = 0.6$. Solid lines: our theory results(Red: X_o , Green: X_1 , Blue: X_2); Symbols: Monte Carlo simulation results (Circles: X_o , Triangles: X_1 , Squares: X_2).

molecules in the vapor phase tend to associate and form closed loop structures. While Galindo et al.[6] shows the importance of tetramer rings using the SAFT-VR equation of state, several studies revealed that 5, 6, 7,b and 8-mer (especially hexamer) rings are dominant structures formed by hydrogen fluoride molecules in the vapor phase [28, 145]. As an advantage of using Marshall's[66] approach and our new theory in ring contribution calculations, we choose the proper bond angle $\alpha_{AB} \approx 120^{\circ}$ that leads the theory to favor formation of rings of size six. The ring equations and the association contribution to the thermodynamic relations were derived in details in section 3.2.2. The parameters (σ , κ , ε_{LJ}/k_B , $\varepsilon^{(HB1)}/k_B$, $\varepsilon^{(HB2)}/k_B$) of our model are obtained by fitting the theory results to the experimental data [2, 3, 4, 5] for liquid density, vapor density and vapor pressure of hydrogen fluoride.

3.3 Results and Discussion

In this section we show the theory results for thermophysical properties of hydrogen fluoride. Our theory results are compared with experimental data on saturated liquid and vapor densities, vapor pressure, and enthalpy of vaporization of hydrogen fluoride.

3.3.1 Application to Hydrogen Fluoride

With the choice of bond angle of $\alpha_{AB} \approx 120^{\circ}$, we fit hydrogen fluoride temperatureindependent diameter (σ), dispersion energy constant (ε/k_B), first hydrogen bond energy ($\varepsilon^{(HB1)}/k_B$), second hydrogen bond energy ($\varepsilon^{(HB2)}/k_B$), bond volume (κ), and the ring factor (ϖ) to the experimental data [2, 3, 4, 5] for saturated liquid density (ρ_L), vapor density (ρ_V), and vapor pressure (P) at the range of $T_{min} = 248.15K$ to $T_{max} = 415.15K$. We believe that fitting to vapor density is a necessity in calculating hydrogen fluoride thermodynamic properties due to its great extension of ring formation. The fitted parameters and $ADD\% \left(ADD\% = \frac{|R_{exp} - R_{theory}|}{R_{exp}} \times 100\right)$, where R is vapor pressure, liquid density, or vapor density, are reported in Table 3.1 and Table 3.2, respectively. To compare the accuracy of our theory in calculating

σ	2.73303511234191
m	1
κ	0.0977111400133387
ε_{LJ}/k_B	95.495615048228
$\varepsilon^{(HB1)}/k_B$	1854.66311612526
$\varepsilon^{(HB2)}/k_B$	2934.73796026587
ω	8.90176926272451

Table 3.1 : Parameters fitted liquid density, vapor density and vapor pressure within the temperature range 190k to 480k. Ring factors are set for bond angle (the angle between two sites) 120 degree.

densities and vapor pressure, we fitted perturbed chain SAFT (PC-SAFT) [8, 9] parameters to the same experimental data and reported the ADD% in Table 3.2. All three properties are better predicted by our theory than PC-SAFT, especially ρ_V and P which are effective in calculation of the vapor phase thermophysical properties. The ratio $\varepsilon^{(HB2)}/\varepsilon^{(HB1)} = 1.58$ is close to the value reported in quantum studies [28] as the ratio of hydrogen bonding energy in rings over dimer chains. ϖ 's value shows that ring contribution to the free energy is larger than what rings of $\beta_c = 27^{\circ}$ report, and that corresponds to considering a larger β_c for association sites on hydrogen fluoride molecules. This is a guidance for future applications of β_c and α_{AB} dependent ring contributions where β_c can be obtained indirectly. Values of σ and (ε/k_B) are similar to those reported by Galindo et al. [6] using SAFT-VR with ring formation.

Figure 3.7 shows the theory results and experimental values for saturated liquid

ADD%	Р	$ ho_L$	$ ho_V$
New Theory	1.6	2.029	6.79
PC-SAFT	11.68	2.17	28.65

Table 3.2 : The error percent in liquid and vapor density and vapor pressure from our new theory and PC-SAFT[8, 9].

Γ ⁽³⁾	1.38E-10
$\Gamma^{(4)}$	1.22E-6
$\Gamma^{(5)}$	5.89E-4
$\Gamma^{(6)}$	2.34E-3
$\Gamma^{(7)}$	2.67E-4
Γ ⁽⁸⁾	2.89E-4
Γ ⁽⁹⁾	3.52E-4
Γ ⁽¹⁰⁾	3.47E-4

Table 3.3 : Values of $\Gamma^{(n)}$ in equation 3.27 averaged over bond angles around $\alpha_{AB} = 120^{\circ}$ for rings of size three to ten used reference [14].



Figure 3.7 : a)Saturated liquid density , and b) Saturated vapor volume diagram of hydrogen fluoride with respect to temperature; symbols are experiments [2, 3, 4, 5] and solid lines are theory results



Figure 3.8 : Vapor pressure diagram of hydrogen fluoride; symbols are experiments [2, 4, 5] and solid line is theory results.

density and vapor volume. Figure 3.8 exhibits vapor pressure calculated from our theory and experimental measurements. In each case experimental data is well correlated. Figure 3.9 presents enthalpy of vaporization (ΔH_{vap}) from experiment [4], our theory, SAFT-VR from Galindo et al. [6] without ring formation and SAFT-VR+n4 which includes formation of cyclic structures of four hydrogen fluoride molecules. The fact that SAFT-VR+n4 does not depend on bond angle and only includes four member rings may lead to an inaccurate vapor state and inaccurate prediction of ΔH_{vap} compared to our theory. In figure 3.10 we see that our theory predicts 6-mer rings $(X_{ring(6)})$ and then 5-mer rings $(X_{ring(5)})$ as the most populated structures in the vapor phase that agrees with previous quantum studies [28]. Figure 3.11 exhibits the fraction of non-bonded (X_o) , bonded once in chain's $\left(X_{1b-chain} = \frac{\rho_{1b-chain}}{\rho}\right)$ and bonded twice in chain's $\left(X_{2b-chain} = \frac{\rho_{2b-chain}}{\rho}\right)$ of associated hydrogen fluoride

molecules in the vapor phase. According to this graph X_o reaches to a maximum around at the same temperature as the maximum in ΔH_{vap} . According to figures 3.10 and 3.11 ring formation in the vapor phase is important at low temperatures. At high temperatures, due to higher vapor densities, chain formation becomes noticeable. Figure 3.12 presents the fraction of molecules involved in chains or not bonded at all in the liquid phase, where ring formation is almost negligible.



Figure 3.9 : Enthalpy of vaporization of hydrogen fluoride; solid line is our theory, and symbols are experiment [4], and dash lines are from Galindo et al. [6] work on SAFTVR and SAFTVR+n4

3.4 Conclusion

We developed a new thermodynamic perturbation theory using Wertheim's twodensity formalism framework to model bond cooperativity and cyclic formation in



Figure 3.10 : Fraction of hydrogen fluoride molecules in rings of associated molecules in vapor phase; all theory results.

hydrogen bonding fluids with two association sites. The theory captures the behavior of associating hard sphere and Lennard Jones species in various conditions of cooperativity and Lennard Jones attraction. The results are in excellent agreement with the previous work on hard spheres by Marshall and Chapman [1], and also with associating Lennard Jones fluid Monte Carlo simulation. We applied the theory to calculate the thermodynamic properties of hydrogen fluoride and the theory predictions are in good agreement with the experimental data. It was found that formation of 6-mer rings and a bond cooperativity ratio of around 1.58 are effective in predicting the enthalpy of vaporization with a higher accuracy compared with the previous SAFT-VR study by Galindo et al.[6]. Extensions on our theory to set the energy of the bonds proportional to the size of the clusters of associated species, studying the cooperativ-



Figure 3.11 : Fraction of hydrogen fluoride molecules not bonded (X_o) , bonded once in a chain $(X_{1b-chain})$, bonded twice in a chain $(X_{2b-chain})$ versus temperature in vapor phase. All theory results.

ity effect in mixtures of associating fluids, and applying the theory to model mixtures of alcohols are the topics of future publications.



Figure 3.12 : Fraction of hydrogen fluoride molecules not bonded (X_o) , bonded once in a chain $(X_{1b-chain})$, bonded twice in a chain $(X_{2b-chain})$ versus temperature in liquid phase. All theory results.

Chapter 4

Combination of Monovalent and Divalent Sites on An Associating Species: Application to Water

4.1 Introduction

TPT1 considers each associating site to saturate after the first bond and associating species form only linear and branched clusters of bonds with similar bonding energies. Although this makes SAFT easy to apply, such simplifying assumptions might be responsible for the challenges the model has in capturing such feature as the maximum in saturated liquid density of water at $4^{\circ}C$ [10], minimum in solubility of alkanes in water [67], and even a maximum in heat of vaporization of Hydrogen Fluoride [4]. In this work we step toward a model that can capture these physics by extending TPT1 beyond such simplifications.

Extensions beyond TPT1 have been the topic of much research in recent years. Kalyuzhnyi et al. [160, 127, 64] and Marshall et al. developed theory to include multiple bonds per site [65, 96, 161, 162, 126, 125], formation of cyclic structures of associated species [14, 156, 130], and cooperative hydrogen bonding [1, 66]. While the results of these theoretical studies have been confirmed by Monte Carlo simulation (MC), the primary motivation has been in modeling patchy colloids [59, 163, 97, 55, 56, 57, 58, 63]. In addition to patchy colloids, one opportunity is to model the oxygen atom of water as a single divalent site which can form two bonds at the same time corresponding to each pair of free electrons. Proposing an accurate perturbation theory for calculating the thermodynamic properties of pure water and its mixtures, has remained a challenge for many years. While in all previous SAFT water models the association contribution is in the TPT1 framework (each site is monovalent and carries the same energy), recently, Marshall has worked out the effect of cooperativity between reference energy and degree of hydrogen bonding [137], and cooperative hydrogen bonding between a hydrogen and oxygen site [27] which follows the cooperativity effects reported by quantum studies [164, 165].

In our current work, we develop a thermodynamic perturbation theory within a multi-density formalism to model associating species with a combination of monovalent and divalent association sites. The model specifically targets water which is represented by a single divalent oxygen site and two monovalent hydrogen sites. First, we test theoretical developments by comparing theory results for a model system with MC simulations. Then, we fit our model's parameters to experimental data on liquid density and vapor pressure [10]. We compare the state of hydrogen bonding in saturated liquid state from our theory with a four-site perturbed chain SAFT (PC-SAFT) model [9, 8] and with molecular dynamics simulations using the iAMOEBA [166], and TIP4P/2005 [167] force field models previously reported by Fouad et al. [11]. We also compare the calculated internal energy of water from our theory with experimental data [10] and PC-SAFT.

4.2 Theory

In this section we develop a perturbation theory for modeling associating fluids with a mixture of monovalent and divalent association sites. We first obtain the Helmholtz free energy contribution due to association, and then we show the validation of the theory versus molecular simulation results. Finally, we apply the theory to the thermodynamic properties of water.

4.2.1 Derivation of Helmholtz free energy of an Associating Fluid with Mixture of Divalent and Monovalent Association Sites

Our work follows the multiple bonding site theory by Marshall and Chapman[65, 125] except that they had only a single divalent site. We limit our theory for the case that one of the sites is divalent, and the rest are monovalent. For the sake of simplicity we call the divalent site an Ox-site and any monovalent site an H-site. The pairwise additive potential of interaction in our system is:

$$\varphi^{(AB)}(12) = \varphi_{segment}(r_{12}) + \sum_{A,B\in\Gamma} \varphi^{(AB)}_{assoc}(12)$$
(4.1)

The notation $(1) = [\vec{r}_1, \Omega_1]$ represents the position \vec{r} and orientation Ω_1 of the sphere 1, and r_{12} is the magnitude of the vector connecting centers of species 1 and 2. $\varphi_{segment}$ is a hard sphere potential that does not allow the segments to overlap with respect to their corresponding hard sphere diameter. Γ is the set of all types of association sites on a species. Bol[123] was the first who introduced a square well potential of interaction for hydrogen bonding, and later Chapman *et al.* [7] used that potential in SAFT. The potential of interaction for association between 1 and 2 is given as:

$$\varphi_{assoc} (12) = \begin{cases} -\varepsilon_{OH} & r_{12} < r_c, \ \theta_{Ox} < \beta_c \ , \ \theta_H < \theta_c \\ 0 & otherwise \end{cases}$$
(4.2)

 r_c is the critical distance between the centers of two patchy colloids beyond which they cannot associate. θ_{Ox} is the angle between $\overrightarrow{r_{12}}$ (vector connecting the centers of 1 and 2) and the vector from the center of the species which is bonding at its Ox-site to the center of its Ox-site, θ_H is defined in a similar way. β_c and θ_c are the



Figure 4.1 : A schematic view of the associating species with one Ox-site and two H-sites. β_c is large enough to form two bonds, and θ_c is small enough that the site saturates by forming only one bond.

critical angles for θ_{Ox} and θ_H , respectively, beyond which association cannot occur. According to equation (4.2) if 1 and 2 are in the positions such that $r_{12} < r_c$, and they are oriented in a way that $\theta_{Ox} < \beta_c$, and $\theta_H < \theta_c$; then, they will associate and the energy of the system will decrease by ε_{OH} . In this work we are not allowing any association between similar sites, $\varepsilon_{HH} = \varepsilon_{OxOx} = 0$. To ensure that any H-site forms only one bond we set $\theta_c = 27^\circ$ and $r_c = 1.1$. Figure 4.1 shows the critical angles of the associating species.

Directly from Wertheim's TPT, the Helmholtz free energy of association in a multi-density formalism [45, 46] is:

$$\frac{A^{assoc}}{Vk_BT} = \rho \ln\left(\frac{\rho_o}{\rho}\right) + \rho + Q - \frac{\Delta c^{(o)}}{V}$$
(4.3)

where ρ is the total number density and ρ_o is the number density of monomers. The



Figure 4.2 : Diagram of associated species corresponding to the first and second order contributions a) Δc_{TPT1} b) Δc_{TPT2} .

term Q is defined as:

$$Q = -\sigma_{\Gamma} + \sum_{\alpha \subset \Gamma} \sigma_{\Gamma-\alpha} c_{\alpha}$$

$$\alpha \subset \Gamma$$

$$\alpha \neq 0$$
(4.4)

The density parameter σ_{α} is defined as:

$$\sigma_{\alpha} = \sum_{\gamma \subset \alpha} \rho_{\gamma} \tag{4.5}$$

where ρ_{γ} is the density of a segment that is bonded at all sites included in the set γ , the improper set ρ_o is included in this sum. And c_{α} in equation (4.4) is defined as

$$c_{\alpha} = \frac{\partial \Delta c^{(o)} / V}{\partial \sigma_{\Gamma - \alpha}} \tag{4.6}$$

 $\Delta c^{(o)}$ is the sum of all irreducible graphs with a single path of association Mayer ffunction bonds between each pair of field points. We assume that association sites are
independent so that bonding at one site does not result in steric hindrance of bonding
at another site. This is most accurate when association sites are widely separated.

Therefore, we limit the graph sum to include only graphs with two and three field points that corresponds to first and second order in perturbation, respectively:

$$\Delta c^{(o)} = \Delta c_{TPT1} + \Delta c_{TPT2} \tag{4.7}$$

Diagrams corresponding to Δc_{TPT1} and Δc_{TPT2} are exhibited in figure 4.2. The first order irreducible graph Δc_{TPT1} which is capable of building any linear and branched cluster is written as:

$$\frac{\Delta c_{TPT1}}{V} = \sum_{i=1\dots n} \frac{\sigma_{\Gamma-H_i} \sigma_{\Gamma-Ox}}{\Omega} \int g_{HS} (12) f_{OH} (12) d(12)$$
(4.8)

n is the number of H sites on a species, $\Omega = 8\pi^2$ is the total number of orientation states it can occupy in orientation space, $g_{HS}(12)$ is the hard sphere pair correlation function, $f_{OH}(12)$ is the Mayer *f*-function of association, and $d(12) = \{\vec{r}_{12}, \Omega_{12}\}$ is the position and orientation vector of particle 2 in a reference coordinate system centered on the center of particle 1. The second order contribution Δc_{TPT2} is written as:

$$\frac{\Delta c_{TPT2}}{V} = \sum_{i=1...n} \sum_{j=1...n} \frac{\sigma_{\Gamma-H_i} \sigma_{\Gamma-O_X} \sigma_{\Gamma-H_j}}{2\Omega^2} \int g_{HS} (123) f_{H_iO} (12) f_{OH_j} (23) d (12) d (23)$$
(4.9)

With the graphs contributing to association determined, equation (4.4) can be written as:

$$Q = -\sigma_{\Gamma} + \sum_{i=1\dots n} \sigma_{\Gamma-H_i} c_{H_i} + \sigma_{\Gamma-Ox} c_{Ox}$$
(4.10)

Here, we define the fraction of segments not bonded at a set of sites α by:

$$X_{\alpha} = \frac{\sigma_{\Gamma - \alpha}}{\sigma_{\Gamma}} \tag{4.11}$$

where according to multi-density formalism each density is defined as:

$$\frac{\rho_{\alpha}}{\rho_o} = \sum_{P(\alpha) = \{\gamma\}} \prod_{\gamma} c_{\gamma} \tag{4.12}$$

 $P(\alpha) = \{\gamma\}$ is the partitioning of α into non-zero sets. The c-terms mentioned above are obtained by taking all ways of turning a field point into a root point in the graphs of equations (4.8) and (4.9):

$$c_{\rm H} = \frac{\sigma_{\Gamma-Ox}}{\Omega} \int g_{HS} (12) f_{OH} (12) d (12) + \sum_{i=1...n} \frac{\sigma_{\Gamma-H_i} \sigma_{\Gamma-Ox}}{\Omega^2} \int g_{HS} (123) f_{H_iO} (12) f_{OH} (23) d (2) d (3)$$
(4.13)

and

$$c_{\text{Ox}} = \sum_{i=1...n} \frac{\sigma_{\Gamma-H_i}}{\Omega} \int g_{HS} (12) f_{OH} (12) d (12) + \sum_{i=1...n} \sum_{j=1...n} \frac{\sigma_{\Gamma-H_i} \sigma_{\Gamma-H_j}}{2\Omega^2} \int g_{HS} (123) f_{H_iO} (12) f_{OH_j} (23) d (12) d (23)$$
(4.14)

Special Case of Two H-sites and One O-site

We take the theory for a special case where there are one Ox-site and two H-sites, and we have four different density factors: ρ_o , $\sigma_{\Gamma-Ox}$, $\sigma_{\Gamma-H_1}$, $\sigma_{\Gamma-H_2}$ and since the bonding at H_1 and H_2 happens randomly, a reasonable approximation is to say $\sigma_{\Gamma-H_1} = \sigma_{\Gamma-H_2}$. These densities are obtained from the following equations which are equivalent to the minimization of the association Helmholtz free energy with respect to each density. According to the definition in equation (4.11):

$$\frac{1}{X_o} = 1 + c_{H_1} + c_{H_2} + c_{Ox} + c_{H_1}c_{H_2} + c_{H_1}c_{Ox} + c_{H_2}c_{Ox} + c_{H_1}c_{H_2}c_{Ox}$$
(4.15)

$$X_{Ox} = X_o \left[1 + c_{H_1} + c_{H_2} + c_{H_1} c_{H_2} \right]$$
(4.16)

$$X_{H_1} = X_o \left[1 + c_{H_2} + c_{Ox} + c_{Ox} c_{H_2} \right]$$
(4.17)

Now, to obtain the c-terms and calculate the fractions, the integrals of association contributions need to be solved. To calculate the first term on the right hand side of (RHS) of equation (4.13) we start with approximating the radial distribution function



Figure 4.3 : Model of a water molecule. Oxygen atom is represented as a divalent site, and hydrogen atoms are monovalent such as modeled in typical SAFT [7, 8, 9].



Figure 4.4 : Cluster of associated water molecules exhibiting the cooperativity in hydrogen bonding.

for which we follow the Chapman's approximation[7] that allows us to estimate the pair correlation function at the association range (from d to r_c) by:

$$r^{2}g(r) = d^{2}g(d) \tag{4.18}$$

and from there the integral of the first order will be simplified to:

$$\frac{\Delta c_{TPT1}}{V} = (\sigma_{\Gamma-Ox}\sigma_{\Gamma-H_1} + \sigma_{\Gamma-Ox}\sigma_{\Gamma-H_2})\Theta_{TPT1}$$
(4.19)

In this integral we fix particle 1 at the center of coordinate system and particle 2 can just occupy the position and orientations allowed for associating to 1. Particle 2 will have the volume element $r_{12}^2 dr_{12} d\cos \theta_{12} d\varphi_{12}$ and the orientation element $d\cos \theta'_2 d\varphi_{12} d\gamma_{12}$ then the integral is simplified to:

$$\Theta_{\text{TPT1}} = f_{OH}g_{HS}\left(d\right)d^{2}\left(r_{c}-d\right)4\pi\kappa_{OH}$$

$$(4.20)$$

In equation above, $\kappa_{OH} = (\cos\beta_c - 1) (\cos\theta_c - 1)/4$ is the probability of finding two spheres oriented sufficiently in a way they can form a bond. To obtain the three body correlation function in the second order contribution, we follow the superposition proposed by Marshall and Chapman[65]:

$$g_{HS}(123) = e_{HS}(12) e_{HS}(23) e_{HS}(13) y_{HS}(123)$$
(4.21)

 y_{HS} (123), the three body cavity correlation function will be determined using the results of the work by Muller and Gubbins[168]:

$$y_{HS}(123) = y_{HS}(12) y_{HS}(23) y_o(123)$$
(4.22)

 $y_{o}(123)$ is approximated by its value at rolling contact:

$$y_o(123) \approx y_o(d, d, 2\sin(\varpi/2)) \equiv y_o(\varpi) \tag{4.23}$$

Here ϖ refers to the average angle between two vectors connecting the centers of two species whose H-sites are bonded to the Ox-sites of a third species. $y_o(\varpi)$ is:

$$y_o(\varpi) = \frac{1 + a_{\varpi}\eta + b_{\varpi}\eta^2}{(1 - \eta)^3}$$
 (4.24)

The constants a_{ϖ} and b_{ϖ} are tabulated in the work by Muller and Gubbins[168] for different angles, and the two-body cavity correlation function is approximated by the same approximation in equation (4.18). Following similar simplification as we did for the first order term we have:

$$\frac{\Delta c_{TPT2}}{V} = \left(\sigma_{\Gamma-Ox}\sigma_{\Gamma-H_1}^2/2 + \sigma_{\Gamma-H_1}\sigma_{\Gamma-Ox}\sigma_{\Gamma-H_2} + \sigma_{\Gamma-Ox}\sigma_{\Gamma-H_2}^2/2\right)I_{TPT2} \quad (4.25)$$

$$I_{\text{TPT2}} = \frac{1}{\Omega^2} \int g_{HS} (123) f_{H_iO} (12) f_{OH_j} (23) d(12) d(23)$$
(4.26)

According to the available bonding volume, and proper orientation for association between two H-sites from two species to an Ox-site on another species, I_{TPT2} is simplified in the following way:

$$I_{\text{TPT2}} = \frac{f_{OH_2}^2}{\Omega^2} \left(g_{HS} \left(d \right) d^2 \kappa_{OH} \upsilon_b \Omega \right)^2 y_o \left(\varpi \right) \Phi_{TPT2}$$
(4.27)

where Φ_{TPT2} stands for the sum of all possible configuration of forming a three body chain as Δc_{TPT2} , and $v_b = 4\pi d^2 (r_c - d)$. Also, in this equation the pair correlation function at contact is used instead of cavity correlation function since at association range $e_{HS} = 1$. Values for Φ_{TPT2} with respect to β_c are reported by Marshall and Chapman [15] using a Monte Carlo integration method.

$$\Phi_{TPT2} = \frac{1}{\left(\kappa_{OH}\upsilon_{b}\Omega\right)^{2}} \int O_{OH}\left(12\right) O_{OH}\left(23\right) e_{HS}\left(12\right) e_{HS}\left(23\right) e_{HS}\left(13\right) d\left(2\right) d\left(3\right)$$
(4.28)

Finally, combining equations (4.6), (4.13), (4.19), and (4.25) we obtain:

$$c_{H_1} = \sigma_{\Gamma - Ox} \Theta_{TPT1} + (\sigma_{\Gamma - Ox} \sigma_{\Gamma - H_1} + \sigma_{\Gamma - Ox} \sigma_{\Gamma - H_2}) I_{TPT2}$$
(4.29)

$$c_{Ox} = (\sigma_{\Gamma-H_1} + \sigma_{\Gamma-H_2}) \Theta_{TPT1} + (\sigma_{\Gamma-H_1}^2/2 + \sigma_{\Gamma-H_1}\sigma_{\Gamma-H_2} + \sigma_{\Gamma-H_2}^2/2) I_{TPT2} \quad (4.30)$$

RHS of equation (4.30) is the sum of both single and double bonding irreducible graphs of oxygen site. The first term on RHS corresponds to single bonding (c_{Ox1}) , and the second term corresponds to double bonding (c_{Ox2}) as shown in equation (4.31). Now, by plugging equations (4.29) and (4.30) into (4.15), (4.16), and (4.17) the fractions are calculated. The fraction of k-times bonded species also obtained as follow:

$$c_{Ox} = c_{Ox1} + c_{Ox2} \tag{4.31}$$

$$X_1 = X_o \left(2c_H + c_{Ox1} \right) \tag{4.32}$$

$$X_2 = X_o \left(c_H c_H + 2c_H c_{Ox1} + c_{Ox2} \right) \tag{4.33}$$

$$X_3 = X_o \left(c_H c_H c_{Ox1} + 2c_H c_{Ox2} \right) \tag{4.34}$$

$$X_4 = X_o \left(c_H c_H c_{Ox2} \right) \tag{4.35}$$

Helmholtz free energy and other thermodynamic properties like chemical potential, pressure and internal energy are easily obtained as shown in the Appendix B.

4.2.2 Theory versus Monte Carlo Simulation

We performed MC simulations over 256 particles in an NVT ensemble. After equilibration, the results are obtained by averaging over each 256×10^6 trial moves after the system reaches equilibrium (a trial move includes an attempt to relocate and reorient an associating species). The range of the association potential is set as $r_c = 1.1d$, and the acceptance ratio is ≈ 0.4 . The energy of association for every bond type is similar and there is no bond cooperativity, in the simulation results.

We begin with plotting the fractions of k-times bonded species. Based on the theory developed in the previous section, each species can bond one to four times.

We denote fractions of species non-bonded: X_o , bonded once: X_1 , bonded twice: X_2 , bonded three-times: X_3 , bonded four-times: X_4 . Figure 4.5 presents how the amount of association in the system varies with respect to the oxygen site angular size, β_c , for two different reduced number densities ($\rho d^3 = \rho^*$) with a fixed reduced association energy $(\varepsilon_{OH}/k_BT = \varepsilon_{OH}^* = 8)$. The points are simulation results and curves are results from theory. Focusing on the plots, when β_c increases, the bond volume of the site enlarges leading to higher chances of bond formation. At $\beta_c = 30^{\circ}$, X_4 is almost zero because the site is barely large enough to form more than one bond. For β_c smaller than 30°, the model reduces to TPT1 with three sites. In the left panel, since the density is low ($\rho^* = 0.2$), the probability of finding species in the proper orientations and positions to form bonds is not very high; therefore, at large β_c , X_3 is still greater than X₄. At this density, X₂ reaches a maximum around $\beta_c = 34^{\circ}$ because as β_c grows, the chance of multiple association at the Ox-site increases. Comparing the plots in figure 4.5 one can observe the effect of density on association. The monomer fraction is not plotted at $\rho^* = 0.6$ since it was negligible. At this density, increasing β_c causes a monotonic increase in the fraction of 4-time bonded species, while X_1 and X_2 continuously decreases with growing β_c . Agreement with simulation is very good at both densities. Observing the variations happening in X_k with changing β_c brings us to an interesting discussion about the impact of using such theory versus a simple three or four-site TPT1 [11]. Therefore, we compare current theory with a four-site TPT1 (two H-site and two Ox-site) at which the H-sites will have the same sizes in both models, but each Ox-sites has a half the bonding volume of the divalent Ox-site in the current theory. We start with noting the similarities and dissimilarities between the two theories in their predictions of fractions of k-times bonded species in figure 4.6. Although, at small β_c 's, the results are very different, in larger angles they



Figure 4.5 : Fractions of k-times bonded species at reduced association energy of $(\varepsilon/k_BT = 8)$ and two densities as a function of oxygen site critical bond angle. Solid lines present current theory results, and symbols show MC simulation results (lines and symbols:: X_o : purple circle; X_1 : light blue plus; X_2 : green diamonds; X_3 : red triangle; X_4 : dark blue squares)



Figure 4.6 : Fraction of k-times bonded beads versus the size of divalent site at $\rho^* = 0.6$ and $\varepsilon_{OH}/k_BT = 8.0$. Solid lines present current theory results, and dash lines show TPT1's results (X₁: light blue; X₂: green; X₃: red; X₄: dark blue)



Figure 4.7 : Reduced internal energy due to association versus β_c for $\varepsilon_{OH}/k_BT = 8.0$ (Solid line: current theory, Dash line: TPT1; Symbol: MC simulation).

tend to converge to the similar values. The key point is that at small β_c 's, our theory reduces to a three-site TPT1 model since the steric hindrance restricts the formation of two bonds at the Ox-site, while in larger β_c 's the steric hindrance loses its importance, and the theory acts like a four-site model. Another way to examine the model differences is to consider the excess internal energy of the system. U^{ASSOC}/Nk_BT is calculated (see Appendix B) and plotted for each density versus the critical angle β_c using both theories. According to the results in figure 4.7 we see that TPT1 model predicts more association at each density (due to greater amount of U^{ASSOC}/Nk_BT) compared with our theory. At large β_c both converge to similar results.

Having validated the theory, we now consider the application to water.

4.2.3 Application to water

In this section we show the applicability of our theory with hard sphere reference fluid to calculate the thermodynamic properties of water. The total Helmholtz free energy is composed of the following contributions:

$$\frac{A}{Nk_BT} = \frac{A^{ID}}{Nk_BT} + \frac{A^{HS}}{Nk_BT} + \frac{A^{DISP}}{Nk_BT} + \frac{A^{ASSOC}}{Nk_BT}$$
(4.36)

where A^{ID} , A^{HS} , A^{DISP} , and A^{ASSOC} are the ideal gas, hard sphere, dispersion and association contributions to the free energy, respectively. The ideal term is exactly known from statistical mechanics, we use the hard sphere term by Boublik [158] and Mansoori et al. [159], and dispersion term by Gross and Sadowski [8, 9] which is used in PC-SAFT.

Modeling a water molecule with a combination of divalent and monovalent association sites, as depicted in figure 4.3, provides the opportunity to include more details in the model. In our model, the oxygen atom is represented by one divalent site which can form up to two hydrogen bonds. In previous studies on water, Marshall [137, 27] emphasized going beyond models that consider similar bond volume and hydrogen bonding energy for all association sites. Here, we propose an asymmetric structure for water where even the energies of the bonds may change due to the bonding status of the molecule.

In our model, the divalent site on oxygen represents the two lone pairs of electrons. In addition, one might expect a different distribution of electrons for an oxygen that is bonded once compared with when it is bonded twice. Therefore, as shown in figure 4.4, in the case where an oxygen site forms only one bond we assign $\varepsilon_{OH}^{(1)}$, and for the case where there are two bonds at the same time the energy of each bond is $\varepsilon_{OH}^{(2)}$. Accordingly, the Mayer *f*-functions in Δc_{TPT1} and Δc_{TPT2} will be $f_{OH}^{(1)} = \exp\left(\varepsilon_{OH}^{(1)}/k_BT\right) - 1$ and $f_{OH}^{(2)} = \exp\left(\varepsilon_{OH}^{(2)}/k_BT\right) - 1$, respectively. Since Δc_{TPT2} involves introducing a value for β_c , we simply assign a large value (from ref. [15]) that can comfortably allow the sites to form two bonds. So, we set $\beta_c = 46^\circ$, and the constants in equation (4.24) are reported in table 4.1.



Table 4.1 : The constants of equation (4.24), and orientation factor (Equation (4.28)) for the choice of $\beta_c = 46^{\circ}$ [15].

4.3 **Results and Discussions**

We fit our model parameters with the consideration of bond cooperativity $\left(\sigma, \kappa, \varepsilon/k_B, \varepsilon_{OH}^{(1)}/k_B, \varepsilon_{OH}^{(2)}/k_B\right)$ to experimental data[10] of liquid density and vapor pressure. Relations for the chemical potential, pressure, and internal energy for the model are presented in Appendix B. The fitted parameters and $ADD\% \left(ADD\% = \frac{|R_{exp} - R_{theory}|}{R_{exp}} \times 1 \right)$ where R is vapor pressure or liquid density, are reported in Table 4.2 and 4.3, respectively. We also fit the PC-SAFT equation of state [8, 9] parameters ($\sigma, \kappa, \varepsilon/k_B, \varepsilon_{OH}/k_B$) to the same experimental data [10] assuming four independent association sites, where ε_{OH}/k_B is the association energy in PC-SAFT, and report the parameters in Tables 4.4 and 4.5.

The values of the hydrogen bonding energies in our theory are such that $\varepsilon_{OH}^{(1)}/k_B >$

Parameters	Values
σ	3.08A
m	1
κ	0.054
ε/k_B	340
$\varepsilon_{OH}^{(1)} / k_B$	1755
$\varepsilon_{OH}^{(2)} / k_B$	1563

Table 4.2 : Parameters of current theory fitted to liquid density and vapor pressure within the temperature range 273K to 528K.

Properties	ADD%
$ ho_L$	3.55
Р	0.65

Table 4.3: ADD% for comparing current theory results and experimental data[10] on liquid density and vapor pressure of water.

Parameters	Values
σ	3.0847A
m	1
ĸ	0.03147
ε/k_B	339.5
ε_{OH}/k_B	1538.3

Table 4.4 : Parameters of PC-SAFT fitted for liquid density, vapor density and vapor pressure within the temperature range 273K to 528K.

Properties	ADD%
ρ_L	4.48
Р	0.5

Table 4.5: ADD% for comparing four-site PC-SAFT results and experimental data[10] on liquid density and vapor pressure of water.



Figure 4.8: Internal energy of pure water in liquid and vapor phase with the reference of saturated liquid at T=273K; lines are theory calculations, and symbols are from experimental data[10].

 $\varepsilon_{OH}^{(2)}/k_B$ which is considered as negative cooperativity [137]. This is consistent with Kumar and Skinner [68] results where they introduced the situation of open trimer clusters of water molecules in which one molecule is a double donor (two bonds at hydrogen atoms) or acceptor (two bonds at the oxygen atom) as the case of anticooperativity. Comparing our association energies $(\varepsilon_{OH}^{(2)}/k_B, \varepsilon_{OH}^{(1)}/k_B)$ with Marshall's water model [27] we see that both energies and their ratio are close to Marshall's model, although his model describes the positive cooperativity that occurs for an open trimer cluster water molecules where one molecule is a donor and acceptro at the same time. Also, the average value $(\varepsilon_{OH}^{(1)}k_B + \varepsilon_{OH}^{(2)}k_B)/2 = 1659K$ is very close to the association energy reported by Wael *et. al.*[11] that is 1631.6K. In addition to the association energies, the bond volume parameter κ obtained in fitting process is similar to what is shown by Marshall [27, 137]. We compare our parameters to PC-SAFT with four association sites where σ and ε/k_B are similar for both theories, and the association energy of PC-SAFT, ε_{OH}/k_B , is very close to $\varepsilon_{OH}^{(2)}/k_B$ in our theory.

The calculated saturated vapor and liquid densities, and vapor pressure from the current theory along with experimental data [10] are plotted in figures 4.9 and 4.10. Internal energy of pure saturated water calculated from our theory and four-site PC-SAFT and measured by experiments [10] are plotted in figures 4.8. The reference for energy calculations is consistent with experiment which is saturated liquid water at 273K, and we simply observe the agreement between our theory and experiments is better than PC-SAFT in the vapor phase. To better understand the reason behind the better performance of our theory on internal energy in vapor phase we calculate the vapor density from both theories and compare it with experiments [10] where our theory gives $ADD\% \approx 5.69$ and PC-SAFT $ADD\% \approx 6.04$. Since our theory agrees better with experiments in vapor phase density, it predicts the amount of hydrogen bonding in vapor phase more accurately; therefore, the change in energy of the fluid from the reference state is more precisely calculated.

Although, the general agreement between theory and experimental measurements is good, the maximum in liquid density observed in experimental data is not reproduced by our theory. We believe that the maximum in liquid density is related to the density and temperature dependence of hydrogen bonding. In particular, geometric constraints appear to require a reduction in density in order to increase the number of hydrogen bonds. A more subtle effect that has also been suggested as responsible for the density maximum is a decrease in available bond volume with decreasing temperature [169]. To explore how well the current model predicts hydrogen



Figure 4.9 : Saturated liquid and vapor density of pure water; sold lines are theory calculations, and symbols are experimental data[10].



Figure 4.10 : Saturated vapor pressure of pure water; sold lines are theory calculations, and symbols are experimental data[10].



Figure 4.11 : Fractions of k-times bonded water molecules in saturated liquid water from current theory, MD simulation TIP4P/2005 and iAMOEBA models [11], four-site water model PC-SAFT[11], and Luck's data on monomer fraction[12].
bonding in saturated liquid water, in figure 4.11 we compare the theoretical results with experimental data and molecular simulation results. It is observed that the current theory agrees with Lucks [12] data on monomer fraction which is similar to the molecular simulation results with the iAMOEBA force field [166] that is one of the better models for liquid water. In general, the fraction of water molecules bonded k times, X_k , from the current theory is closer to iAMOEBA results than to simulations using TIP4P/2005 [167], one of the best force fields for water properties. We also show results for PC-SAFT using a water model with four independent association sites that lack bond cooperativity. As shown by both theories and simulation in figure 4.11, X_3 shows a maximum on increasing temperature from 300K to 500K. This transition is shown qualitatively by the current model and by PC-SAFT. At low temperatures, the ratio of association energy to $k_B T$ is high and most water molecules are bonded three or four times with the fraction bonded four times monotonically decreasing with increasing temperature. At high temperatures, the ratio of association energy to $k_B T$ is low so that water molecules tend to be either once or twice bonded. This transition results in a maximum in X_3 . The two simulation models produce qualitatively similar results. Given that the theories produce lower monomer fractions than iAMOEBA, we expect that the theories will produce higher fractions bonded in each case. This is true for the current theory except for the fraction bonded four times. This is a consequence of our bond cooperativity and the competition between the oxygen site bonding once or twice. On the other hand, the PC-SAFT model without bond cooperativity agrees more closely with iAMOEBA results, but over-estimates the fraction bonded four times except at high temperatures.

4.4 Conclusion

We developed an asymmetric model in multi-density formalism framework where an associating species has a combination of monovalent and divalent sites. We verified our theory by comparing theory results on extent of association, and excess internal energy of the fluid with corresponding MC simulations, and the agreement was excellent. To observe the effect of implementing a divalent site instead of two monovalent sites, we compared the current theory results with corresponding four-site model using TPT1 and we found that at the limit of associating sites with large bonding volumes both theories converge to similar results.

We applied the theory to calculate the thermo-physical properties of water, since the oxygen atom can be considered as a single association site with two available pairs of free electrons to share for two hydrogen bonds, and fitted the model's parameters to experimental data on liquid density and vapor pressure. The calculated thermodynamic properties of water in saturated phases are in a good agreement with experimental data, and an improvement is observed when comparing theory results with PC-SAFT four-site equation of state. The great advantage of such theory is the flexibility it carries by allowing a user to vary the hydrogen bonding energies with respect to the state of hydrogen bonding, and also tuning the geometry of the divalent site to obtain a more accurate model. These are all additional flexibilities compared with PC-SAFT and generally any SAFT version equation of state.

The current theory represents water molecules as asymmetric associating species where the energy of hydrogen bonding is determined by the state of bonding of molecules. The authors believe that there is still room for improving the model specifically by testing the theory for water using a Lennard Jones reference fluid which is the topic of a future publication. In addition, application of the model for mixtures of water/alkanes and water/alcohols are subjects of future studies.

Chapter 5

A Density Functional Theory for Colloids with Two Multiple Bonding Associating Sites

5.1 Introduction

Recent papers have extended the theory for associating fluids beyond Wertheims TPT to a level that removes the limitations [64, 127, 128, 65, 96, 126, 125]. While the focus of most of these studies is on homogenous fluids, in current work, we extend the theory beyond Wertheims TPT for an inhomogeneous fluid. We specifically consider an inhomogeneous colloidal fluid in which each colloid has two association sites that can each form two bonds.

Chapman [7] proposed a density functional theory (DFT) framework to extend Wertheims first order TPT (TPT1) to inhomogeneous fluids. To describe hard spheres with multiple association sites, the hard sphere contribution is calculated either by Rosenfelds Fundamental Measure Theory (FMT) [69], or Tarazonas weighted density approach [70]. Segura et al. [48] considered two different approaches to the association free energy functional. In the first method, the free energy functional is derived within TPT1. In the second approach, the bulk form of TPT1 is used for inhomogeneous fluids using weighted densities. Both approaches have shown promising results in various DFT applications [48, 71, 72, 73, 74]. In addition to associating spherical molecules, both forms of the DFT proposed by Segura, et al. have been extended to model polymers and associating polyatomic molecules [48, 71, 73, 75, 76, 77, 78, 79, 80]. The DFT has found extensive application in studying interfacial phenomena and phase behavior of associating polyatomic fluids in confined systems or close to interfaces by Tripathi and Chapman [74, 76, 49] and Bymaster and Chapman [72]. Further, using weighted densities or FMT with the bulk association free energy has found application for associating molecules in a variety of publications by Segura and Chapman [48, 81, 82, 83], Sokolowski et al.[84, 85, 86, 87, 88, 89, 90, 91, 92, 93, 94], Wu et al. [71, 80, 95].

Similar to hydrogen bonding fluids, patchy colloids have strong, orientation dependent, short-range attractions. These colloids are synthesized through different methods; for example, glancing angle deposition [97, 55, 56], polymer swelling [57], stamping DNA [58] to the surface of the colloid, etc. Due to their reversible bottom up design, patchy colloids show promise to be synthesized to present a set of predetermined properties, and to be utilized in a wide range of applications, like 3-D photonic crystals [163], empty liquids [63, 170], self-healing materials [61], and modeling of protein phase behavior [171, 172]. Kern and Frenkel [124] applied the square well potential model for association proposed by Bol [123] to the patch-patch interactions in patchy colloidal fluids. Wertheims TPT is proven to be a practical theory for the patchy particle systems because it can capture the anisotropic attractions between patches and bond saturation effectively. Targeting these interactive systems, researchers were successful in extending the theory beyond the constraint of Wertheims TPT. Kalyuzhnyi et al. [127, 128] included formation of multiple bonds per patch using a multi-density formalism [160], that allows species with a single patch to form long chains. Later, Marshall and Chapman (MA) realized that at low temperatures closed loop structures become important, so they included the effect of self-assembled ring structures in both homogenous [65] and inhomogeneous fluids near an interface [96]. Moreover, MA promoted the multi-bonding per site theory to the ultimate case where a patch covers the whole surface of a colloid. This model allows the spherical patchy colloid to interact with another single [126] or multi-patch [125] particle that results in assembling of star polymers. Additional effects such as the impact of the angle between association sites on cluster formation [14, 130]; reentrant phase behavior of fluids with two multi-time bonding patches [64]; and bond cooperativity in hydrogen bonding fluids [1, 66] are the other extensions introduced that go beyond Wertheims TPT.

In this chapter, we extend Wertheims TPT for a patchy colloidal system with two patches, each able to form a maximum of two bonds. The theory is developed in a density functional form to predict the fluid behavior between planar hard walls. Marshall and Chapman [65] developed the theory for confined colloids with a single association site that could bond twice; this work extends this model to allow two multiple bonding sites. The association model allowing multiple bonds leads to a competition between chains and rings. We plot the theory predictions for the density profile and fractions of species with different numbers of bonds versus the distance from one wall. The results are verified with Monte Carlo simulation. In section II the theory and model are developed. In section III results are presented, and the conclusions are provided in section IV.

5.2 Model and Theory

In this section we develop an equation of state for a fluid of particles with two identical associating sites, where each can form more than one bond. The theory predicts the extent of association in a pore using a density functional theory approach. The potential of interaction between a pair of colloids is a sum of hard sphere and association interactions:

$$\varphi(12) = \varphi_{HS}(12) + \varphi_{AA}(12) \tag{5.1}$$

The notation $(1) \equiv [\vec{r_1}, \Omega_1]$ stands for position $[(\vec{r_1})$ and orientation (Ω_1) vectors of colloid 1. $\varphi_{HS}(12)$ is the hard sphere potential and is written as:

$$\varphi_{HS}(12) = \begin{cases} \infty, & r_{12} < d \\ 0, & otherwise \end{cases}$$
(5.2)

 r_{12} indicates the distance between centers of colloids 1 and 2, and d is the diameter of a colloid. The association potential is a square well potential (as shown in figure 5.1) that requires two square well sites to be close enough to each other and in the correct orientation to form a bond of energy $-\varepsilon_{AA}$. This can be written as:

$$\varphi_{AA}(12) = \begin{cases} -\varepsilon_{AA}, & r_{12} \leq r_c, \ \theta_{A(1)} \leq \theta_c, \ \theta_{A(2)} \leq \theta_c \\ 0, & otherwise \end{cases}$$
(5.3)

where, r_c and θ_c are the critical distance and angle of association, respectively, beyond which association cannot happen. $\theta_{A(1)}$ is the angle between the vector connecting centers of colloids 1 and 2, and the vector from the center of colloid 1 to the center of its site, A ($\theta_{A(2)}$ is defined in the similar way). We set the critical angle θ_c at 35 degrees that allows for the formation of two bonds in maximum [96]. In this work the colloids have two association sites with centers located 180 degree from each other. Association can happen between any pair of sites, and the energy of association is the same for every bond formed.

In the density functional theory framework, the density profile at equilibrium is obtained by minimizing the grand free energy with respect to density $\rho(\vec{r})$ of a species:



Figure 5.1 : Schematic view of an associating species in the fluid; the sites are similar and no restriction is imposed on the association between sites.



Figure 5.2 : Schematic view of the contributions in $\Delta c^{(o)}$, a) first order dimer, b) twice-bonding sites in form of rings, c) twice-bonding sites in form of chain.

$$\frac{\delta\Theta\left[\rho\left(\vec{r}\right)\right]}{\delta\rho\left(\vec{r}\right)}\Big|_{\rho=\rho_{eq}} = 0$$
(5.4)

where ρ_{eq} is the density profile at equilibrium, and by definition the grand free energy is:

$$\Theta\left[\rho\left(\vec{r}\right)\right] = A\left[\rho\left(\vec{r}\right)\right] + \int \rho\left(\vec{r}\right)\left(V_{ext}\left(\vec{r}\right) - \mu\right)d\vec{r}$$
(5.5)

where $A[\rho(\vec{r})]$ is the Helmholtz free energy functional, V_{ext} is the external field applied to the fluid, and is the chemical potential of the bulk fluid. The Helmholtz free energy includes three contributions: the ideal, hard sphere, and association contributions:

$$A[\rho(\vec{r})] = k_B T \int \rho(\vec{r}) (ln\rho(\vec{r}) - 1) d\vec{r} + A^{HS}[\rho(\vec{r})] + A^{ASSOC}[\rho(\vec{r})]$$
(5.6)

The first term in equation 5.6 is the ideal contribution which is known exactly from statistical mechanics. k_B is the Boltzmanns constant and T is the temperature. The second term is the Helmholtz free energy of the hard sphere fluid from the White Bear [173] version of fundamental measure theory [69, 174]. And using Wertheims multi-density formalism [45, 46], the association Helmholtz free energy functional A^{ASSOC} is written as:

$$\frac{A^{ASSOC}}{k_B T} = \int d(1) \left(\rho(1) \ln \frac{\rho_o(1)}{\rho(1)} + \rho(1) + Q(1) \right) - \Delta c^{(o)}$$
(5.7)

 $\rho(1)$ and $\rho_o(1)$ are the total number density and the monomer density of particles at position 1. The term $\Delta c^{(o)}$ is the sum of all irreducible graphs with a single path of association bonds between each pair of points. As will be described in this section, $\Delta c^{(o)}$ includes graphs of dimers, and twice bonded sites in the form of three-body chains and three-body rings [96]. The term Q is defined as:

$$(1) = -\sigma_{\Gamma}(1) + \sum_{\alpha \subset \Gamma} \sigma_{\Gamma-\alpha}(1) c_{\alpha}(1)$$

$$\alpha \subset \Gamma$$

$$\alpha \neq 0$$
(5.8)

where, Γ is the set of all associating sites on one colloid, and the density parameter $\sigma_{\Gamma-\alpha}$ is defined as the density of colloids not bonded at the set of sites α , and in general σ_{β} (the density of species bonded at the set of site β) is:

$$\sigma_{\beta}\left(1\right) = \sum_{\gamma \subset \beta} \rho_{\gamma}\left(1\right) \tag{5.9}$$

where ρ_{γ} is the density of segments that are bonded at all sites included in the set γ , the improper set ρ_o is included in this sum. The derivatives of $\Delta c^{(o)}$ with respect to density parameters are written by Wertheim as:

$$c_{\alpha}\left(1\right) = \frac{\partial \Delta c^{(o)}}{\partial \sigma_{\Gamma-\alpha}\left(1\right)} \tag{5.10}$$

Using the terms we have introduced, the Helmholtz free energy of association for our potential model with association sites A_1 and A_2 can be written as:

$$\frac{A^{ASSOC}}{k_B T} = \int d(1) \left(\rho(1) \ln \frac{\rho_o(1)}{\rho(1)} + \rho(1) - \sigma_{A_1}(1) - \sigma_{A_2}(1) + \frac{\sigma_{A_1}(1) \sigma_{A_2}(1)}{\rho_o(1)} \right) - \Delta c^{(o)}$$
(5.11)

where σ_{A_1} is the density parameter for the association site A_1 (σ_{A_2} is defined in the similar way), $\Delta c^{(o)}$ is the sum over chain and ring contributions:

$$\Delta c^{(o)} = \Delta c_{chain} + \Delta c_{ring} \tag{5.12}$$

We approximate the chain term as a sum of dimer and trimer chain contributions. Within this approximation only two-body and three-body correlation functions are included; dimer and trimer chains are the most accurate, but all linear and branched chain lengths are included in this level of approximation:

$$\Delta c_{chain} = \Delta c_{TPT1} + \Delta c_{TPT2} \tag{5.13}$$

The chain and ring contributions are schematically shown in figure 5.2. Each contribution in equations 5.12 and 5.13 is defined in the following way:

$$\Delta c_{TPT1} = \sum_{i=1,2} \sum_{j=1,2} \frac{1}{2} \int \sigma_{\Gamma-A_i}(1) \,\sigma_{\Gamma-A_j}(2) \,y_{HS}(12) \,f_{AA}(12) \,d(1) \,d(2) \tag{5.14}$$

$$\Delta c_{TPT2} = \sum_{i=1,2} \sum_{j=1,2} \sum_{k=1,2} \frac{1}{2} \int \sigma_{\Gamma-A_i} (1) \sigma_{\Gamma-A_j} (2) \sigma_{\Gamma-A_k} (3) y_{chain} (123) \dots$$

$$f_{A_i A_j} (12) f_{A_j A_k} (23) d (1) d (2) d (3)$$
(5.15)

$$\Delta c_{ring} = \sum_{i=1,2} \sum_{j=1,2} \sum_{k=1,2} \frac{1}{6} \int \sigma_{\Gamma-A_i} (1) \sigma_{\Gamma-A_j} (2) \sigma_{\Gamma-A_k} (3) y_{ring} (123) \dots f_{A_i A_j} (12) f_{A_i A_k} (13) f_{A_j A_k} (23) d(1) d(2) d(3)$$
(5.16)

By definition, the Mayer *f*-function for the association is $f_{A_iA_j}(12) = \exp(\varphi_{A_iA_j}(12)/k_BT) -$ 1. Each contribution includes a sum over all possible configurations of association. Since the associating sites are similar, we can use $f_{AA}(12)$ instead of $f_{A_iA_j}(12)$. $y_{HS}(12), y_{chain}(123)$ and $y_{ring}(123)$ are the two-body, three-body chain and threebody ring cavity correlation functions, respectively. By minimizing A^{ASSOC} with respect to the density factors we obtain:

$$1 - \frac{\sigma_{A_2}(1)}{\rho_o(1)} = -\frac{\delta \Delta c^{(o)}}{\delta \sigma_{A_1}(1)}$$
(5.17)

$$\frac{\rho(1)}{\rho_o(1)} - \frac{\sigma_{A_1}(1)\,\sigma_{A_2}(1)}{\rho_o(1)^2} = \frac{\delta\Delta c^{(o)}}{\delta\rho_o(1)} \tag{5.18}$$

Defining the fractions of beads not bonded at a set of sites α as:

$$M_{\alpha}(1) = \sigma_{\Gamma-\alpha}(1) / \sigma_{\Gamma}(1)$$
(5.19)

One needs to calculate the c-terms to evaluate the density factors. According to equation 5.10 the c-terms for each site are functions of orientation and position. Segura et al. [48, 168] showed that angle average of this function provides good agreement with molecular simulation of confined fluids. We ignore the angular dependence and divide the c-terms among the following four different states of bonding; bonded once at first order, bonded once at second order, bonded twice at second order and bonded in a ring. These terms are written as follows:

$$c_{A_{1}}\left(\vec{r}_{1}\right) = c_{A_{1}}^{T1}\left(\vec{r}_{1}\right) + c_{A_{1}}^{T2(1)}\left(\vec{r}_{1}\right) + c_{A_{1}}^{T2(2)}\left(\vec{r}_{1}\right) + c_{A_{1}}^{T(ring)}\left(\vec{r}_{1}\right)$$
(5.20)

$$c_{A_1}^{T1}\left(\vec{r}_1\right) = \sum_{j=1,2} \int \sigma_{\Gamma-A_j}(2) y_{HS}(12) f_{AA}(12) d(2)$$
(5.21)

$$c_{A_1}^{T2(1)}\left(\vec{r}_1\right) = \sum_{j=1,2} \sum_{k=1,2} \int \sigma_{\Gamma-A_j}(2) \sigma_{\Gamma-A_k}(3) y_{chain}(123) f_{AA}(12) f_{AA}(23) d(2) d(3)$$
(5.22)

$$c_{A_{1}}^{T2(1)}\left(\vec{r}_{1}\right) = \sum_{j=1,2} \sum_{k=1,2} \frac{1}{2} \int \sigma_{\Gamma-A_{j}}(2) \sigma_{\Gamma-A_{k}}(3) y_{chain}(123) f_{AA}(12) f_{AA}(23) d(2) d(3)$$
(5.23)

$$c_{A_{1}}^{T(ring)}\left(\vec{r}_{1}\right) = \sum_{j=1,2} \sum_{k=1,2} \int \sigma_{\Gamma-A_{j}}(2) \sigma_{\Gamma-A_{k}}(3) y_{ring}(123) f_{AA}(12) f_{AA}(23) f_{AA}(31) d(2) d(3)$$
(5.24)

The terms $c_{A_1}^{T_1}$, $c_{A_1}^{T_2(1)}$, $c_{A_1}^{T_2(2)}$, and $c_{A_1}^{T(ring)}$ are the derivatives of Δc_{TPT1} , Δc_{TPT2} at the end segment, Δc_{TPT2} at the middle segment, and Δc_{ring} , respectively. A similar set of equations is considered for c_{A_2} . Combining bonding states derivatives, different fractions of species are calculated. Accordingly, the fractions of k-times bonded colloids divided by the monomer fractions are obtained:

$$\frac{X_1\left(\vec{r}_1\right)}{X_o\left(\vec{r}_1\right)} = c_{A_1}^{T1}\left(\vec{r}_1\right) + c_{A_2}^{T1}\left(\vec{r}_1\right) + c_{A_1}^{T2(1)}\left(\vec{r}_1\right) + c_{A_2}^{T2(1)}\left(\vec{r}_1\right)$$
(5.25)

$$\frac{X_{2}(\vec{r}_{1})}{X_{o}(\vec{r}_{1})} = c_{A_{1}}^{T1}(\vec{r}_{1}) * c_{A_{2}}^{T1}(\vec{r}_{1}) + c_{A_{1}}^{T2(2)}(\vec{r}_{1}) + c_{A_{1}}^{T1}(\vec{r}_{1}) * c_{A_{2}}^{T2(1)}(\vec{r}_{1}) + c_{A_{2}}^{T2(2)}(\vec{r}_{1}) + \dots \\
\dots c_{A_{2}}^{T1}(\vec{r}_{1}) * c_{A_{1}}^{T2(1)}(\vec{r}_{1}) + c_{A_{2}}^{T(ring)}(\vec{r}_{1}) + c_{A_{1}}^{T(ring)}(\vec{r}_{1}) + c_{A_{1}}^{T(ring)}(\vec{r}_{1})$$
(5.26)

$$\frac{X_{3}(\overrightarrow{r}_{1})}{X_{o}(\overrightarrow{r}_{1})} = c_{A_{1}}^{T1}(\overrightarrow{r}_{1}) * c_{A_{2}}^{T2(2)}(\overrightarrow{r}_{1}) + c_{A_{2}}^{T1}(\overrightarrow{r}_{1}) * c_{A_{1}}^{T2(2)}(\overrightarrow{r}_{1}) + c_{A_{1}}^{T1}(\overrightarrow{r}_{1}) * c_{A_{2}}^{T(ring)}(\overrightarrow{r}_{1}) + \dots \\
\dots c_{A_{2}}^{T1}(\overrightarrow{r}_{1}) * c_{A_{1}}^{T(ring)}(\overrightarrow{r}_{1}) + c_{A_{2}}^{T2(1)}(\overrightarrow{r}_{1}) * c_{A_{1}}^{T2(2)}(\overrightarrow{r}_{1}) + c_{A_{1}}^{T2(1)}(\overrightarrow{r}_{1}) * \dots \\
\dots c_{A_{2}}^{T2(2)}(\overrightarrow{r}_{1}) + c_{A_{2}}^{T2(1)}(\overrightarrow{r}_{1}) * c_{A_{1}}^{T(ring)}(\overrightarrow{r}_{1}) + c_{A_{1}}^{T2(1)}(\overrightarrow{r}_{1}) * c_{A_{2}}^{T(ring)}(\overrightarrow{r}_{1}) \\
\dots c_{A_{2}}^{T2(2)}(\overrightarrow{r}_{1}) + c_{A_{2}}^{T2(1)}(\overrightarrow{r}_{1}) * c_{A_{1}}^{T(ring)}(\overrightarrow{r}_{1}) + c_{A_{1}}^{T2(1)}(\overrightarrow{r}_{1}) * c_{A_{2}}^{T(ring)}(\overrightarrow{r}_{1}) \\
\dots c_{A_{2}}^{T2(2)}(\overrightarrow{r}_{1}) + c_{A_{2}}^{T2(1)}(\overrightarrow{r}_{1}) * c_{A_{1}}^{T(ring)}(\overrightarrow{r}_{1}) + c_{A_{1}}^{T2(1)}(\overrightarrow{r}_{1}) * c_{A_{2}}^{T(ring)}(\overrightarrow{r}_{1}) \\
\dots c_{A_{2}}^{T2(2)}(\overrightarrow{r}_{1}) + c_{A_{2}}^{T2(1)}(\overrightarrow{r}_{1}) * c_{A_{1}}^{T(ring)}(\overrightarrow{r}_{1}) + c_{A_{1}}^{T2(1)}(\overrightarrow{r}_{1}) * c_{A_{2}}^{T(ring)}(\overrightarrow{r}_{1}) \\
\dots c_{A_{2}}^{T2(2)}(\overrightarrow{r}_{1}) + c_{A_{2}}^{T2(1)}(\overrightarrow{r}_{1}) * c_{A_{1}}^{T(ring)}(\overrightarrow{r}_{1}) + c_{A_{1}}^{T2(1)}(\overrightarrow{r}_{1}) * c_{A_{2}}^{T(ring)}(\overrightarrow{r}_{1}) \\
\dots c_{A_{2}}^{T2(2)}(\overrightarrow{r}_{1}) + c_{A_{2}}^{T2(1)}(\overrightarrow{r}_{1}) * c_{A_{1}}^{T(ring)}(\overrightarrow{r}_{1}) + c_{A_{2}}^{T2(1)}(\overrightarrow{r}_{1}) * c_{A_{2}}^{T(ring)}(\overrightarrow{r}_{1}) \\
\dots c_{A_{2}}^{T2(2)}(\overrightarrow{r}_{1}) + c_{A_{2}}^{T2(1)}(\overrightarrow{r}_{1}) * c_{A_{1}}^{T(ring)}(\overrightarrow{r}_{1}) + c_{A_{2}}^{T2(1)}(\overrightarrow{r}_{1}) * c_{A_{2}}^{T2(1)}(\overrightarrow{r}_{1}) \\
\dots c_{A_{2}}^{T2(2)}(\overrightarrow{r}_{1}) + c_{A_{2}}^{T2(1)}(\overrightarrow{r}_{1}) * c_{A_{2}}^{T(ring)}(\overrightarrow{r}_{1}) + c_{A_{2}}^{T2(1)}(\overrightarrow{r}_{1}) + c_{A_{2}}^{T2(1)}(\overrightarrow{r}_{1}) * c_{A_{2}}^{T2(1)}(\overrightarrow{r}_{1}) \\
\dots c_{A_{2}}^{T2(1)}(\overrightarrow{r}_{1}) + c_{A_{2$$

$$\frac{X_4(\vec{r}_1)}{X_o(\vec{r}_1)} = c_{A_1}^{T2(2)}(\vec{r}_1) * c_{A_2}^{T2(2)}(\vec{r}_1) + c_{A_1}^{T(ring)}(\vec{r}_1) * c_{A_2}^{T(ring)}(\vec{r}_1) + \dots \dots c_{A_1}^{T2(2)}(\vec{r}_1) * c_{A_2}^{T(ring)}(\vec{r}_1) + c_{A_2}^{T2(2)}(\vec{r}_1) * c_{A_1}^{T(ring)}(\vec{r}_1)$$
(5.28)

where $X_o(\vec{r}_1)$ is the fraction of monomer and $X_k(\vec{r}_1)$ is the fraction of bonded k-times. With the following mass action equation, the density factors are evaluated:

$$X_{o}\left(\vec{r}_{1}\right) + X_{1}\left(\vec{r}_{1}\right) + X_{2}\left(\vec{r}_{1}\right) + X_{3}\left(\vec{r}_{1}\right) + X_{4}\left(\vec{r}_{1}\right) = 1$$
(5.29)

Since bond formation happens randomly at any site of a colloid we can say $M_A(\vec{r_1}) = M_{A_1}(\vec{r_1}) = M_{A_2}(\vec{r_1})$. The c-terms are simplified to:

$$c_A^{T1}\left(\vec{r}_1\right) = \frac{\left(1 - \cos\theta_c\right)^2}{2} f_{AA} \int \rho\left(\vec{r}_2\right) M_A\left(\vec{r}_2\right) y\left(\vec{r}_1, \vec{r}_2\right) \lambda\left(r_{12}\right) d\vec{r}_2$$
(5.30)

$$c_{A}^{T2(1)}\left(\vec{r}_{1}\right) = 4f_{AA}^{2} \int \rho\left(\vec{r}_{2}\right) M_{A}\left(\vec{r}_{2}\right) \rho\left(\vec{r}_{2}\right) M_{A}\left(\vec{r}_{3}\right) y_{chain}\left(\vec{r}_{1},\vec{r}_{2},\vec{r}_{3}\right) \Upsilon\left(\Omega_{1},\Omega_{2},\Omega_{3}\right) d\vec{r}_{2}d\vec{r}_{3}$$

$$(5.31)$$

$$c_{A}^{T2(2)}\left(\vec{r}_{1}\right) = 2f_{AA}^{2} \int \rho\left(\vec{r}_{2}\right) M_{A}\left(\vec{r}_{2}\right) \rho\left(\vec{r}_{2}\right) M_{A}\left(\vec{r}_{3}\right) y_{chain}\left(\vec{r}_{1},\vec{r}_{2},\vec{r}_{3}\right) \Upsilon\left(\Omega_{1},\Omega_{2},\Omega_{3}\right) d\vec{r}_{2}d\vec{r}_{3}$$
(5.32)

$$c_{A}^{T(ring)}\left(\vec{r}_{1}\right) = 2f_{AA}{}^{3} \int \rho\left(\vec{r}_{2}\right) M_{A}\left(\vec{r}_{2}\right) \rho\left(\vec{r}_{3}\right) M_{A}\left(\vec{r}_{3}\right) y_{ring}\left(\vec{r}_{1},\vec{r}_{2},\vec{r}_{3}\right) \Psi\left(\Omega_{1},\Omega_{2},\Omega_{3}\right) d\vec{r}_{2}d\vec{r}_{3}$$

$$(5.33)$$

where $f_{AA} = \exp(\varepsilon_{AA}/k_BT) - 1$. Now, with these simplifications we can rewrite the contribution terms:

$$\Delta c_{TPT1} = \frac{\left(1 - \cos\theta_c\right)^2}{2} f_{AA} \int \rho\left(\vec{r_1}\right) M_A\left(\vec{r_1}\right) \rho\left(\vec{r_2}\right) M_A\left(\vec{r_2}\right) y\left(\vec{r_1}, \vec{r_2}\right) \lambda\left(r_{12}\right) d\vec{r_1} d\vec{r_2}$$
(5.34)

$$\Delta c_{TPT2} = 4f_{AA}{}^{2} \int \rho\left(\vec{r}_{1}\right) M_{A}\left(\vec{r}_{1}\right) \rho\left(\vec{r}_{2}\right) M_{A}\left(\vec{r}_{2}\right) \rho\left(\vec{r}_{3}\right) M_{A}\left(\vec{r}_{3}\right) \dots$$

$$\dots y_{chain}\left(\vec{r}_{1},\vec{r}_{2},\vec{r}_{3}\right) \Upsilon\left(\Omega_{1},\Omega_{2},\Omega_{3}\right) d\vec{r}_{1}d\vec{r}_{2}d\vec{r}_{3}$$
(5.35)

$$\Delta c_{ring} = \frac{8}{6} f_{AA}{}^3 \int \rho\left(\vec{r_1}\right) M_A\left(\vec{r_1}\right) \rho\left(\vec{r_2}\right) M_A\left(\vec{r_2}\right) \rho\left(\vec{r_3}\right) M_A\left(\vec{r_3}\right) \dots$$

$$\dots y_{ring}\left(\vec{r_1}, \vec{r_2}, \vec{r_3}\right) \Psi\left(\Omega_1, \Omega_2, \Omega_3\right) d\vec{r_1} d\vec{r_2} d\vec{r_3}$$
(5.36)

 $\Upsilon(\Omega_1, \Omega_2, \Omega_3)$ and $\Psi(\Omega_1, \Omega_2, \Omega_3)$ are the orientational factors in each integral which are defined in the following way: Υ is the total number of ways that a threebody chain can be formed, and Ψ is the total number of ways that a three-body ring can be formed:

$$\Upsilon\left(\Omega_{1},\Omega_{2},\Omega_{3}\right) = \frac{1}{\Omega^{3}} \int \lambda\left(r_{12}\right)\lambda\left(r_{23}\right)U\left(\Omega_{1},\Omega_{2}\right)U\left(\Omega_{2},\Omega_{3}\right)H\left(r_{13}-d\right)d\Omega_{1}d\Omega_{2}d\Omega_{3}$$
(5.37)

$$\Psi\left(\Omega_{1},\Omega_{2},\Omega_{3}\right) = \frac{1}{\Omega^{3}} \int \lambda\left(r_{12}\right)\lambda\left(r_{23}\right)\lambda\left(r_{13}\right)U\left(\Omega_{1},\Omega_{2}\right)U\left(\Omega_{2},\Omega_{3}\right)U\left(\Omega_{1},\Omega_{3}\right)d\Omega_{1}d\Omega_{2}d\Omega_{3}$$
(5.38)

 λ controls two colloids to be in proper positions, and U assures they are in appropriate orientation in order to form a bond. H(x) is the heavy side step function, and the total number of orientation is $\Omega = 8\pi^2$.

$$\lambda(r_{12}) = \begin{cases} 1, & d < r_{12} < r_c \\ 0, & otherwise \end{cases}$$
(5.39)

$$U(\Omega_1, \Omega_2) = \begin{cases} 1, & \theta_{A(1)} \le \theta_c \text{ and } \theta_{A(2)} \le \theta_c \\ 0, & \text{otherwise} \end{cases}$$
(5.40)

The ring and chain integrals, Υ and Ψ , are solved for a homogenous fluid by Monte Carlo integration using the approach proposed by Marshall and Chapman [96].

According to the restriction imposed by the Mayer f-function, the inhomogeneous two-body cavity correlation function in the first order contribution term (Eq. 5.34) needs to be calculated within the bonding shell $(r_c - d)$. We estimate this correlation function using a coarse grained approximation since in these integrals one particle is usually fixed and the other one can be anywhere inside the bonding area. The pair function is approximated by:

$$\overline{y(\vec{r_1})} = \frac{\int d\vec{r_2} y(\vec{r_1}, \vec{r_2}) \lambda(r_{12})}{\int d\vec{r_2} \lambda(r_{12})}$$
(5.41)

where the function $\lambda(r_{12})$ assures the average is taken over the bonding region. Because the labeling of variables in the correlation function is random, we have $y(\vec{r_1}, \vec{r_2}) = y(\vec{r_2}, \vec{r_1})$. We approximate the inhomogeneous cavity distribution function $y(\vec{r_1}, \vec{r_2})$ by the geometric mean of homogenous cavity correlation functions at $\vec{r_1}$ and $\vec{r_2}$. The geometric mean is the equivalent to averaging the potential of mean force at the two points.

$$y(\vec{r_1}, \vec{r_2}) \approx \left(\overline{y(\vec{r_1})} \times \overline{y(\vec{r_2})}\right)^{1/2}$$
 (5.42)

We further assume that $r^2 \overline{y(r)}$ is approximately d^2 times the contact value of the homogeneous cavity function. This approximation is most accurate at intermediate densities. The result is an approximation for the radial dependence of the inhomogeneous cavity correlation function given by $r^2 y(\vec{r_1}, \vec{r_2}) \approx \left(d^2 \overline{y_c(\vec{r_1})} \times d^2 \overline{y_c(\vec{r_2})} \right)^{1/2}$ is determined using the cavity function at contact in homogeneous fluids $(1 - 0.5\eta)/(1 - \eta)^3$, with a coarse grained density:

$$\overline{y_c\left(\vec{r}_1\right)} \approx y_c\left(\bar{\rho}\left(\vec{r}_1\right)\right) \tag{5.43}$$

where the coarse grained density is averaged over the bonding shell:

$$\bar{\rho}\left(\vec{r}_{1}\right) = \frac{3}{4\pi d^{3}} \int d\vec{r}_{2}\rho\left(\vec{r}_{2}\right) H\left(d - r_{12}\right)$$
(5.44)

This approximation has been shown to give promising results for associating and polyatomic molecules [75]. The three body cavity correlation functions of chain and ring are estimated, respectively:

$$y(\vec{r_1}, \vec{r_2}, \vec{r_3})|_{chain} = y(\vec{r_1}, \vec{r_2}) y(\vec{r_2}, \vec{r_3}) y_o^c(\vec{r_1}, \vec{r_2}, \vec{r_3})$$
(5.45)

$$y(\vec{r_1}, \vec{r_2}, \vec{r_3})|_{ring} = y(\vec{r_1}, \vec{r_2}) y(\vec{r_2}, \vec{r_3}) y_o^r(\vec{r_1}, \vec{r_2}, \vec{r_3})$$
(5.46)

The two-body cavity functions are evaluated by equation 5.42, and the angle dependent cavity functions of chain and ring, $y_o^c(\vec{r_1}, \vec{r_2}, \vec{r_3})$ and $y_o^r(\vec{r_1}, \vec{r_2}, \vec{r_3})$, are calculated with Muller and Gubbinss approach [168] which was proposed for bulk fluids:

$$y_o\left(\varpi\right) = \frac{1 + a\eta + b\eta^2}{\left(1 - \eta\right)^2} \tag{5.47}$$

The values for the constants a and b are tabulated in reference [168], at each average bond angle (ϖ), for the homogenous fluid. In a triatomic chain or ring, ϖ (represented as ϖ_{chain} or ϖ_{ring} , respectively) is the average bond angle between colloids 1 and 3 which are in contact with colloid 2 [96]. For an inhomogeneous fluid, equation 5.47 is used with a coarse grained density from equation 5.44. The three body angle dependent cavity functions for an inhomogeneous fluid can be written as:

$$lny_{o}^{c}(\vec{r}_{1},\vec{r}_{2},\vec{r}_{3}) = \frac{1}{3}ln\left[y_{o}\left(\bar{\rho}\left(\vec{r}_{1}\right),\varpi_{chain}\right) \times y_{o}\left(\bar{\rho}\left(\vec{r}_{2}\right),\varpi_{chain}\right) \times y_{o}\left(\bar{\rho}\left(\vec{r}_{3}\right),\varpi_{chain}\right)\right]$$
(5.48)

$$lny_{o}^{r}(\vec{r}_{1},\vec{r}_{2},\vec{r}_{3}) = \frac{1}{3}ln\left[y_{o}^{r}(\bar{\rho}(\vec{r}_{1}),\varpi_{ring}) \times y_{o}^{r}(\bar{\rho}(\vec{r}_{2}),\varpi_{ring}) \times y_{o}^{r}(\bar{\rho}(\vec{r}_{3}),\varpi_{ring})\right]$$
(5.49)

where $y_o^r(\varpi_{ring}) = y_o(\varpi_{ring})/y_c$. ϖ_{chain} and ϖ_{ring} are considered to be that of bulk system and are tabulated in Marshall and Chapman publication [65]. With the fractions we derived using bonding states derivatives, the Helmholtz free energy of association can be written as:

$$\frac{A^{ASSOC}}{k_B T} = \int d\vec{r_1} \rho(\vec{r_1}) \left(ln X_o(\vec{r_1}) + 1 - M_{A_1}(\vec{r_1}) - M_{A_2}(\vec{r_1}) + \frac{M_{A_1}(\vec{r_1}) M_{A_2}(\vec{r_1})}{X_o(\vec{r_1})} \right) - \Delta c^{(o)}$$
(5.50)

Now taking the functional derivative of the Helmholtz free energy with respect to density we have:

$$\frac{\delta A^{assoc}/k_B T}{\delta \rho\left(\vec{r}\right)} = ln X_o\left(\vec{r}\right) - \frac{\delta \Delta c^{(o)}}{\delta \rho\left(\vec{r}\right)}$$
(5.51)

$$\frac{\delta\Delta c^{(o)}}{\delta\rho\left(\vec{r}\right)} = \frac{\delta\Delta c_{TPT1}}{\delta\rho\left(\vec{r}\right)} + \frac{\delta\Delta c_{TPT2}}{\delta\rho\left(\vec{r}\right)} + \frac{\delta\Delta c_{ring}}{\delta\rho\left(\vec{r}\right)}$$
(5.52)

$$\frac{\delta\Delta c_{TPT1}}{\delta\rho\left(\vec{r}\right)} = \int d\vec{r}_1 \rho(\vec{r}_1) M_{A_1}(\vec{r}_1) c_A^{T1}\left(\vec{r}_1\right) \frac{\partial lny\left(\bar{\rho}\left(\vec{r}_1\right)\right)}{\partial\rho\left(\vec{r}\right)}$$
(5.53)

$$\frac{\delta\Delta c_{TPT2}}{\delta\rho\left(\vec{r}\right)} = \int d\vec{r}_{1}\rho(\vec{r}_{1})M_{A_{1}}\left(\vec{r}_{1}\right)c_{A}^{T2(1)}\left(\vec{r}_{1}\right)\left[2\frac{\partial lny\left(\bar{\rho}\left(\vec{r}_{1}\right)\right)}{\partial\rho\left(\vec{r}\right)} + \frac{\partial lny_{o}\left(\bar{\rho}\left(\vec{r}_{1}\right),\varpi_{chain}\right)}{\partial\rho\left(\vec{r}\right)}\right]$$
(5.54)

$$\frac{\delta\Delta c_{ring}}{\delta\rho\left(\vec{r}\right)} = \frac{2}{3} \int d\vec{r}_{1}\rho(\vec{r}_{1})M_{A_{1}}(\vec{r}_{1})c_{A}^{T(ring)}\left(\vec{r}_{1}\right) \left[2\frac{\partial lny\left(\bar{\rho}\left(\vec{r}_{1}\right)\right)}{\partial\rho\left(\vec{r}\right)} + \frac{\partial lny_{o}\left(\bar{\rho}\left(\vec{r}_{1}\right),\varpi_{ring}\right)}{\partial\rho\left(\vec{r}\right)}\right]$$
(5.55)

The other information we need in order to finalize our density functional theory calculation is the chemical potential of the bulk which is derived in detail in the Appendix.

5.3 Simulation

To validate results from DFT, new NVT Monte Carlo simulations were conducted for patchy colloids in a pore. Most of the simulation details were given in previous study by Marshall et al.[96]. In this work, each colloid carries two patches, and the angle between vectors connecting the centers of each patch to the center of colloid is 180 degrees (see figure 5.1). Due to the fact that each particle can bond 4 times, it is difficult to obtain the equilibrated results. To speed up the equilibrium process, the configurationally biased Monte Carlo simulation technique was employed. At each trail move, 10 orientations were sampled to identify a probable trial configuration and the acceptance probability of the move was corrected for the biasing. The details of configurationally biased Monte Carlo technique are given in the book by Frenkel et al.[175]. Each simulation was allowed to equilibrate for 1.5×10^9 trail moves. The final simulation results were obtained by taking the averages over 0.5×10^9 trail moves.

To demonstrate the accuracy of the theory and to demonstrate that the wall contact theorem is satisfied, new NPT Monte Carlo simulations were performed for 256 particles[65, 176]. Unlike the NVT simulations performed in this work, the periodic boundary condition was applied in all directions. Each simulation was allowed to equilibrate for 4×10^8 trial moves. The final simulation results were obtained by



Figure 5.3 : Predictions of the density profile, scaled by the bulk number density for a bulk reduced density of $\rho_b^* = 0.2$ for association energies, ε_{AA}/k_BT , of 4, 5, and 6. Solid line: density functional theory, Symbols: Monte Carlo simulation results with error bars.

taking the averages over 10^8 trial moves. For all simulations, the angle change and displacement parameters were adjusted to tune the acceptance ratio in the range of 30% - 40%.

5.4 **Results and Discussion**

In this section we compare predictions from density functional theory with new Monte Carlo simulation results for the density profile of colloids with two associating sites. each with angular cutoff of size $\theta_c = 35^\circ$, close to a hard wall in a pore. Figure 5.3 shows excellent agreement of the theory (curves) with simulation results (symbols) for the density profile of the fluid, scaled by bulk density, versus the distance from one wall to the middle of the pore. The bulk reduced number density of the fluid is, $(\rho_b^* = \rho_b d^3)$, $\rho_b^* = 0.2$ and results are shown for association energies, ε_{AA}/k_BT , of 4, 5, and 6. Near the wall, the density profile fluctuates from the bulk value since the wall imposes a constraint over the positions that each colloid can occupy. At low association energies of $\varepsilon_{AA}/k_BT = 4$, the density at contact with the wall, $\rho(0)$, is higher than the bulk fluid density because of the packing effect of hard spheres near a rigid surface. Increasing association energy causes a decrease in the contact density $\rho(0)$ since the bulk pressure is decreasing. At $\varepsilon_{AA}/k_BT = 5$, the contact density is smaller than $\rho(0)$ for an energy of 4, but still greater than the bulk density. However, for $\varepsilon_{AA}/k_BT = 6$, $\rho(0)$ is even lower than bulk density, which shows that colloids deplete from the wall under these conditions. Increasing association energy results to the formation of clusters of associated species. The hard wall introduces a restriction over the possible positions and orientations of colloidal clusters. Therefore, at higher association energies, particles partition into the bulk to form more bonds and larger clusters. The theory agrees well with simulation at all association energies.



Figure 5.4 : Same as figure 3 with a bulk reduced density $\rho_b^*=0.5.$



Figure 5.5 : Theory (solid lines) and Monte Carlo (symbols with error bars) results for the fractions of k-time bonded species (i.e., X2 is the fraction of species bonded twice) at a bulk reduced number density of $\rho_b^* = 0.5$ and an association energy of $\varepsilon_{AA}/k_BT = 6$.

Interestingly, although the theory captures the density distribution, the theory uses orientation factors and distribution functions that were calculated for a homogeneous fluid at a weighted density. In a sense, the only information about the pore surface provided to the association term in the Helmholtz free energy functional is that there are no colloids available to bond in the wall.

The results for a higher density case are plotted in figure 5.4, where the average bulk reduced number density is 0.5. Similar to the previous figure, three profiles for three different association energies of $\varepsilon_{AA}/k_BT = 4$, 5, and 6 are exhibited. Comparing figure 5.3 to figure 5.4 shows two effects of the higher density case. On one hand, the higher density increases the amount of association since colloids are more compact and the chances of finding suitable bonding partners are higher. On the other hand, the higher density increases the wall density because of a higher bulk



Figure 5.6 : Theory (solid lines) results for fractions of species with at least one site bonded twice that are present in rings or chains at a reduced density of $\rho_b^* = 0.5$ and association energy $\varepsilon_{AA}/k_BT = 6$.

pressure. In figure 5.4, increasing the association energy to $\varepsilon_{AA}/k_BT = 6$ reduces $\rho(0)$, but since the average bulk density is high, unlike figure 5.3, the wall density does not reduce to values lower than bulk density. Theory (curves) is in good agreement with simulation (points).

To provide a more detailed description of the impact of higher association energies in a fluid near a hard wall, the fractions of colloids in different bonding states are plotted in figure 5.5 versus the distance from the wall. This figure shows that at $\varepsilon_{AA}/k_BT = 6$, in the bulk region, twice bonded colloids (X2) are the dominant structure, and then, X1 and X3, respectively. Twice bonded colloids includes contributions from chains and rings. However, approaching the wall, the concentration of clusters is reduced because, although larger clusters are energetically favored, larger clusters are penalized by geometric constraints near the wall. According to this graph, approach-



Figure 5.7 : Fractions of k-time bonded species (i.e., X2 is the fraction of species bonded twice) in bulk from Theory: solid lines and Monte Carlo simulation: symbols at a reduced bulk number density $\rho_b^* = 0.5$.

ing the wall the fractions of two, three, and four-time bonded particles are decreased, whereas monomer and one-time bonded fractions are increased. The theory is in very good agreement with the simulation results. Notice that the theory accurately captures the characteristic distance of a hard sphere diameter where larger clusters are depleted in favor of monomers and one-time bonded colloids, although the wall fractions show some deviation from simulation results. As described before, geometric distributions provided to the association free energy functional were calculated for a homogeneous fluid at a weighted density. Further information about the fractions of colloids with at least one site bonded twice as either in a ring or chain is plotted in Figure 5.6. This figure shows these rings and chains deplete at the hard wall. Excellent agreement between simulation and theory for the distribution of colloids that are monomers, bonded once, twice, etc. in the bulk fluid is shown versus inverse



Figure 5.8 : Same as figure 3 with a bulk reduced density $\rho_b^*=0.764.$



Figure 5.9 : Theory (solid lines) and Monte Carlo (symbols with error bars) results for fractions of k-time bonded species (i.e., X2 is the fraction of species bonded twice) at a bulk reduced number density of $\rho_b^* = 0.764$ and an association energy of $\varepsilon_{AA}/k_BT = 6$.

temperature in Figure 5.7.

The density profile and fractions of colloids bonded in different states are plotted in figures 5.8 and 5.9 for a fluid with $\rho_b^* = 0.764$ with $\varepsilon_{AA}/k_BT = 4$, 5, and 6 (figure 5.9 shows the results for $\varepsilon_{AA}/k_BT = 6$). Due to being at a higher bulk density, the density profiles show more structure and higher contact density in each case compared with lower density systems. Agreement between theory and simulation results is very good for the density profiles. At this higher density, the extent of association is also higher. At an association energy of $\varepsilon_{AA}/k_BT = 6$ in figure 5.9, the fractions bonded ktimes are plotted as a function of distance from the pore wall. The monomer fraction is very small at this condition and not plotted. The theory predicts that, within one diameter of the wall, the fractions bonded at k-sites either rise or drop from their bulk value similar to that seen for the case of a reduced bulk density of 0.5 in figure 5.5.



Figure 5.10 : Theory (solid lines) and Monte Carlo (symbols) results for bulk pressure due to association versus bulk density for association energies, ε_{AA}/k_BT , of 4, 5, and 6.

Near the wall, the simulations show a decrease in the fraction bonded 3 and 4 times and an increase in the fraction bonded once, but this occurs at a smaller distance from the wall than predicted by theory. The trends of the theory are in general agreement with the simulation results, but the range over which the wall affects association is not reproduced.

As a verification of the accuracy of the theory for bulk fluid properties, the contribution of only the association term to the pressure is plotted in figure 5.10 versus density for the association energies studied. In this case of a fluid interacting with a hard wall, the wall contact theorem states that the bulk pressure equals the wall density, $P/k_BT = \rho(0)$. In figure 5.10, we compare the change to the bulk pressure due to association from DFT calculations, $(P - P^{HS}) d^3 = k_BT d^3 (\rho(0) - \rho_{HS}(0))$,



Figure 5.11 : Theoretical predictions of the density profile from a two-site (solid line) model and a four-site (dash line) model at a reduced bulk density of $\rho_b^* = 0.764$ and association energy, ε_{AA}/k_BT , of 6.

with NPT simulation results and we find the theory to be in excellent agreement with the simulation results.

In our theory, the orientational factors and distribution functions describe the steric hindrance (SH) that controls whether a site can bond once or twice. Figure 5.11 and 5.12 exhibit a comparison between our theory versus a corresponding foursite (FS) model in which each association site can form only one bond, but each site has a half of the bond volume of a site in our model. In the FS model, sites are assumed to be located far enough apart that the impact of SH is not a concern, so the system can be modeled by a TPT1 theory as shown by Segura et al.[48]. Figure 5.11, shows the difference in density profiles where it is observed $\rho(0)$ has a lower value for the FS model due to a lower bulk pressure, but the density profile is similar between the two models. Since in the FS model there is no SH effect, the extent of



Figure 5.12 : Theoretical predictions of fractions of k-time bonded colloids from a two-site model (solid line) and four-site (dash line) model. $\rho_b^* = 0.764$ and association energy, ε_{AA}/k_BT , of 6.

association is expectedly higher than in our two site model. This is seen in figure 5.12 where the FS model shows much greater fractions of colloids bonded three and four times compared with the two site SH model. The general shapes of the bonding distribution curves are similar for the two models. For the same bond volumes and association energies, the FS model has greater association than the two site SH model; the greater association leads to lower wall densities for the FS model.

5.5 Conclusion

We extended Wertheims multi-density formalism for colloids with two patches that can each bond multiple times. This has been further developed in the form of a free energy functional and applied in a density functional theory to predict the overall density distribution and distribution of associated states as a function of distance from a pore wall. The theory is generally in very good agreement with MC simulation results for the density profile and the fractions of species in various bonding states versus the distance from the pore wall. The temperature range studied was limited by time necessary to produce equilibrium configurations in simulation. At lower temperatures, we expect the overall density profile to be accurate, but we expect bonding fractions to show deviation, particularly near a pore wall. Our experience in applying the first order theory to confined polymers (the lowest temperature state of complete bonding)[75, 177] has been very good agreement between theory and simulation for fluid density distribution. Extension of the density functional theory using approaches to further relax approximations in Wertheims TPT1, such as geometric bond angle constraints, cooperative hydrogen bonding, spherically symmetric sites, etc. as described in Marshall et al.[125, 14, 1] for bulk fluids, and mixtures of patchy colloidal fluids will be the subjects of future research.

Chapter 6

A Density Functional Theory for Association of Fluid Molecules with A Functionalized Surface: Fluid-Wall Single and Double Bonding

6.1 Introduction

Due to the importance of adsorption phenomena in many industrial applications, describing the distribution of molecules at heterogeneous surfaces has been a long standing challenge. For example, Chmiel et al used Tarazona DFT [98, 99, 100] to model a Lennard Jones fluids near a wall with adsorbing strips. Tripathi [49, 101] developed a DFT to model systems of associating fluids close to a rigid functionalized surface with discrete association sites. In addition to the theoretical studies, such systems were investigated by several molecular simulation methods, like Muller et al who performed MC simulation for adsorption of water over activated carbons [102, 103, 104].Lee and Rossky [105] investigated the structure and dynamics of water on hydrophobic and hydrophilic solid surfaces.

In this chapter, we extend Wertheim's TPT to model a single site associating fluid close to a rigid planar surface functionalized with association sites. A DFT is developed, and the fluid behavior near to the wall is studied under different conditions of density, and temperature. Tripathi [49] developed his DFT for fluids interacting with wall sites that could form only one bond; however, in our work the wall sites are large enough that two bonds can form. Such theory can be applied for modeling the adsorption of molecular fluids on a hard wall with divalent active sites, and association of patchy colloids to rigid surfaces with large patches. The theory predictions for density profile, state of bonding, and surface coverage are reported and verified with MC simulation results, and they are in good agreement.

6.2 Model and Theory

In this section we develop a density functional theory for a single association site fluid close to a hard planar wall with association sites on its surface. The angular cutoffs of the association sites of the fluid and the wall are $\theta_{c_{c}F} = 27^{\circ}$ and $\theta_{c_{e}W} = 35^{\circ}$, respectively. According to previous studies [65] for $\theta_{c_{e}W} > 30^{\circ}$ more than one bond per site can occur; therefore, wall sites can form two bonds. We limit the association to happen only between fluid and wall site, so the fluid particles interact only through hard sphere interactions φ_{FF} (12) = φ_{HS} (12):

$$\varphi_{\rm HS}(12) = \begin{cases} \infty, & r_{12} < d \\ 0, & otherwise \end{cases}$$
(6.1)

d is the diameter of a fluid segment.

The fluid-wall site potential of interaction is:

$$\varphi_{\rm FW}\left(12\right) = \varphi_{\rm FW}^{\rm assoc}\left(12\right) \tag{6.2}$$

where 1 and 2 stand for the position and orientation of a fluid species and a hypothetical sphere which carries the wall site (with the same diameter d).

$$\varphi_{\rm FW}^{\rm assoc}\left(12\right) = \begin{cases} -\varepsilon_{\rm FW} , & r_{12} \le r_{\rm c} , \ \theta_{\rm F(1)} \le \theta_{\rm c_F} , \ \theta_{\rm W(2)} \le \theta_{\rm c_W} \\ 0 , & otherwise \end{cases}$$
(6.3)



Figure 6.1 : Scheme view of possible bonding states between fluid and wall. Silver spheres represent wall site segments and blue spheres exhibit fluid species. The brown line shows the wall position.

 $r_c = 1.1d$, is the critical distance beyond which association cannot happen. $\theta_{F(1)}$ is the angle between the vector connecting centers of the fluid segment at 1 and wall particle at 2, and the vector from the center of fluid sphere to the center of its site $(\theta_{W(2)})$ is defined in the similar way for a wall site sphere). According to 6.3 if a fluid species is within a proper distance and orientation of a wall site, a bond will be formed between them, and the energy of the system reduces by a ε_{FW} . A scheme view of the fluid near to the wall is depicted in figure 6.1. The wall site is oriented perpendicular to the wall. We will consider the case where the wall sites are spaced far enough apart to be independent, but the wall sites can associate with two fluid particles at the same time as shown in figure 6.2.

In the density functional theory framework, the density profile at equilibrium is obtained by minimizing the grand free energy with respect to the density of the fluid, $\rho^{(\mathrm{F})}\left(\tilde{\mathrm{r}}\right)$:

$$\frac{\delta\Theta\left[\rho^{(\mathrm{F})}\right]}{\delta\rho^{(\mathrm{F})}\left(\tilde{\mathbf{r}}\right)}\bigg|_{\rho^{(\mathrm{F})}=\rho^{(\mathrm{F})}_{\mathrm{eq}}} = 0$$
(6.4)

where $\rho_{eq}^{(F)}$ is the density profile of the fluid at equilibrium, and by definition the grand free energy is:

$$\Theta\left[\rho^{(\mathrm{F})}\right] = \mathrm{A}\left[\rho^{(\mathrm{F})}\right] + \int \rho^{(\mathrm{F})}\left(\tilde{\mathrm{r}}\right)\left(\mathrm{V}_{\mathrm{ext}}\left(\tilde{\mathrm{r}}\right) - \mu\right)\mathrm{d}\tilde{\mathrm{r}}$$
(6.5)

where $A\left[\rho^{(F)}\right]$ is the Helmholtz free energy functional, V_{ext} is the external field applied to the fluid, and μ is the chemical potential of the bulk which is the hard sphere reference fluid. Since the wall is planar, it is oriented in the x-y plane and z is the axis normal to the wall:

$$V_{\text{ext}} = \begin{cases} \infty & \text{if } z \le 0\\ 0 & \text{otherwise} \end{cases}$$
(6.6)

The Helmholtz free energy includes three contributions: the ideal, hard sphere, and association contributions:

$$A\left[\rho^{(F)}\right] = k_{B}T \int \rho^{(F)}\left(\tilde{r}\right) \left(\ln\rho^{(F)}\left(\tilde{r}\right) - 1\right) d\tilde{r} + A^{HS}\left[\rho^{(F)}\right] + A^{ASSOC}\left[\rho^{(F)}\right]$$
(6.7)

The first term in equation 6.7 is the ideal contribution which is known exactly from statistical mechanics. k_B is the Boltzmanns constant and T is the temperature. The second term is the Helmholtz free energy of the hard sphere fluid from the White Bear [173] version of fundamental measure theory [69, 174]. Using Wertheims twodensity formalism [43, 44], the association Helmholtz free energy functional, A^{ASSOC}, is written as:



Figure 6.2 : Geometrical presentation of a wall site forming two bonds with two fluid species.
$$\frac{A^{ASSOC}\left[\rho^{(F)}\right]}{k_{B}T} = \sum_{k} \int d\left(1\right) \left(\rho^{(k)}\left(1\right) \ln \frac{\rho_{o}^{(k)}\left(1\right)}{\rho^{(k)}\left(1\right)} + \rho^{(k)}\left(1\right) - \rho_{o}^{(k)}\left(1\right)\right) - \Delta c^{(o)} \quad (6.8)$$

 $\rho^{(k)}(1)$ and $\rho_{o}^{(k)}(1)$ are, respectively, the total and monomer reduced number density of the species k (fluid and wall sites) at position 1. The term $\Delta c^{(o)}$ is the sum of all irreducible graphs with a single path of association bonds between each pair of points. As will be described in this section, $\Delta c^{(o)}$ includes graphs of a wall site bonded to one and two fluid segments:

$$\Delta c^{(o)} = \Delta c_{\rm TPT1} + \Delta c_{\rm TPT2} \tag{6.9}$$

Each contribution in equation 6.9 is defined in the following way:

$$\Delta c_{\rm TPT1} = \int \rho_{\rm o}^{\rm (F)}(1) \,\rho_{\rm o}^{\rm (W)}(2) \,F_{\rm FW}(12) \,g_{\rm FW}^{\rm ref}(r_{12}) \,d(1) \,d(2) \tag{6.10}$$

$$\Delta c_{\rm TPT2} = \frac{1}{2} \int \rho_{\rm o}^{\rm (F)}(1) \,\rho_{\rm o}^{\rm (W)}(2) \,F_{\rm FW}(12) \,\rho_{\rm o}^{\rm (F)}(3) \,F_{\rm FW}(23) \,g_{\rm FWF}^{\rm ref}(r_{123}) \,d(1) \,d(2) \,d(3)$$
(6.11)

By definition, the Mayer *f*-function of association is $F_{FW}(12) = \exp(-\varphi_{FW}(12)/k_BT) - 1$. $\rho_o^{(W)}$ is the monomer density of the wall sites and $g_{FW}^{ref}(r_{12})$ and $g_{FWF}^{ref}(r_{123})$ are the two-body and three-body correlation functions between fluid and wall spheres, respectively. We approximate the three-body correlation function for a cluster consisted of two fluid segments bonded to a wall site, with the superposition of the pair correlation functions between wall and each fluid species, and a hard sphere interaction exponential between the fluid segments. Assuming the wall site at position 2 and fluid particles at 1 and 3:

$$\frac{X_{d}^{(F)}(\tilde{r}_{1})}{X_{o}^{(F)}(\tilde{r}_{1})} = \frac{(1 - \cos\theta_{c_{-}F})}{2} f_{FW} \int \rho^{(W)}(\tilde{r}_{2}) X_{o}^{(W)}(\tilde{r}_{2}) \lambda(r_{12}) g_{FW}^{ref}(r_{12}) d\tilde{r}_{2}$$
(6.12)

where $e_{HS}(13) = \exp(-\varphi_{HS}(13)/k_BT)$. With such approximation the limitation of available bonding configurations for a second fluid particle to join an already bonded wall site imposed by the previously bonded fluid particle is taken into account. We define monomer fraction of the fluid as $X_o^{(F)}(1) = \rho_o^{(F)}(1)/\rho^{(F)}(1)$, so the fraction of the fluid segments bonded to the one-time bonded wall sites, $X_d^{(F)}$, is obtained as:

$$\frac{X_{d}^{(F)}(\tilde{r}_{1})}{X_{o}^{(F)}(\tilde{r}_{1})} = \frac{(1 - \cos\theta_{c_F})}{2} f_{FW} \int \rho^{(W)}(\tilde{r}_{2}) X_{o}^{(W)}(\tilde{r}_{2}) \lambda(r_{12}) g_{FW}^{ref}(r_{12}) d\tilde{r}_{2}$$
(6.13)

where $\rho^{(W)}$ and $X_o^{(W)}$ are the total density and monomer fractions of the wall sites, and $f_{FW} = \exp(\varepsilon_{FW}/k_BT) - 1$ and in our model the position and orientation of the wall sites are fixed. $\lambda(r_{12})$ specifies the position range where the association between fluid and wall site can happen

$$\lambda \left(\mathbf{r}_{12} \right) = \begin{cases} 1, & \mathbf{r}_{12} < \mathbf{r}_{c} \\ 0, & otherwise \end{cases}$$
(6.14)

Following Tripathis approach [49, 101] we perform a rearrangement and density weighted average on equation 6.13 over the planes parallel to the wall in the bonding region, and define wall site density as

$$\rho^{(W)}(\mathbf{r}) = \left\langle \sum_{i}^{N_{W}} \delta\left(\mathbf{r} - \mathbf{r}_{i}\right) \right\rangle = \sum_{i}^{N_{W}} \delta\left(\mathbf{r} - \mathbf{r}_{i}\right)$$
(6.15)

The ensemble average $\langle \rangle$ is eliminated since the positions of the sites are fixed on the wall. N_W is the total number of association sites on the wall, and r_i is the position of the ith site on the wall. Equation 6.13 is written as

$$\frac{\int_{z_{1}} X_{d}^{(F)}(\tilde{r}_{1})\rho^{(F)}(\tilde{r}_{1})ds_{1}}{\int_{z_{1}} \rho^{(F)}(\tilde{r}_{1})ds_{1}} = \frac{\int_{z_{1}} X_{o}^{(F)}(\tilde{r}_{1})\rho^{(F)}(\tilde{r}_{1})ds_{1}}{\int_{z_{1}} \rho^{(F)}(\tilde{r}_{1})ds_{1}} \frac{(1-\cos\theta_{c,F})}{2} f_{FW} \int \rho^{(W)}(\tilde{r}_{2}) X_{o}^{(W)}(\tilde{r}_{2}) \lambda(r_{12}) g_{FW}^{ref}(r_{12}) d(2)$$
(6.16)

where ds_1 is the surface area element at constant z_1 . Here, we believe due to the similarities between our model system and Tripathis [49, 101] (the size of the wall sites is finite and relatively small, and the wall sites are assumed to be far enough from each other that there is no interaction between them), the monomer density approximation used by Tripathi [49] is still valid for the current theory:

$$\overline{X}_{o}^{(F)}(z_{1})\overline{\rho}^{(F)}(z_{1}) = \overline{\overline{X}}_{o}^{(F)}(z_{1})\overline{\overline{\rho}}^{(F)}(z_{1})$$

$$(6.17)$$

in which $\overline{\overline{X}}_{o}^{(F)}(z_{1})$ and $\overline{\overline{\rho}}^{(F)}(z_{1})$ are the averaged monomer fraction and total density of the fluid segments over a disc within the bond volume of the wall site and at the distance z_{1} from the wall, respectively. $\overline{X}_{o}^{(F)}(z_{1})$ and $\overline{\rho}^{(F)}(z_{1})$ are the average monomer fraction and total density of the fluid segments over the entire plane of the wall at the distance z_{1} from the wall. According to this approximation, the monomer density of the fluid is uniform over the entire plane parallel to the wall at any distance z_{1} . In other words, the density distribution of monomers as a function of distance from the wall is independent of positions parallel to the wall. Using 6.17, 6.16 is simplified to

$$\overline{X}_{d}^{(F)}(z_{1}) = \overline{X}_{o}^{(F)}(z_{1}) \frac{(1 - \cos\theta_{c.F})}{2} \pi \left(r_{c}^{2} - z_{1}^{2}\right) f_{FW} \rho^{(W)} X_{o}^{(W)} g_{FW}^{ref}(z_{1})$$
(6.18)

where the wall site density is simply the ratio of the number of wall sites to the surface area of the wall, $\rho^{(W)} = N_W/S_W$, and $X_o^{(W)}$ is the fraction of wall sites that are not bonded.

The pair correlation function $g_{FW}^{ref}(z_1)$ is calculated similar to Tripathis approach [49] using corresponding hard sphere fluid with the same bulk density:

$$g_{FW}^{ref}(z_1) = \frac{\rho^{(HS-F)}(z_1)}{\rho^{(HS-F)}_{average}}$$
(6.19)

where $\rho^{(\text{HS}_F)}(z_1)$ is the density of the hard sphere reference fluid at the distance z_1 from the wall, and $\rho^{(\text{HS}_F)}_{\text{average}}$ is the averaged density of the reference fluid in the system.

The fraction of fluid molecules bonded to two-time bonded wall sites, $X_{tr}^{(F)}(\tilde{r}_1)$, is obtained as

$$\frac{X_{tr}^{(F)}(\tilde{r}_{1})}{X_{o}^{(F)}(\tilde{r}_{1})} = \rho^{(W)}X_{o}^{(W)}\int f_{FW}(12)\,\rho^{(F)}(\tilde{r}_{3})\,X_{o}^{(F)}(\tilde{r}_{3})\,f_{FW}(23)\,g_{FWF}^{ref}(r_{123})\,d\tilde{r}_{3} \qquad (6.20)$$

By taking the similar averages to equation 6.18 over the planes parallel to the wall at z_1 and z_3 , equation 6.20 is simplified to:

$$\overline{X}_{tr}^{(F)}(z_{1}) = \overline{X}_{o}^{(F)}(z_{1}) \rho^{(W)} X_{o}^{(W)}(f_{FW})^{2} g_{FW}^{ref}(z_{1}) \pi (r_{c}^{2} - z_{1}^{2})$$

$$\int_{z_start}^{r_{c}} \pi (r_{c}^{2} - z_{3}^{2}) \overline{\rho}^{(F)}(z_{3}) \overline{X}_{o}^{(F)}(z_{3}) g_{FW}^{ref}(z_{3}) \Gamma (z_{1}, z_{3}) dz_{3}$$
(6.21)

where z_start = 0.5d ($\cos\theta_{c_W} + 1$) and the function $\Gamma(z_1, z_3)$ is defined as below:

$$\Gamma\left(\mathbf{z}_{1},\mathbf{z}_{3}\right) = \frac{1}{\Omega^{2}} \int_{z_{1},z_{3}} \lambda\left(\mathbf{r}_{12}\right) \lambda\left(\mathbf{r}_{23}\right) \mathrm{U}\left(\Omega_{1},\Omega_{2}\right) \mathrm{U}\left(\Omega_{2},\Omega_{3}\right) \mathrm{H}\left(\mathbf{r}_{13}-\mathrm{d}\right) \mathrm{d}\Omega_{1} \mathrm{d}\Omega_{3} \qquad (6.22)$$

H(x) is the Heaviside step function, $\Omega = 4\pi$ is the total number of orientation configurations of a fluid segment, and $U(\Omega_1, \Omega_2)$ is given as:

$$U(\Omega_{1}, \Omega_{2}) = \begin{cases} 1, & \theta_{F(1)} \leq \theta_{c_F} \text{ and } \theta_{W(2)} \leq \theta_{c_W} \\ 0, & otherwise \end{cases}$$
(6.23)

where the orientation of the wall site is fixed at the wall and parallel to the z-axis. $\Gamma(z_1, z_3)$ represents the probability of having two fluid segments within the bond volume of a wall site at distances z_1 and z_3 from the wall that are properly oriented to form bonds with the wall site without overlapping with each other. 6.2 gives a geometrical presentation of bonding of two fluid segments at a wall site. We calculate values of this integral for each pair of z_1 and z_3 using Monte Carlo integration method which is close to the approach that was first created by Marshall and Chapman [96], and then used by Haghmoradi et al.[161] for divalent associating fluids.

Using an identical methodology, fractions of one-time, $X_d^{(W)}$, and two-times, $X_{tr}^{(W)}$, bonded wall sites are obtained as:

$$X_{d}^{(W)} = f_{FW} X_{o}^{(W)} \frac{(1 - \cos\theta_{c_{F}})}{2} \int_{z_{a} tart}^{r_{c}} dz_{1} \pi \left(r_{c}^{2} - z_{1}^{2}\right) \overline{\rho}^{(F)}(z_{1}) \overline{X}_{o}^{(F)}(z_{1}) g_{FW}^{ref}(z_{1})$$
(6.24)

$$X_{tr}^{(W)} = \frac{(f_{FW})^2}{2} X_o^{(W)} \int_{z_start}^{r_c} dz_1 \overline{\rho}^{(F)}(z_1) \overline{X}_o^{(F)}(z_1) g_{FW}^{ref}(z_1) \pi (r_c^2 - z_1^2) \int_{z_start}^{r_c} dz_3 \pi (r_c^2 - z_3^2) \overline{\rho}^{(F)}(z_3) \overline{X}_o^{(F)}(z_3) g_{FW}^{ref}(z_3) \Gamma (z_1, z_3)$$
(6.25)

Now that all possible fractions of the fluid and wall sites are defined, we need to solve the following mass action equations to obtain the monomer fractions of the fluid and wall sites:

$$\overline{X}_{o}^{(F)}(z_{1}) + \overline{X}_{d}^{(F)}(z_{1}) + \overline{X}_{tr}^{(F)}(z_{1}) = 1$$

$$(6.26)$$

$$X_o^{(W)} + X_d^{(W)} + X_{tr}^{(W)} = 1 aga{6.27}$$

Now that we have all fractions of bonding states derived we move forward to calculate the density profile of the fluid using equation 6.4

$$\rho^{(\mathrm{F})}\left(z_{1}\right) = \exp\left(\frac{\mu}{\mathrm{k}_{\mathrm{B}}\mathrm{T}} - \frac{\delta}{\delta\rho^{(\mathrm{F})}\left(z_{1}\right)}\frac{\mathrm{A}^{\mathrm{ASSOC}}\left[\rho^{(\mathrm{F})}\right]}{\mathrm{k}_{\mathrm{B}}\mathrm{T}} - \frac{\delta}{\delta\rho^{(\mathrm{F})}\left(z_{1}\right)}\frac{\mathrm{A}^{\mathrm{HS}}\left[\rho^{(\mathrm{F})}\right]}{\mathrm{k}_{\mathrm{B}}\mathrm{T}} - \frac{\mathrm{V}_{\mathrm{ext}}\left(\tilde{\mathrm{r}}\right)}{\mathrm{k}_{\mathrm{B}}\mathrm{T}}\right) \tag{6.28}$$

The derivative of the association Helmholtz free energy with respect to the local density of the fluid segments is written as

$$\frac{\delta}{\delta\rho^{(\mathrm{F})}(\mathrm{z}_{1})}\frac{\mathrm{A}^{\mathrm{ASSOC}}\left[\rho^{(\mathrm{F})}\right]}{\mathrm{k}_{\mathrm{B}}\mathrm{T}} = \ln\frac{\rho_{\mathrm{o}}^{(\mathrm{F})}(\mathrm{z}_{1})}{\rho^{(\mathrm{F})}(\mathrm{z}_{1})} - \frac{\delta\Delta\mathrm{c}^{(\mathrm{o})}}{\delta\rho^{(\mathrm{F})}(\mathrm{z}_{1})}$$
(6.29)

Since association happens only at the distances close to the wall, which is very small compared with the whole system range, we approximate the second term on the right hand side of 6.29 as:

$$\frac{\delta\Delta c^{(o)}}{\delta\rho^{(F)}(z_1)} = 0 \tag{6.30}$$

This approximation is equivalent to our approximation in equation 6.17 that the monomer density remains the same as the reference fluid density profile close to the wall as observed by Tripathis simulations [49].

In the next section the theory and simulation will be compared for a case of a fluid next to a hard wall.

6.3 Result and Discussion

In this section we compare predictions from density functional theory with new NVT Monte Carlo simulation results that we conducted for the density profile of fluid segments with one associating sites, with angular cutoff of size $\theta_{c_{-F}} = 27^{\circ}$, close to



Figure 6.3 : Density profile of fluid segments versus distance from the wall. Solid lines: theory; symbols: Monte Carlo simulation. The insets highlight the fluid density within the bonding region. a) $\varepsilon^* = 9$, $\rho_W^* = 0.14$, $\rho^{(\text{bulk})^*} = 0.14$ b) $\varepsilon^* = 9$, $\rho_W^* = 0.25$, $\rho^{(\text{bulk})^*} = 0.11$ c) $\varepsilon^* = 9$, $\rho_W^* = 0.39$, $\rho^{(\text{bulk})^*} = 0.09$

a planar hard wall that has association site on its surface with angular cutoff of size $\theta_{c_{-W}} = 35^{\circ}$. Similar to the theory, the spheres that carry the wall sites are considered to be hypothetical in simulation and z_start in simulation and theory are completely consistent. Simulation details were given in the previous study by Segura et al.[81].

Figure 6.3 shows excellent agreement of the theory (curves) with simulation results (symbols) for the density profile of the fluid versus the distance from the wall to the bulk region. The association energy between wall sites and fluid segments is, $(\varepsilon_{\rm FW}/k_{\rm B}T = \varepsilon^*)$, $\varepsilon^* = 9$ and the results are shown for the bulk fluid and wall site reduced number density of, $(\rho_{bulk}^* = \rho_b d^3 \text{ and } \rho^{(W)^*} = \rho^{(W)} d^2), \rho_{bulk}^* = \rho^{(W)} d^2$ 0.14 with $\rho^{(W)^*} = 0.14$, $\rho^*_{\text{bulk}} = 0.11$ with $\rho^{(W)^*} = 0.25$ and $\rho^*_{\text{bulk}} = 0.09$ with $\rho^{(W)^*} = 0.14$ 0.39 in cases a, b, and c, respectively. Since there is no fluid-fluid association, the fluid beyond the bonding region behaves as a hard sphere fluid. In figure 6.3, the insets highlight the bonding region where wall-fluid association causes a sharp increase in the density profile. According to figure 6.3, at constant association energy, enhancing the wall site density intensifies the adsorption of the fluid segments on the wall. The simulation results exhibited in this figure are produced with a fixed number of particles within the simulation box. As shown in figure 6.3, increasing $\rho^{(W)*}$ reduces ρ_{bulk}^* because the more attraction at the wall brings more adsorption of the fluid segments on the surface and less particles in the bulk region. In this figure one can observe that the agreement between our theory and simulation becomes slightly worse with increasing $\rho^{(W)*}$. The reason is that, as the density of wall sites and fluid segments close to the wall become large, the assumption of independent wall sites breaks down. This phenomena is explained in detail later in this section with introduction of distributions of fractions of fluid segments in different bonding states.

The effect of ρ_{bulk}^* on the density profile is investigated in figure 6.4, while $\varepsilon^* = 9$



Figure 6.4 : Density profile of fluid segments versus distance from the wall. Solid lines: theory; dash line: TPT1 theory; symbols: Monte Carlo simulation. The insets highlight the fluid density within the bonding region. a) $\varepsilon^* = 9$, $\rho_W^* = 0.14$, $\rho^{(\text{bulk})^*} = 0.14$ b) $\varepsilon^* = 9$, $\rho_W^* = 0.14$, $\rho^{(\text{bulk})^*} = 0.24$ c) $\varepsilon^* = 9$, $\rho_W^* = 0.14$, $\rho^{(\text{bulk})^*} = 0.38$.



Figure 6.5 : Density profile of fluid segments versus distance from the wall. Solid lines: theory; dash line: TPT1 theory; symbols: Monte Carlo simulation. The insets highlight the fluid density within the bonding region. a) $\varepsilon^* = 9$, $\rho_W^* = 0.14, \rho^{(bulk)^*} = 0.14$ b) $\varepsilon^* = 10$, $\rho_W^* = 0.14, \rho^{(bulk)^*} = 0.14$ c) $\varepsilon^* = 11$, $\rho_W^* = 0.14, \rho^{(bulk)^*} = 0.14$



Figure 6.6 : Density profile of fluid segments versus distance from the wall. Solid lines: theory; dash line: TPT1 theory; symbols: Monte Carlo simulation. The insets highlight the fluid density within the bonding region. a) $\varepsilon^* = 8$, $\rho_W^* = 0.39$, $\rho^{(bulk)^*} = 0.6$ b) $\varepsilon^* = 9$, $\rho_W^* = 0.39$, $\rho^{(bulk)^*} = 0.6$ c) $\varepsilon^* = 10$, $\rho_W^* = 0.39$, $\rho^{(bulk)^*} = 0.6$.

and $\rho^{(W)*} = 0.14$ are constant. Due to packing effects of hard spheres near a rigid surface, increasing ρ_{bulk}^* from 0.24 to 0.38 and 0.52, in cases a, b and c, brings a higher probability of finding particles close to the wall, and that increases the chances of finding fluid segments at proper position and orientation to form bonds with the wall sites. So, higher wetting effect and amount of association causes a sharper increase in density profiles and this is well predicted by our theory and confirmed with simulation. Dashed curves plotted in figure 6.4 present the density profiles assuming one bond per wall site which under predicts the density near the wall. As explained before, in large $\rho^*_{\rm bulk}$ many fluid segments are available for bond formation, so the chances of double bonding at the wall sites are greater and that intensifies the adsorption of the fluid on the wall compared with the case where wall sites can form only single bonds. Figure 6.5 exhibits how the density profile can be affected by ε^* , while bulk and wall site densities are constant $\rho_{\text{bulk}}^* = 0.14$ with $\rho^{(W)*} = 0.14$. Increasing ε^* from 9 to 10, and 11 increases the amount of fluid-wall association which adsorbs more fluid segments on the wall. The same effect is studied in figure 6.6 but for larger bulk and wall site densities that result in more adsorption of the fluid to the wall than figure 6.5. Figure 6.6 shows that in higher amounts of associations and adsorptions, especially in liquid states, the single bond per wall site theory fails to predict the correct density profile; however, there is good agreement between our theory and MC simulation results.

In figure 6.7, 6.8, and 6.9 we study the bonding status of fluid segments to obtain more insights about the system behavior. In figure 6.7 one can observe that increasing wall site density which comes with a reduction in bulk fluid density (similar to figure 6.3) brings more fluid-wall associations. As discussed before, since there is no fluidfluid association, beyond the bond area of the wall sites the fluid segments behave exactly like hard spheres; however, a sharp change will occur once they reach the



Figure 6.7 : Distribution of fluid segments at different bonding status versus distance from the wall. Solid lines: theory; symbols: Monte Carlo simulation. Blue: $X_b^{(F)}$, red: $X_o^{(F)}$, green: $X_{tr}^{(F)}$ and circles: $X_o^{(F)}$, rectangles: $X_b^{(F)}$, triangles: $X_{tr}^{(F)}$ a) $\varepsilon^* = 9$, $\rho_W^* = 0.06$, $\rho^{(bulk)^*} = 0.15$ b) $\varepsilon^* = 9$, $\rho_W^* = 0.14$, $\rho^{(bulk)^*} = 0.14$ c) $\varepsilon^* = 9$, $\rho_W^* = 0.25$, $\rho^{(bulk)^*} = 0.11$ d) $\varepsilon^* = 9$, $\rho_W^* = 0.39$, $\rho^{(bulk)^*} = 0.09$.

bonding region of the wall sites. This phenomenon is clearly observed in the bonded $(X_b^{(F)})$ and non-bonded $(X_o^{(F)})$ fluid particles fractions curves. In lower wall site and bulk densities, the change is smoother than high densities because of a lower amount of fluid-wall association. Additional curves showing the fractions $(X_{tr}^{(F)})$ of fluid segments bonded to twice-bonded wall sites is plotted. Although $X_{tr}^{(F)}$ is not significant in all four cases of this figure, increasing $\rho^{(W)*}$ reduces $X_{tr}^{(F)}$ because at low $\rho^{(W)^*}$ there are less wall sites available for bonding; therefore, to minimize the energy of the system the sites try to form more bonds resulting in more double bonded wall sites. However, increasing $\rho^{(W)^*}$ with the same number of fluid particles creates higher chances of association; consequently, the fluid particles, instead of restricting themselves in certain positions and orientations to share a wall site with another particle, bond to a non-bonded wall site to retain a higher degree of freedom. Figure 6.8 shows the effect of ρ_{bulk}^* at constant $\varepsilon^* = 9$, $\rho^{(W)^*} = 0.14$ on fluid-wall association. According to the results increasing the bulk density corresponds to a higher packing of spheres on the wall that brings more segments for association. At constant number of wall sites, with larger number of fluid particles there are more species available for bond formation, and in order to maximize the energy benefit, the wall sites form double bonds and $X_{tr}^{(F)}$ grows. Increasing bulk density which enhances wetting causes lower $X_b^{(F)}$ and higher $X_o^{(F)}$ because the number of the wall sites is fixed and there are more segments at the wall so the maximum capacity of sites are consumed, while still non-bonded segments are available. The effect of increasing ε^* from 8 to 9 and 10 at constant ${\rho^{(W)}}^* = 0.39$ and $\rho^*_{\text{bulk}} = 0.6$ on bonding status of fluid segments is exhibited in figure 6.9. According to figure 6.6 at such high $\rho^{(W)*}$ and ρ^{*}_{bulk} the fluid is strongly adsorbed to the surface. This is an interesting figure to show the limitations of our theory where $\rho^{(W)*}$, ρ^{*}_{bulk} , and $\rho^{(F)}(0)$ (fluid density at contact with the wall)

are at their highest values among all cases we have reported in this manuscript. In our theory, we assume the wall sites are independent of each other and there is no steric hindrance between them. Also, $\Gamma(z_1, z_3)$ which evaluates the probability of formation of two bonds at a wall site does not carry any effect from the density of the fluid at z_1 or z_3 , and existence of another wall site at their vicinity. Therefore, at such condition of high $\rho^{(F)}(0)$ and $\rho^{(W)^*}$ a difference between theory predictions and MC results is expected. $X_{tr}^{(F)}$ at $\varepsilon^* = 8$, 9 is well reported by theory and verified by simulations, but at $\varepsilon^* = 10$ while theory shows a monotonic increase, simulation presents a constant value in distances very close to the wall. We believe this happens because of the steric hindrance between the fluid segments bonded to the wall sites close to each other which does not leave enough space for all of the wall sites to consume their maximum capacity in bond formation.

Effects of association energy and bulk fluid density on surface coverage, $X_b^{(W)}$, are exhibited in figure 6.10 where increasing each factor results in a growth in $X_b^{(W)}$. To compare our theory with Tripathis [49, 101], we calculated $X_b^{(W)}$ using his approach, and we found the results agree with our theory. In an attempt to calculate the surface coverage using only bulk fluid properties we derived $X_b^{(W)}$ in a simplified form by approximating the surface coverage as follow:

$$X_{\rm b}^{\rm (W)} = \frac{P_{\rm bulk} \kappa f_{\rm FW}}{1 + P_{\rm bulk} \kappa f_{\rm FW}}$$
(6.31)

where P_{bulk} is the bulk fluid pressure and it depends on the bulk fluid density, $\kappa = \nu_{\rm b} \left(1 - \cos\theta_{\rm c,F}\right)/2$ and $\nu_{\rm b}$ is the bond volume of a wall site. This is the Langmuir adsorption equation. The predictions from equation 6.31 are close to DFT calculation and MC results.



Figure 6.8 : Distribution of fluid segments at different bonding status versus distance from the wall. Solid lines: theory; symbols: Monte Carlo simulation. Blue: $X_b^{(F)}$, red: $X_o^{(F)}$, green: $X_{tr}^{(F)}$ and circles: $X_o^{(F)}$, rectangles: $X_b^{(F)}$, triangles: $X_{tr}^{(F)}$ a) $\varepsilon^* = 9$, $\rho_W^* = 0.14, \rho^{(\text{bulk})^*} = 0.14$ b) $\varepsilon^* = 9$, $\rho_W^* = 0.14, \rho^{(\text{bulk})^*} = 0.24$ c) $\varepsilon^* = 9$, $\rho_W^* = 0.14, \rho^{(\text{bulk})^*} = 0.38$ d) $\varepsilon^* = 9$, $\rho_W^* = 0.14, \rho^{(\text{bulk})^*} = 0.52$.



Figure 6.9 : Distribution of fluid segments at different bonding status versus distance from the wall. Solid lines: theory; symbols: Monte Carlo simulation. Blue: $X_b^{(F)}$, red: $X_o^{(F)}$, green: $X_{tr}^{(F)}$ and circles: $X_o^{(F)}$, rectangles: $X_b^{(F)}$, triangles: $X_{tr}^{(F)}$ a) $\varepsilon^* = 8$, $\rho_W^* = 0.39, \rho^{(bulk)^*} = 0.6$ b) $\varepsilon^* = 9$, $\rho_W^* = 0.39, \rho^{(bulk)^*} = 0.6$ c) $\varepsilon^* = 10$, $\rho_W^* = 0.39, \rho^{(bulk)^*} = 0.6$.

6.4 Conclusion

We extended Wertheims two-density formalism beyond its first order to model a system of fluid particles with a small association site which can form only one bond near to a functionalized rigid surface with large association sites that can bond to two fluid particles simultaneously. We studied the effects of the reduced bulk fluid and wall site densities, and temperature on fluid segments density profile, extent of association, competition between single and double bonding of fluid segment at the wall sites versus distance from the wall. The theory predictions are compared with new Monte Carlo simulation results and they are in good agreement. The theory accurately predicts that increasing either association energy, bulk fluid or wall site densities intensifies the adsorption and the amount of fluid-wall association. We found that the assumption of independent sites on the wall surface faces limitations at high wall site densities. The theory captures the surface coverage over a wide range of temperature and bulk density and predicts the distribution of singly or doubly bonded wall sites. In addition, for such systems that we studied, especially in the range of high association energy and fluid density close to the wall, theory requires approximately two orders of magnitude less computation time than molecular simulation even in the absence of fluid-fluid association.

The theory can be applied for association of molecular fluids to surfaces with functional divalent groups, as well as, patchy colloids near to surfaces functionalized with large patches. Extensions of the current theory for systems of the fluid with multiple association sites, fluid-fluid association, and capturing the effect of steric hindrance between wall sites for surfaces with high site densities are topics of future publications.



Figure 6.10 : a) Surface coverage $X_b^{(W)}$ versus $\varepsilon^* \left(\rho^{(W)^*} = 0.14, \rho_{\text{bulk}}^* = 0.14\right)$. b) Surface coverage $X_b^{(W)}$ versus $\rho_{\text{bulk}}^* \left(\varepsilon^* = 0.14, \rho^{(W)^*} = 0.14\right)$. Solid lines: theory; Dash lines: equation 6.31; symbols: MC simulation results.

Chapter 7

Concluding Remarks and Future Work

In this thesis Wertheim's thermodynamic perturbation theory was developed beyond its first order for different systems of associating fluids in bulk and near to the interfaces. To verify the theory developments, the results were compared with new monte carlo simulations and experimental measurements data, where the agreements in all of the cases were excellent.

7.1 Concluding Remarks

In chapter 2, a thermodynamic perturbation theory was developed for a binary mixture of fluids with two identical associating sites. According to the limitation we imposed on the association, the specific types of chains and rings with even number of colloids were formed. While in Wertheim's theory, fluids with more than one associating site are treated within a multi-density formalism[45, 46, 106] in which including the steric hindrance effect for such fluids is very difficult, in chapter 2 we utilized a two-density formalism that including the steric hindrance effect at any order of perturbation theory was simpler and more transparent. Two-density formalism had shown promising results for single-site fluids in previous studies [43, 44, 65]. In this work we extended this framework to an equimolar mixture of colloids with two association sites. Extensions of the current theory for the case where two species have different bond angles, and for a non-equimolar binary mixture will be the subjects of future studies.

In chapter 3, Wertheim's two-density formalism was extended to model bond cooperativity and cyclic formation effect in hydrogen bonding fluids. The theory captures the behavior of associating hard sphere and Lennard Jones species in various conditions of cooperativity and Lennard Jones attraction. We applied the theory to calculate the thermodynamic properties of hydrogen fluoride, and it was found that formation of 6-mer rings and a bond cooperativity ratio of around 1.58 are effective in predicting the enthalpy of vaporization with a higher accuracy compared with the previous SAFT-VR study by Galindo et al.[6]. Extensions on our theory to set the energy of the bonds proportional to the size of the clusters of associated species, studying the cooperativity effect in mixtures of associating fluids, and applying the theory to model mixtures of alcohols are the topics of future works.

We developed an asymmetric model within Wertheim's thermodynamic perturbation theory in chapter 4 where an associating species has a combination of monovalent and divalent sites. To observe the effect of implementing a divalent site instead of two monovalent sites, we compared the current theory results with corresponding four-site model using TPT1 and we found that at the limit of associating sites with large bonding volumes both theories converge to similar results. We applied the theory to calculate the thermo-physical properties of water, since the oxygen atom can be considered as a single association sites with two available pairs of free electrons to share for two hydrogen bonds, and fitted the model's parameters to experimental data on liquid density and vapor pressure. The great advantage of such theory is the flexibility it carries by allowing a user to vary the hydrogen bonding energies with respect to the state of hydrogen bonding, and also tuning the geometry of the divalent site to obtain a more accurate model. These are all additional flexibilities compared with PC-SAFT and generally any SAFT version equation of state. The current theory represents water molecules as asymmetric associating species where the energy of hydrogen bonding is determined by the state of bonding of molecules. The authors believe that the model has a great potential for improvement specifically by testing the theory for water using a Lennard Jones reference fluid which is the topic of a future study. In addition, application of the model for mixtures of water/alkanes and water/alcohols are subjects of future studies.

In Chapter 5, we extended multi-density formalism for colloids with two divalent patches. This has been further developed in the form of a free energy functional and applied in a density functional theory to predict the overall density distribution and distribution of associated states as a function of distance from a pore wall. The temperature range studied was limited by time necessary to produce equilibrium configurations in simulation. At lower temperatures, we expect the overall density profile to be accurate, but we expect bonding fractions to show deviation, particularly near a pore wall. Our experience in applying the first order theory to confined polymers (the lowest temperature state of complete bonding)[75, 177] has been very good agreement between theory and simulation for fluid density distribution. Extension of the density functional theory using approaches to further relax approximations in Wertheims TPT1, such as geometric bond angle constraints, cooperative hydrogen bonding, spherically symmetric sites, etc. as described in Marshall et al.[125, 14, 1] for bulk fluids, and mixtures of patchy colloidal fluids will be the subjects of future research.

In chapter 6, Wertheim's TPT was extended beyond its first order to model a system of fluid particles with a small association site which can form only one bond near to a functionalized rigid surface with large association sites that can bond to



Figure 7.1 : An exhibition of system of association fluids with two association sites near to a functionalized surface, where the active surface sites are close to each that bonding at one site limits the available space for the other site.

two fluid particles simultaneously. We studied the effects of the reduced bulk fluid and wall site densities, and temperature on fluid segments density profile, extent of association, competition between single and double bonding of fluid segment at the wall sites versus distance from the wall. The theory accurately predicts that increasing either association energy, bulk fluid or wall site densities intensifies the adsorption and the amount of fluid-wall association. We found that the assumption of independent sites on the wall surface faces limitations at high wall site densities. The theory captures the surface coverage over a wide range of temperature and bulk density and predicts the distribution of singly or doubly bonded wall sites. The theory can be applied for association of molecular fluids to surfaces with functional divalent groups, as well as, patchy colloids near to surfaces functionalized with large patches. Extensions of the current theory for systems of the fluid with multiple association sites, fluid-fluid association, and capturing the effect of steric hindrance between wall sites for surfaces with high site densities (as depicted in figure 7.1) are topics of future research.

7.2 Future Work

The current studies on associating fluids in this thesis has revealed the great potential for extensions of the theory for more complex systems. The theoretical developments for confined fluids [161] using density functional theory formalism are only position dependent. The orientation dependency of the system was taken care of by averaging over all possible orientations of fluid species in the orientation space. However, this may not be the best assumption, and one study can be focused on developing an association theory in density functional theory framework for an associating fluid confined between two parallel hard walls and at the same time influences by an external orienting fluid that is not position dependent. This can be considered as an extension to Marshall's work [13] where he modeled a fluid with two association sites in bulk region influenced by and external orienting field. In that work, Marshall used Wertheim TPT1 in a DFT framework which the final equations were only function of orientation of fluids species with respect to the external field. Adding position dependency to this work makes the situation more complex which is considered as future work. A scheme of the suggested system is depicted in figure 7.2, where the fluid between two parallel rigid surfaces is in equilibrium with the fluid in the bulk region. To avoid the effect of the areas close to the ends of the walls, the dimensions of the walls are assumed to much larger than fluid species diameter. The primary equations for this system is developed in the following section.

7.2.1 Theory

We consider an associating fluid with spherical species of diameter d, and two monovalent conical associating sites placed at two opposite poles of the sphere (separated by 180°), and label them as A and B. Also, association is restricted to happen only between A and B. The potential of interaction will be the sum of hard sphere and association attraction. The association attraction potential is described by square well potential [123, 109, 124] as follow:

$$\phi_{AB}(12) = \begin{cases} -\varepsilon_{AB}, & r_{12} \le r_c, \ \beta_{A1} \le \beta_c, \ \beta_{B2} \le \beta_c \\ 0, & otherwise \end{cases}$$
(7.1)

The notation $(1) \equiv [\vec{r_1}, \Omega_1]$ stands for position $[(\vec{r_1})$ and orientation (Ω_1) vectors of sphere 1. r_{12} indicates the distance between centers of spheres 1 and 2. r_c and β_c are the critical distance and angle of association, respectively, beyond which association



Figure 7.2 : An exhibition of the associating fluid in bulk region and at the area confined by two parallel hard walls, and an external orienting field which emerges. In this picture the direction of the field is perpendicular to both walls.



Figure 7.3 : A schematic comparison that shows the effect of orienting field on a fluid with two associating sites near to a rigid surface.



Figure 7.4 : Presentation of the associating species in and oriental field, with the orientation direction represented by \vec{E} . The species orientation is describe by the vector connecting the center of the species j to the center of its associating site $(\vec{r_A}^{(j)})$ [13].

cannot happen. $\beta_{A(1)}$ is the angle between the vector connecting centers of spheres 1 and 2, and the vector from the center of the sphere 1 to the center of its site, A ($\beta_{B(2)}$ is defined in the similar way). If two spheres are properly positioned and oriented relative to each-other they will associate and the energy of the system reduces by ε_{AB} .

The grand free energy (Θ) of the system is a function of the fluid species number density (ρ) , and the number density is a function of position (\vec{r}) and orientation (Ω) of the species. Θ is defined as follow:

$$\Theta\left[\rho\left(\vec{r},\Omega\right)\right] = A\left[\rho\left(\vec{r},\Omega\right)\right] + \int \rho\left(\vec{r},\Omega\right)\left(V_{ext}\left(\Omega\right) - \mu\right)d\vec{r}d\Omega$$
(7.2)

where A is the Helmholtz free energy, $V_{ext}(\Omega)$ is the external field, and μ is the chemical potential of the fluid. The Helmholtz free energy is comprised of the ideal gas, hard sphere and association contribution as follow:

$$A\left[\rho\left(\vec{r},\Omega\right)\right] = k_B T \int \rho\left(\vec{r},\Omega\right) \left(\ln\left(\rho\left(\vec{r},\Omega\right)\Lambda^3\right) - 1\right) d\vec{r} d\Omega + A^{HS}\left[\rho\left(\vec{r},\Omega\right)\right] + A^{ASSOC}\left[\rho\left(\vec{r},\Omega\right)\right]$$

$$(7.3)$$

In this system, the external field is only a function of orientation and has no position dependency:

$$\frac{V_{ext}\left(\Omega\right)}{k_BT} = \frac{\Phi_E\left(\Omega\right)}{k_BT} = -C^* \cos\gamma \tag{7.4}$$

 C^* is the magnitude of the field, and γ is the angle between field vector (\vec{E}) and the fluid species orientation vector $(\vec{r_A}^{(j)})$ which is the vector connecting the center of the sphere to the center of its association site A (depicted in figure 7.4).

According to Wertheim's theory [45, 46], the Helmholtz free energy due to asso-

ciation for a fluid with two association sites is written as:

$$A^{ASSOC}[\rho] = k_B T \int d(1) \left(\rho(1) \ln \frac{\rho_o(1)}{\rho(1)} - \sigma_A(1) - \sigma_B(1) - \frac{\sigma_A(1) \sigma_B(1)}{\rho_o(1)} + \rho(1) \right) - \Delta c^{(o)}$$
(7.5)

 $\Delta c^{(o)}$ is the sum of all graphs of associated species. According to the specifics of the associating sphere Wertheim's TPT1 is considered as the best approximation for this system:

$$\Delta c^{(o)} = \int \sigma_A(1) \,\sigma_B(2) \,f_{AB}(12) \,g(12) \,d(1) \,d(2) \tag{7.6}$$

Defined by Wertheim, for a fluid with two associating sites (A and B), σ_A is the density of the fluid species that are not bonded at B (σ_B is defined similarly), $f_{AB}(12) = \exp\left[-\phi_{AB}(12)/k_BT\right] - 1$ is the Mayer *f*-function of association and g(12) is the pair correlation function. The bulk chemical potential is consisted of:

$$\frac{\mu}{k_B T} = \frac{\mu^{ID}}{k_B T} + \frac{\mu^{HS}}{k_B T} + \frac{\mu^{ASSOC}}{k_B T}$$
(7.7)

It is assumed that the parallel hard walls, which provide a frame for external field, are surrounded by the bulk fluid (see figure 7.2), where the fluid species are freely move into and out of the space between the walls, and the edge effects are neglected. Therefore an equilibrium between the fluid in the bulk region and the fluid confined between the walls is considered. The calculation of the bulk chemical potential will be trivial and will be similar to the previous studies [161].

According to density functional theory, in equilibrium there exists a unique density profile for fluid species, and the density profile is obtained by minimizing the grand free energy with respect to the fluid density:

$$\frac{\delta\Theta\left[\rho\right]}{\delta\rho\left(\vec{r},\Omega\right)}\Big|_{\rho^{(F)}=\rho^{(F)}_{eq}} = 0$$
(7.8)

where the density is obtained as:

$$\rho\left(\vec{r},\Omega\right) = exp\left(\frac{\mu}{k_BT} - \frac{\delta}{\delta\rho\left(\vec{r},\Omega\right)}\frac{A^{ASSOC}\left[\rho\right]}{k_BT} - \frac{\delta}{\delta\rho\left(\vec{r},\Omega\right)}\frac{A^{HS}\left[\rho\right]}{k_BT} - \frac{\Phi_E\left(\Omega\right)}{k_BT}\right)$$
(7.9)

where we expect the functional derivative of the hard sphere contribution to the Helmholtz free energy with respect to density simplifies to a position derivative, while the functional derivative of the association contribution will be both position and orientation derivative.

$$\frac{\delta}{\delta\rho\left(\vec{r},\Omega\right)}\frac{A^{ASSOC}\left[\rho\right]}{k_{B}T} = \ln X_{o}\left(\vec{r},\Omega\right) - \frac{\delta\Delta c^{(o)}}{\delta\rho\left(\vec{r},\Omega\right)}$$
(7.10)

where X_o is the fraction of monomers. The second term on RHS of equation 7.10 is simply derived by the approximation $g(12) = g_{HS}(\vec{r_1}, \vec{r_2})$ which is the correlation function of hard sphere reference fluid that is only function of position since in hard sphere fluid the orientation of species are not correlated [13]. The derivative is written as:

$$\frac{\delta\Delta c^{(o)}}{\delta\rho\left(\vec{r},\Omega\right)} = \int \sigma_A\left(\vec{r}_1,\Omega_1\right)\sigma_B\left(\vec{r}_2,\Omega_2\right)f_{AB}\left(\vec{r}_1,\vec{r}_2,\Omega_1,\Omega_2\right)\frac{\delta g_{HS}\left(\vec{r}_1,\vec{r}_2\right)}{\delta\rho\left(\vec{r},\Omega\right)}d\vec{r}_1d\Omega_1d\vec{r}_2d\Omega_2\tag{7.11}$$

Using the mass action equation (as shown by SAFT equation of state [107]), the fraction of fluid molecules non-bonded at site A is calculated as:

$$\frac{1}{X_A(\vec{r_1}, \cos\gamma)} = 1 + \int \rho\left(\vec{r_2}, \cos\gamma'\right) X_B\left(\vec{r_2}, \cos\gamma'\right) f_{AB}\left(\vec{r_1}, \vec{r_2}, \Omega_1, \Omega_2\right) g_{HS}\left(\vec{r_1}, \vec{r_2}\right) d\vec{r_2} d\Omega_2$$
(7.12)

Switching $A \to B$ obtains the similar mass action equation for site B. Once X_o and X_A are obtained the density profile is known as function of position and orientation, then the distribution of the fluid species at each orientation and position can be obtained by:

$$\Upsilon\left(\vec{r},\Omega\right) = \frac{\rho\left(\vec{r},\Omega\right)}{\int \rho\left(\vec{r},\Omega\right) d\Omega}$$
(7.13)

The next step in this work will be obtaining a simplified form for X_A as a function of the relative position and orientation of the fluid species with respect to the walls and the external field \vec{E} which will be studied in future studies.

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Appendix A

Derivation of Thermodynamic Properties for An Associating Fluid with Two Divalent Sites, Confined Between Two Parallel Hard Walls

To calculate the chemical potential the bulk limit, we provide the homogeneous form of the Helmholtz free energy as:

$$\frac{A^{assoc}}{Nk_BT} = lnX_o + 1 - M_{A_1} - M_{A_2} + \frac{M_{A_1}M_{A_2}}{X_o} - \frac{\Delta c^{(o)}}{N}$$
(A.1)

where all the terms in this equation are equivalent to the inhomogeneous form of the same terms we derived in theory section. The bulk chemical potential is written:

$$\frac{\mu^{assoc}}{k_B T} = ln X_o - \frac{\partial \Delta c^{(o)} / V}{\partial \rho}$$
(A.2)

Plugging the bulk limit of $\frac{\partial \Delta c^{(o)}/V}{\partial \rho}$ from theory section of chapter 5 into equation A.2 the complete form of the chemical potential is obtained:

$$\frac{\mu^{assoc}}{k_B T} = ln X_o - \eta M_{A_2} c_{A_1}^{T1} \frac{\partial lny(d)}{\partial \eta} - \eta M_{A_2} c_{A_1}^{T2(1)} \left[2 \frac{\partial lny(d)}{\partial \eta} + \frac{\partial lny(\bar{\omega}_{chain})}{\partial \eta} \right]$$

$$- \eta M_{A_2} c_{A_1}^{T2(ring)} \left[\frac{8}{6} \frac{\partial lny(d)}{\partial \eta} + \frac{4}{6} \frac{\partial lny(\bar{\omega}_{ring})}{\partial \eta} \right]$$
(A.3)

From here, calculating the pressure equation is straight forward:

$$P^{assoc} = \rho \mu^{assoc} - A^{assoc} / V \tag{A.4}$$

Appendix B

Calculation of Pressure, Chemical Potential, and Internal Energy for Water Model

In this appendix we derive the chemical potential, excess internal energy, and pressure from the results of the theory section. The chemical potential is derived from the general relation:

$$\frac{\mu^{ASSOC}}{k_B T} = ln \frac{\rho_o}{\rho} - \frac{\partial \Delta c^{(o)}/V}{\partial \rho}$$
(B.1)

And the derivative of the contribution due to the association which is composed of derivative of the first and second order terms is:

$$\frac{\partial \Delta c_{TPT1}/V}{\partial \rho} = \left(\sigma_{\Gamma-O}\sigma_{\Gamma-H_1} + \sigma_{\Gamma-O}\sigma_{\Gamma-H_2}\right) \frac{\partial \Theta_{TPT1}}{\partial \rho} \tag{B.2}$$

$$\frac{\partial \Delta c_{TPT2}/V}{\partial \rho} = \left(\sigma_{\Gamma-O}\sigma_{\Gamma-H_1}^2/2 + \sigma_{\Gamma-H_1}\sigma_{\Gamma-O}\sigma_{\Gamma-H_2} + \sigma_{\Gamma-O}\sigma_{\Gamma-H_2}^2/2\right)\frac{\partial I_{TPT2}}{\partial \rho} \quad (B.3)$$

And the derivatives of the integrals in B.2 and B.3 are:

$$\frac{\partial \Theta_{\text{TPT1}}}{\partial \rho} = \Theta_{\text{TPT1}} \left(\frac{\partial lng_{HS}(d)}{\partial \eta} \right) \tag{B.4}$$

$$\frac{\partial I_{\text{TPT2}}}{\partial \rho} = I_{TPT2} \left(2 \frac{\partial lng_{HS}(d)}{\partial \eta} + \frac{\partial lny(\varpi)}{\partial \eta} \right)$$
(B.5)

Knowing the chemical potential the pressure is calculated through the relation

$$\frac{P^{ASSOC}}{Nk_BT} = \frac{\rho\mu^{ASSOC}}{k_BT} - \frac{A^{ASSOC}}{Vk_BT}$$
(B.6)

And the internal energy due to association is obtained through equation

$$\frac{U^{ASSOC}}{Nk_BT} = \frac{\partial}{\partial\beta} \frac{\beta A^{ASSOC}}{N} \tag{B.7}$$

$$\frac{\frac{\partial}{\partial\beta}\frac{\beta A^{ASSOC}}{N} = \frac{\dot{\rho}_o}{\rho_o} + 2\left(\frac{\dot{\sigma}_{\Gamma-H}}{\sigma_{\Gamma-H}}\right)\left(\frac{\sigma_{\Gamma-H}c_H}{\rho}\right) + 2\left(\frac{\sigma_{\Gamma-H}\dot{c}_H}{\rho}\right) + \left(\frac{\dot{\sigma}_{\Gamma-O}}{\sigma_{\Gamma-O}}\right)\left(\frac{\sigma_{\Gamma-O}c_O}{\rho}\right) + \left(\frac{\sigma_{\Gamma-O}\dot{c}_O}{\rho}\right) - \frac{\partial\Delta c^{(o)}/N}{\partial\beta}$$
(B.8)

$$\frac{\partial}{\partial\beta}\frac{\Delta c_{TPT1}}{N} = \frac{1}{\rho}\left(\frac{\dot{\sigma}_{\Gamma-O}}{\sigma_{\Gamma-O}} + \frac{\dot{\sigma}_{\Gamma-H}}{\sigma_{\Gamma-H}} + \frac{\dot{f}_{OH}}{f_{OH}}\right)\frac{\Delta c_{TPT1}}{V}$$
(B.9)

$$\frac{\partial}{\partial\beta}\frac{\Delta c_{TPT2}}{N} = \frac{1}{\rho} \left(\frac{\dot{\sigma}_{\Gamma-O}}{\sigma_{\Gamma-O}} + 2\frac{\dot{\sigma}_{\Gamma-H}}{\sigma_{\Gamma-H}} + 2\frac{\dot{f}_{OH}}{f_{OH}}\right)\frac{\Delta c_{TPT2}}{V}$$
(B.10)

Using equation (4.15) we have

$$\frac{\dot{\rho}_o}{\rho_o} = -\left(\frac{\rho_o}{\rho}\right) \left[\dot{c}_{H_1} + \dot{c}_{H_2} + \dot{c}_O + \dot{c}_{H_1}c_{H_2} + c_{H_1}\dot{c}_{H_2} + \dot{c}_{H_1}c_O + c_{H_1}\dot{c}_O + \dot{c}_{H_2}c_O + c_{H_2}\dot{c}_O + \dot{c}_{H_1}c_{H_2}c_O + c_{H_1}\dot{c}_{H_2}c_O + c_{H_1}c_{H_2}\dot{c}_O\right]$$
(B.11)

$$c_{H_1}\dot{c}_O + \dot{c}_{H_2}c_O + c_{H_2}\dot{c}_O + \dot{c}_{H_1}c_{H_2}c_O + c_{H_1}\dot{c}_{H_2}c_O + c_{H_1}c_{H_2}\dot{c}_O$$

$$\frac{\dot{\sigma}_{\Gamma-O}}{\rho_o} = \frac{\dot{\rho}_o}{\rho_o} \left[\sigma_{\Gamma-O} / \rho_o \right] + \left[\dot{c}_{H_1} + \dot{c}_{H_2} + \dot{c}_{H_1} c_{H_2} + c_{H_1} \dot{c}_{H_2} \right]$$
(B.12)

$$\frac{\dot{\sigma}_{\Gamma-H_1}}{\rho_o} = \frac{\dot{\rho}_o}{\rho_o} \left[\sigma_{\Gamma-H_1} / \rho_o \right] + \left[\dot{c}_O + \dot{c}_{H_2} + \dot{c}_O c_{H_2} + c_O \dot{c}_{H_2} \right]$$
(B.13)

$$\dot{c}_{H_1} = \dot{\sigma}_{\Gamma-O}\Theta_{\text{TPT1}} + \left(\frac{\dot{f}_{OH}}{f_{OH}}\right)\sigma_{\Gamma-O}\Theta_{\text{TPT1}} + \left(\dot{\sigma}_{\Gamma-O}\sigma_{\Gamma-H_1} + \sigma_{\Gamma-O}\dot{\sigma}_{\Gamma-H_1} + \dot{\sigma}_{\Gamma-O}\dot{\sigma}_{\Gamma-H_2}\right)I_{\text{TPT2}} + 2\left(\frac{\dot{f}_{OH}}{f_{OH}}\right)\left(\sigma_{\Gamma-O}\sigma_{\Gamma-H_1} + \sigma_{\Gamma-O}\sigma_{\Gamma-H_2}\right)I_{\text{TPT2}}$$
(B.14)

$$\dot{c}_{O} = (\dot{\sigma}_{\Gamma-H_{1}} + \dot{\sigma}_{\Gamma-H_{2}}) \Theta_{\text{TPT1}} + (\sigma_{\Gamma-H_{1}} + \sigma_{\Gamma-H_{2}}) \left(\frac{\dot{f}_{OH}}{f_{OH}}\right) \Theta_{\text{TPT1}} + (\dot{\sigma}_{\Gamma-H_{1}}\sigma_{\Gamma-H_{1}} + \dot{\sigma}_{\Gamma-H_{1}}\sigma_{\Gamma-H_{2}} + \sigma_{\Gamma-H_{1}}\dot{\sigma}_{\Gamma-H_{2}} + \dot{\sigma}_{\Gamma-H_{2}}\sigma_{\Gamma-H_{2}}) I_{\text{TPT2}} + 2 \left(\frac{\dot{f}_{OH}}{f_{OH}}\right) (\sigma_{\Gamma-H_{1}}^{2}/2 + \sigma_{\Gamma-H_{1}}\sigma_{\Gamma-H_{2}} + \sigma_{\Gamma-H_{2}}^{2}/2) I_{\text{TPT2}}$$
(B.15)

since the choice between H_1 , H_2 is completely random then equations will be simplified:

$$\dot{c}_{H_1} = c_{H_1} \left(\frac{\dot{\sigma}_{\Gamma-O}}{\sigma_{\Gamma-O}} + \frac{\dot{f}_{OH}}{f_{OH}} \right) + \left(2\sigma_{\Gamma-O}\sigma_{\Gamma-H_1} \right) I_{\text{TPT2}} \left(\frac{\dot{\sigma}_{\Gamma-H}}{\sigma_{\Gamma-H}} + \frac{\dot{f}_{OH}}{f_{OH}} \right) \tag{B.16}$$

$$\dot{c}_O = \left(\frac{\dot{\sigma}_{\Gamma-H}}{\sigma_{\Gamma-H}} + \frac{\dot{f}_{OH}}{f_{OH}}\right) \left(c_O + 2\sigma_{\Gamma-H}^2 I_{TPT2}\right) \tag{B.17}$$

From here Enthalpy of the fluid is calculated as:

$$H^{ASSOC} = U^{ASSOC} + P^{ASSOC}V \tag{B.18}$$

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