RICE UNIVERSITY

Statistical thermodynamics of multi-body effects in associating fluids: A cluster size distribution theory

by

Artee Bansal

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE
Doctor of Philosophy

APPROVED, THESIS COMMITTEE:

Dr. Walter G. Chapman, Chair
Associate Dean for Energy
William W. Akers Chair Professor
Chemical and Biomolecular Engineering

Dr. Kenneth R. Cox
Professor in the Practice
Director of Undergraduate Studies
Chemical and Biomolecular Engineering

Dr. Mason B. Tomson
Professor of Engineering
Civil and Environmental Engineering

Dr. Francisco Vargas
Assistant Professor
Chemical and Biomolecular Engineering

Houston, Texas
October, 2017
ABSTRACT

Statistical thermodynamics of multi-body effects in associating fluids: A cluster size distribution theory

by

Artee Bansal

Associating fluids are central to all natural and engineered systems. Notable examples are water, the matrix of life, and solvents typically encountered in industrial processes. In contrast to simple liquids, in associating fluids attractive interactions play a decisive role in the structure and thermodynamics of the fluid.

Patchy colloids, particles with engineered directional interactions, are characterized by short range directional interactions and are archetypes of associating fluids. For these molecules with short range directional interactions, by varying the shape, number, and position of the patches, different self assembled geometries leading to complex structures can be obtained. Thus these systems have drawn intense scrutiny in designing materials from the nanoscale level. But despite the simplicity in describing and engineering the inter-molecular interactions in such systems, a general theory to predict the phase behavior is not yet available.

Statistical associating fluid theory (SAFT) has proven useful in modeling associating fluids of both scientific and industrial importance. In SAFT, the fluid properties are obtained by incorporating the role of association over the reference system properties. The properties of the reference are typically based on modeling two-particle or three-particle distribution functions. As the complexity of the interaction increases in
the physical system, such as may result from multiple bonding and size asymmetries, multi-body interactions become more important and information about two-body or three-body correlations in the reference no longer suffices. The difficulty in determining these interactions arises due to the limited knowledge in describing multi-body correlation functions particularly for three-body and higher correlations, also at separations other than contact value.

In this work, we develop a new type of perturbation theory that allows us to incorporate multi-body effects given the properties of the reference. Drawing upon SAFT and quasichemical theory, theoretical models for the molecular level interactions are developed to describe the thermodynamic properties and structure of these self-assembling mixtures.

We first study mixtures of spherically symmetric solute in patchy colloid solvents, a model for solvated ions and supramolecular star molecules. We present a “complete reference” perturbation theory that can describe multiple bonding at a single patch by representing higher order correlation functions in the hard sphere reference fluid in terms of average $n$-ordered clusters. Studies for symmetric and asymmetric colloidal mixtures show excellent agreement with the computer experiments for these systems. We also perform a quasichemical theory based analysis to develop a physically transparent, statistical mechanical model to describe the occupancy probabilities in the hard sphere fluids for different packing fractions. This model corrects multi-body effects obtained for isolated clusters by incorporating the role of the cluster-bulk interface and the bulk medium effects.

Next we model associating fluids entirely within the quasichemical organization of the potential distribution theorem and explore a range of bonding configurations from a solute that can bond only once, to a solute that can bond multiple solvents but only on one-hemisphere of its surface, i.e. a Janus particle, and to a solute with a sticky patch that covers its entire surface. Quasichemical theory leads to the identification of the occupancy of a patch conditional on the total occupancy of the spherical
observation volume, all in the reference fluid, as an important quantity within the theory. Based on this study we extend Wertheim’s theory beyond second order thermodynamic perturbation to study different multiple bonding geometries of a single site on the solute molecules. Again excellent agreement with computer simulations is obtained for different patch geometries. Our theoretical equilibrium phase studies also show the importance of these mixtures in obtaining very low density gels.

Lastly, the application of these multi-body effects to model ion-solvent interactions in electrolyte systems is indicated with a SAFT model for electrolyte systems. We also present various future directions of our approach.
Acknowledgements

My sincere gratitude to my advisor Dr. Walter G. Chapman, for his patience, his immense knowledge, and for motivating me to do my best. I truly enjoyed working in a research environment where original thinking and initiative is encouraged. I could not have imagined having a better advisor and mentor.

I want to extend a special thanks to Dr. Dilip N. Asthagiri, whose expertise, direction, and support were critical to the success of my research project. Dr. Chapman and Dr. Asthagiri have also helped me immensely in improving my scientific writing skills. I would also like to thank the rest of my thesis committee: Dr. Kenneth R. Cox, Dr. Mason B. Tomson, and Dr. Francisco Vargas, for their insightful comments and encouragement.

I am fortunate to have worked with a talented group of people during my PhD. My sincere thanks to Dr. Essmail Djmali and Dr. Pradeep Venkatraman, for various discussions on the electrolyte work. I also want to thank my seniors Dr. Bennett Marshall and Dr. Deepti Ballal, for many discussions that helped in my research project. I thank my fellow group members: Amin, Arjun, Jinlu, Kevin, Leo, Shun, Yiwei, and Yuchong, for the stimulating discussions we have had in the last five years.

Many thanks to my friends in Houston: Aarthi, Abhinav, Arun, Mayank, Mohit, Nithya, Sharan, Srijaya, Sumit, and Vivek, for helping me enjoy my life outside of work and stay sane.

Last but not least, I could not have finished my thesis without the continuous support and encouragement from my parents, my siblings, and my husband. Particularly, I thank my husband, Vitin, for his unconditional love and support and for instilling the confidence in me.
Contents

Abstract ii
List of Illustrations xi
List of Tables xvi

1 Introduction 1
1.1 Extant models of associating fluids 4
   1.1.1 Thermodynamic perturbation theory for associating fluids 4
   1.1.2 Molecular distributions and multi-body correlations in hard
       sphere fluids 6
   1.1.3 Extensions beyond TPT1 8
1.2 A new perturbation approach for associating fluids 10
1.3 Overview 11

2 Molecular distribution and average cluster size around a
   solute in the hard sphere system 15
2.1 Theory 17
   2.1.1 Molecular distributions and average n-ordered clusters 17
   2.1.2 Quasi-chemical theory 20
   2.1.3 Self-consistent mean field approach 21
   2.1.4 Physically derived models for coordination distribution functions 24
2.2 Methods 26
   2.2.1 Monte Carlo simulations 26
   2.2.2 Cluster partition function 27
### 2.3 Results

- **2.3.1 Symmetric hard sphere mixtures**: 28
- **2.3.2 Effect of the size asymmetry**: 31
- **2.3.3 Effect of the size of the observation volume**: 33

### 2.4 Conclusions

- 35

### 2.5 Appendix

- **2.5.1 Expression for $K_n$**: 36
- **2.5.2 MaxEnt model for $\{x_n\}$**: 38

### 3 Symmetric mixtures of patchy and spherically symmetric colloids

- **3.1 Theory**: 45
  - **3.1.1 Marshall-Chapman theory**: 47
  - **3.1.2 The complete reference approach**: 51
- **3.2 Methods**: 53
  - **3.2.1 Monte Carlo simulation of associating system**: 53
  - **3.2.2 Cluster partition function**: 55
- **3.3 Results and Discussions**: 55
  - **3.3.1 Average cluster distribution**: 55
  - **3.3.2 Solute-solvent versus solvent-solvent association**: 56
  - **3.3.3 $\beta\mu^{asso}$ of solute**: 57
  - **3.3.4 Variation of average bonding with association energy**: 59
  - **3.3.5 Solute concentration effect**: 61
- **3.4 Conclusion**: 62
- **3.5 Appendix**: 63
  - **3.5.1 Expression for $Q^{(k)}$**: 63

### 4 Asymmetric mixtures of patchy and spherically symmet-
# ric colloids

4.1 Theory ............................................. 66  
   4.1.1 Asymmetric mixtures with different association geometries .. 66  
4.2 Methods ............................................ 71  
   4.2.1 Monte Carlo Simulations ............................ 71  
4.3 Results and discussions ............................... 73  
   4.3.1 Infinite Dilution .................................. 73  
   4.3.2 Varying association strengths ..................... 75  
   4.3.3 Chemical potential and energy entropy contributions ....... 76  
   4.3.4 Concentrated systems ............................. 78  
4.4 Concluding discussions .............................. 78  
4.5 Appendix ............................................ 80  
   4.5.1 Spherical Code ................................... 81  

5 Quasichemical perspective of association .............. 83  

5.1 Quasichemical theory .................................. 85  
   5.1.1 Quasichemical perspective of associating fluids ............ 87  
   5.1.2 Single site solute .................................. 94  
5.2 Methods ............................................. 96  
   5.2.1 Monte Carlo Simulations ............................ 96  
   5.2.2 Calculation of $\Theta(k|n)$ .......................... 97  
5.3 Results and Discussions ................................ 98  
   5.3.1 Patch geometries for the solute ..................... 98  
   5.3.2 Simplifications — Single bonding patch .................. 102  
   5.3.3 Simplifications — Spherically symmetric patch ............ 104  
5.4 Conclusions ........................................... 106  
5.5 Appendix ............................................ 107  
   5.5.1 Equilibrium constant ............................... 107
6 Cluster size distribution theory for associating fluids 111

6.1 Theory ................................................................. 113
  6.1.1 Multiple bonding of a single site on solute ................. 115
  6.1.2 Thermodynamic perturbation theory ...................... 118
  6.1.3 Analytical model for hard sphere distribution .......... 121

6.2 Methods ............................................................... 122
  6.2.1 Monte Carlo Simulations ..................................... 122

6.3 Results and Discussions ........................................... 123
  6.3.1 Janus solute particles ...................................... 124
  6.3.2 Other multi-bonding geometries for solute ............ 128
  6.3.3 Phase equilibrium .......................................... 130

6.4 Conclusions ......................................................... 132

6.5 Appendix .............................................................. 133
  6.5.1 Thermodynamic framework ................................. 133
  6.5.2 One patch solvent molecule ............................... 136
  6.5.3 Two patch solvent molecule ............................... 136
  6.5.4 Thermodynamic properties in associating mixtures .... 139
  6.5.5 Analytical expressions for density derivatives of hard sphere distribution ........................................ 140

7 New ion-hydration model for electrolyte systems 143

7.1 Theory ................................................................. 144
  7.1.1 Association with spherically symmetric and patchy colloid model 145
  7.1.2 Semiresstricted non-primitive MSA ....................... 148

7.2 Methods ............................................................... 151
  7.2.1 Insights from molecular simulation ...................... 151

7.3 Results ............................................................... 153
7.3.1 Ion-specific parameters for alkali halides . . . . . . . . . . . . 154
7.3.2 Application of new theory for calculating dielectric constant . 157
7.4 Conclusions . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 160

8 Concluding discussions & future directions 161
8.1 Future directions . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 165
  8.1.1 Revisiting electrolyte model . . . . . . . . . . . . . . . . . . . . . . 165
  8.1.2 Complex patch geometries . . . . . . . . . . . . . . . . . . . . . . 166
  8.1.3 Water model . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 167
  8.1.4 Inhomogeneous systems . . . . . . . . . . . . . . . . . . . . . . . . 167
Illustrations

1.1 A schematic of short-range directional interactions between molecules. 5
1.2 A graphical representation for the distribution \((x_n)\) around a distinguished solute in the hard sphere system. 7
1.3 A schematic showing different multiple bonding site geometries for a solute molecule. 8
1.4 Different bonding states of a spherically symmetric colloid. 9

2.1 Schematic of \(F^{(n)}\), the average number of \(n\)-solvent cluster (\(n\)-mer) around a solute molecule. 18
2.2 A graphical representation for the distribution \((x_n)\) around a distinguished solute in the hard sphere system. 19
2.3 Average occupancy \(n_{\text{avg}}^{HS}\) and exclusion probability \(\ln x_0\) for symmetric hard sphere mixture. 29
2.4 Occupancy distributions \(x_n\) and cluster size distributions \(F^{(n)}\) for different densities for symmetric hard sphere mixtures. 30
2.5 Average occupancy \((n_{\text{avg}}^{HS})\) and exclusion probability \((\ln x_0)\) for different size ratios and different reduced densities. 31
2.6 Cluster size distribution \(F^{(n)}\) for different size ratios at a density of \(\rho d^3 = 0.8\). 32
2.7 Variation of average occupancy \((n_{\text{avg}}^{HS})\) for different size ratios with packing fraction. 33
<table>
<thead>
<tr>
<th>Section</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.8</td>
<td>Average occupancy $n_{HS}^{avg}$ and exclusion probability $\ln x_0$ for different observation volumes $r_c$ for symmetric hard sphere mixtures, at different densities.</td>
</tr>
<tr>
<td>2.9</td>
<td>Occupancy distributions $x_n$ for different observation volumes for symmetric hard sphere mixtures, at different densities.</td>
</tr>
<tr>
<td>3.1</td>
<td>Association between solute and solvent and solvent molecules.</td>
</tr>
<tr>
<td>3.2</td>
<td>Representation of graph sums for all the possible arrangements due to association of the solvent around a solute.</td>
</tr>
<tr>
<td>3.3</td>
<td>Example graph sum to illustrate the joint role of occupancy and bonding.</td>
</tr>
<tr>
<td>3.4</td>
<td>Comparison of average number of n-mers ($F^{(n)}$).</td>
</tr>
<tr>
<td>3.5</td>
<td>Distribution of bonding states of the solute when the strength of solvent-solvent interaction is $7k_BT$ and zero.</td>
</tr>
<tr>
<td>3.6</td>
<td>Chemical potential for charging a solute molecule in a patchy solvent environment for different reduced densities.</td>
</tr>
<tr>
<td>3.7</td>
<td>Distribution of bonding states of solute at $\rho d^3 = 0.8$ and different association energies between solute-solvent molecules.</td>
</tr>
<tr>
<td>3.8</td>
<td>Variation of average bonding number ($n_{avg}$) with the association energy between molecules ($\epsilon$) for $\rho d^3 = 0.8$. Solute is infinitely dilute.</td>
</tr>
<tr>
<td>3.9</td>
<td>Variation of average bonding number ($n_{avg}$) with the association energy between solute-solvent molecules ($\epsilon^{(p,p)}$)(left) and solvent-solvent molecules ($\epsilon^{(s,p)}$)(right) for $\rho d^3 = 0.8$. Solute is infinitely dilute.</td>
</tr>
<tr>
<td>3.10</td>
<td>Variation of average bonding number ($n_{avg}$) with the concentration of solute in the solution for $\rho d^3 = 0.8$. Energy of association between molecules is $7k_BT$.</td>
</tr>
</tbody>
</table>
4.1 Association between solute and solvent (a) and solvent molecules (b). Different cases with solute larger and smaller than solvent molecules are studied. ................................................................. 67

4.2 Schematic of $F^{(3)}$, the average number of $n = 3$-solvent cluster ($n = 3$-mer) around a solute. ................................................................. 68

4.3 Average bonding numbers $n_{avg}$ in associated mixtures for asymmetric cases with different relative size of solute molecules. ...................... 74

4.4 Variation of average bonding numbers ($n_{avg}$) with the relative strengths of solute-solvent and solvent-solvent association strengths. . 76

4.5 Chemical potential for charging a solute molecule in a patchy solvent environment for different reduced densities and different size ratios. . 77

4.6 Variation of residual chemical potential of solute ($\mu_{s}^{asso}$), partial molar energy ($E_{s}^{asso}$) and entropy ($S_{s}^{asso}$) with temperature for a system with no solvent-solvent association interactions. The interactions between solute-solvent for different temperatures is determined by $\frac{\epsilon^{(s,p)}}{k_B T} = 2087.05/T$. ................................................................. 78

4.7 Variation of average bonding number of solute ($n_{avg}$) with the concentration of solute for size ratio, $d_s/d_p$, 1.1 and 0.8. ................. 79

4.8 Left: Maximum number of coordination states possible and their respective maximum permissible patch angle for different size ratios $d_s/d_p$. Right: Diagram to compute the angle between two solvent particles to get the maximum number of coordination states .............. 82

5.1 Schematic of the quasichemical organization of the potential distribution theorem. ................................................................. 86

5.2 Different patch geometries of the solute with single or multiple bonding conditions. ................................................................. 90
5.3 A schematic to describe conditional probability $Q(i|n)$ for a Janus particle. ........................................ 93

5.4 Comparison of the occupancy distribution for different patch geometries on the solute. Average occupancy is also compared for different densities for various patch geometries of solute. ............ 99

5.5 Comparison of bonding distribution for different patch geometries on the infinitely dilute solute. ........................................ 100

5.6 Comparison of bonding distribution of an infinitely dilute solute, when the solute and solvent have same patch geometries. No solvent-solvent association is allowed. ................................. 101

5.7 Comparison of occupancy and bonding distribution for a single bonding condition on solute patch. ........................................ 103

5.8 Comparison of the occupancy distribution, bonding fractions, and chemical potential of an infinitely dilute solute with spherically symmetric association. ........................................ 106

6.1 Different patch geometries ($\theta_{i,(B)}^{(c)}$) of the solute molecules. .......... 114

6.2 A schematic for association between $B$ patch on solute and patch $A$ on solvent. ......................................................... 114

6.3 Effect of concentration of the solute ($x^{(\sigma)}$) on the association for solute molecules. ..................................................... 125

6.4 Effect of concentration of solute on the bonding fractions of the solvent molecule and the internal energy per particle due to association $E^{AS}/Nk_B T.$ ..................................................... 126

6.5 Effect of strength of solvent-solvent association $\epsilon^{(p,p)}$, when the solute-solvent association strength is fixed at $\epsilon^{(\sigma,p)} = 7k_B T.$ ........... 128
6.6 Variation of the bonding distribution of solute with the patch sizes on the solute. Variation of average bonding numbers for the solute molecules ($n_{avg}^{bond}$); average length of arms ($L_{arm}$) and fraction of chains originating from the patch on solute molecules ($\Psi$) is also shown.

6.7 Patchy solvent molecules with two $A$ sites are considered to study the equilibrium phase behavior.

6.8 Vapor-liquid coexistence curves for three different concentrations of patchy solvent molecules. The solute has a spherically symmetric $B$ site and solvent molecules have two $A$ patches. AA, AB association is allowed and $\epsilon^{(\sigma,p)} = 3 \cdot \epsilon^{(p,p)}$. Symbols represent critical point.

6.9 Vapor-liquid coexistence curves for three different size geometries of solute molecules in $2A$ patch solvent. Solute size of $\theta_{(c,\sigma)} = 60^\circ, 90^\circ, 180^\circ$ (bottom to top) are presented. Concentration of the solvent is $x^{(p)} = 0.65$. Symbols represent critical point.

7.1 Association between patchy-spherical and patchy-patchy colloids.

7.2 Density of aqueous NaCl at 298.15 K.

7.3 Comparison of short range interactions in ions.

7.4 Activity coefficients of alkali halides at 298.15 K.

7.5 Distribution of solvent around a sodium ion.

7.6 Density prediction of NaCl aqueous solution at different temperatures.

7.7 Density prediction for NaBr aqueous solution at different temperatures.

7.8 Concentration dependence of dielectric constant of aqueous NaCl solution at 298.15 K.

8.1 Different complex patch geometries for solute molecules.
Tables

2.1 Parameters for Eq. 2.12 and Eq. 2.13 for different $\rho d^3$, based on a self-consistent mean field approach. ......................................................... 24

2.2 Parameters for Eq. 2.16 ($\zeta_1, \zeta_2$) and Eq. 2.18 ($\zeta$) for different densities $\rho d^3$ and packing fractions ($\eta$). The observation volume is defined by $r_c = 1.1d$ and $d$. ................................................................. 29

2.3 $\ln(x_n)$ in hard sphere reference system obtained by reweighted sampling for different reduced densities ($\rho \sigma^3$). The solute and solvent molecules have the same size ($d$) and the observation shell is defined by $r_c = 1.1d$. ................................................................. 40

2.4 $\ln(x_n)$ in asymmetric hard sphere systems obtained by reweighted sampling for different size ratios of the solute and solvent molecules at different reduced densities ($\rho \sigma^3$). The observation shell is defined by $r_c = 1.1\bar{d}$ and $\bar{d} = (d_\sigma + d_p)/2$. Solute is infinitely dilute. ....... 41

2.5 Isolated cluster probabilities $P^{(n)}$ for different observation volumes. The solute and solvent molecules have same size. ......... 42

2.6 Isolated cluster probabilities $P^{(n)}$ for different relative sizes of the solute as compared to the solvent molecules. The observation shell is defined by $r_c = 1.1\bar{d}$ and $\bar{d} = (d_\sigma + d_p)/2$. ......... 43

4.1 Comparison of average bonding numbers ($n_{avg}$) of solute for extreme size ratios. ................................................................. 75
5.1 Maximum bonding numbers corresponding to different patch geometries of the solute.

5.2 Conditional isolated cluster probabilities, $\Theta(k|n)$ of having exactly $k$ molecules in the patch region given $n$ molecules in the spherical shell around the solute, for the critical angle on the solute, $\theta_{(c,\sigma)} = 35^\circ, 40^\circ$ and $50^\circ$. The spherical observation shell is defined by $r_c = 1.1d$ and $d$.

5.3 Conditional isolated cluster probabilities, $\Theta(k|n)$ of having exactly $k$ molecules in the patch region given $n$ molecules in the spherical shell around the solute, for the critical angle on the solute, $\theta_{(c,\sigma)} = 60^\circ$ and $90^\circ$. The spherical observation shell is defined by $r_c = 1.1d$ and $d$.

6.1 Patch size of the solute ($\theta_{c,\sigma}$) and the corresponding maximum bonding number ($N_{\text{bond}}^{\text{max}}$). The solute and solvent molecules have the same size $d$ and the critical distance for association is $r_c = 1.1d$.

7.1 SAFT model parameters for pure water with two sites.

7.2 Ion-specific parameters for aqueous NaCl and NaBr obtained with an improved ion-solvent association. $\epsilon_{iw}$ is the association strength for ion-water association and $\kappa_{iw}$ is the corresponding volume factor.
Chapter 1

Introduction

Many of the fluids encountered in natural and engineered systems are characterized by molecules with strong, directional association between species. Examples cross most areas of science and include liquid water, aqueous ions, proteins, patchy colloids, supra-molecular polymers that are obtained from monomers interacting with hydrogen bonds, surfactants and material such as asphaltenes. Although these associating systems are ubiquitous, predicting the phase behavior of such materials remains a fundamental open challenge in molecular sciences.

An association interaction is weaker than covalent bonds but stronger than van der Waals attractions. Resulting from these interactions are a distribution of long-lived associated clusters of molecules. One of the most common examples of associating fluids is water, where the hydrogen bonding between water molecules results in a mixture of associated networks of water molecules that determine the properties of water. As another example, consider the problem of modeling electrolytes. Disregarding molecular ions for the time being, we can imagine the ion as a spherical particle that can associate isotropically with other ions and with water, where the water molecules can be thought of as particles with specific directional interactions. In the extremely low dilution limit, the properties of such a system are adequately described by the well-known Debye-Huckel model [6]. In this model, the ions constituting the electrolytes are described as point charges and the molecular nature of the liquid is ignored, with the effect of the liquid incorporated using a dielectric con-
stant. But it is well-known that this so-called mean-field model of electrolytes cannot
describe the vast range of ion-specific effects seen in aqueous phase processes. But
almost all of the aqueous phase processes of practical interest require one to acknow-
ledge the molecular nature of the ions and liquid water. For example, in the extreme
case of modeling the properties of electrolytes at extreme temperature and pressure,
a problem of significant interest given the move towards deep off-shore oil-and-gas ex-
ploration, we encounter systems with salt concentrations in excess of 300,000 mg/L
total dissolved solids (TDS); indubitably one cannot rely on a mean-field description
of the ions and must acknowledge the molecular characteristics of the ions and liquid
water.

Extant models of electrolytes at high concentration almost always derive from a
virial-type expansion originally due to Pitzer [7]. In these models, the excess chem-
ical potential of the ion is approximated based on a hard-sphere exclusion and then
considers the impact of ion-ion correlations at various orders. For example, pair-
interaction between ions will contribute a factor to the excess chemical potential and
this is incorporated using a specific term in the Pitzer-type expansion. Likewise,
triplet correlations will contribute a factor and so on. Even in this model, the role
of water is accounted for in an effective sense on the basis of a dielectric constant.
Moreover, the pair-, triplet-, etc. expansion is nearly always treated as solely a fram-
ework that can be used to fit data. While these fits can work well in the regime of
parameterization, they are largely inutile outside the domain of parameterization,
greatly limiting the utility of these models. A fundamental physics, based approach
to modeling such complex systems is sorely needed.

A primary motivation for the present work was indeed based on my initial efforts
to model electrolyte systems as those noted above. However, we quickly realized that
the chemical and physical complexity in these systems, particularly related to multi-body interactions, poses a daunting challenge in the development of a molecularly-detailed theory that can meet the challenge of being a purely predictive framework. In particular, in this thesis, we focus on the modeling of multi-body interactions to enable the development of models for such systems.

Patchy colloids, particles with engineered directional interactions, are archetypes of associating systems [8–12] and offer a useful model system to study the physics of multi-body interactions. In these molecules, by varying the shape, number, and position of the patches, different self-assembled geometries leading to complex structures can be obtained [8, 9, 11, 13–21]. In recent years, such particles have been the focus of intense experimental investigations that have sought to design new nanostructured materials with interesting optical, electronic, and mechanical properties [8–10, 13, 14, 22–31]. Complementing these experimental studies, molecular simulations have also sought to understand how the anisotropy of interactions determines the emergent structure [17, 32–36] and the phase behavior [37, 39–43]. The patchy colloids are simpler to explore experimentally and in particle simulations and are thus the system of choice to anchor the theoretical developments in this thesis. Since the physics of ion-water association [69–71] is analogous to the solute - patchy solvent association considered in this work, the present work also opens an avenue to investigate fundamental questions pertaining to the behavior of ions in water (for example, see Refs. [72, 73]). Also, the multi-bonding colloidal solutes have applications in various fields like advanced surfactant molecules, gelation, specific drug delivery, supramolecular polymers, ion-hydration, and viscosity modifiers [12, 74–79]. In particular, studies have shown advantages of Janus particles as surfactant molecules and in stabilizing emulsions and foams [75, 80, 81] as compared to homogeneous molecules.
of the same size.

1.1 Extant models of associating fluids

The thermodynamic behavior of simple fluids, for which the most important intermolecular forces are repulsion and weak van der Waals attractions, is well established. Molecular theories have been developed describing the structure and physical properties of simple liquids (like liquefied noble gases) due to the non directional and non-saturating nature of the intermolecular forces. Perturbation theories have been developed for simple fluids by separating the interaction potential into a part containing all the repulsive forces and a part containing all the attractive forces [44]. This is based on the understanding that in dense simple liquids, repulsive interactions dominate and determine the structure of the fluid. In complex fluids-the associating fluids noted above being prototypes - the intermolecular forces are stronger and hence molecules can form relatively long lived dimers and larger clusters. The repulsive forces alone no longer determine the structure and the perturbation approaches developed for weak attraction forces do not converge for these complex systems with strong attraction forces.

1.1.1 Thermodynamic perturbation theory for associating fluids

In the early 1980s, Wertheim in a series of papers developed a theory [45–48] to describe the physics of short-range association given the properties of a non-associating reference fluid, typically a hard sphere or Lennard-Jones fluid. The associating molecules are envisioned as having sticky-patches on their surfaces over which they bond; the range of attraction is very short relative to the size of the particle (see Fig. 1.1), and a multi-density formalism is developed where each bonding state of a
molecule is assigned a singlet density. To account for the directional nature and large energy of the association early in the theory, Wertheim used a graph approach building on the work by Lockett [49] to remove unphysical graphs due to steric hindrance in the fugacity expansion of the grand partition function. Chapman et. al. [50, 51] developed the statistical associating fluid theory (SAFT) which is based on an extension to Wertheim’s theory to treat chain molecules in mixtures of associating fluids. Wertheim’s theory [45–48] and its extension in the form of the statistical associating fluid theory (SAFT) [50, 51] have proven effective [16, 40, 52, 53] in describing systems with short-range, directional (i.e. specific) interactions and are thus of natural interest in describing patchy colloids.

![Figure 1.1: A schematic of short-range directional interactions between molecules. The large circles represent the repulsive cores of spherical molecules. The A and B sites allow association when the sites overlap.](image)

The structure of Wertheim’s theory or SAFT is such that one can obtain accurate extent of association and thermodynamics even for systems with strong inter-particle interactions provided the representation of the reference is adequate. Within this perturbation approach, the total potential is represented as a sum of the reference and association contributions \( u(r) = u_{HS}(r) + u_{AS}(r) \). The association contribution is obtained by approximating the monomer-monomer pair correlation function with the reference pair-correlation function and a single bonding condition is assumed for each associating site. This first order thermodynamic perturbation theory (TPT1)
works well when the attraction is of short-range and the sticky patches are restricted to bond only once. As the complexity of the interaction increases in the physical system, such as may result from multiple bonding at a site and size asymmetries, multi-body interactions become more important and information about pair-correlations in the reference no longer suffices.

1.1.2 Molecular distributions and multi-body correlations in hard sphere fluids

The hard sphere fluid forms the reference for many perturbation theories as the mutual volume exclusion due to the finite size of the particles influences the structure of dense fluids. Molecular distribution functions express the probabilities of observing different configurations of sets of n molecules out of the total number of molecules. Because of the presence of interactions between different molecules, no real system exhibits a random distribution in configuration space and correlation functions are defined corresponding to these distribution functions.

\[ \rho(\vec{r}_1 \cdots \vec{r}_n) = \rho^n g(\vec{r}_1 \cdots \vec{r}_n) \] (1.1)

where \( g(\vec{r}_1 \cdots \vec{r}_n) \) is the \( n \)-body correlation function for the distribution function \( \rho(\vec{r}_1 \cdots \vec{r}_n) \). For this study, we are interested in the distribution of solvent molecules in a defined observation shell around a distinguished solute molecule. Notice that for this system, \( \rho^n g_{HS}(\vec{r}_1 \cdots \vec{r}_n|0)\, d\vec{r}_1 \cdots d\vec{r}_n \) is the probability that the \( n \) volume elements \( d\vec{r}_1 \cdots d\vec{r}_n \) around \( \vec{r}_1 \cdots \vec{r}_n \) simultaneously contain the centers of particles.

Another important quantity in hard sphere systems is the coordination distribution around a solute molecule. The coordination distribution \( x_n \) gives the probability of having exactly \( n \) solvent molecules in the coordination volume of a solute (v) de-
Figure 1.2: A graphical representation for the distribution \( (x_n) \) around a distinguished solute in the hard sphere system. Left to right: Probability of having no solvent \( (x_0) \), one solvent \( (x_1) \), and two solvent \( (x_2) \) molecules in the coordination volume of the solute.

Defined by the spherical region of radius \( r_c \). Figure 1.2 shows coordination distribution of an infinitely dilute solute. We focus on a distinguished solute and observe frequencies of the various coordination states \( n \) of this solute in a given observation volume.

For molecular theories of associating fluids that include attractive forces as a perturbation, the pair correlation and higher order correlation functions in the hard sphere reference are needed at separations different than the contact value. When the patch on a solute molecule can associate with multiple solvent molecules (see Fig. 1.3), it is important to study the multi-body correlations that determine the packing of solvent particles around the solute in the reference fluid [54]. The difficulty in determining these interactions arises due to the limited knowledge in describing multi-body correlation functions, particularly for 3—body and higher correlations, at contact and at other separations. Despite extensive studies on mixtures of hard spheres with different diameters [55–60], a compact form for higher body correlations beyond the contact value is still unavailable. Further, for systems with large size asymmetries, even the pair-correlation information obtained using the Boublik-Mansoori-Carnahan-Starling-Leland equation is inadequate [61]. We next discuss these multi-bonding geometries where the pair correlation information is not sufficient to describe the association.
between molecules.

### 1.1.3 Extensions beyond TPT1

![Diagram showing different multiple bonding site geometries](image)

Figure 1.3: A schematic showing different multiple bonding site geometries for a solute molecule. Cases where TPT1 fails for short-range directional interactions between molecules.

For sufficiently small value of the observation shell \( r_c = 1.1d \) and for patch size \( \theta_{c,\sigma} \leq 27^\circ \), each patch can be bonded only once. For \( \theta_{c,\sigma} = 35^\circ \) the maximum number of the bonds per patch is two, for \( \theta_{c,\sigma} = 40^\circ \) the patch can bond upto three times, and for \( \theta_{c,\sigma} = 60^\circ \) each patch can bond simultaneously five particles. For larger bonding patches, such as for Janus particles i.e. \( \theta_{c,\sigma} = 90^\circ \) and for spherically symmetric particles \( \theta_{c,\sigma} = 180^\circ \) bonding of 7 and 12 molecules respectively is possible. Figure 1.3 shows different site geometries on a solute molecule that allow multiple bonding at a single site. As is evident from the figure, multi-body correlation information is important to correctly include the steric effects in the reference fluid for higher bonding \( (n > 1) \) states. Marshall et. al. [62, 63] extended Wertheim’s theory/SAFT to account for double bonding of larger patch sizes. To approximate the three body correlations in the reference fluid, they used a linear superposition of the pair correlation and a three body correction based on the functional form given by Muller and
Gubbins [64] for three hard spheres in rolling contact and the data given by Attard et. al. [65]. This second order perturbation theory (TPT2) was developed by neglecting the three and higher bonding contributions and works well for systems where patches are restricted to bound a maximum of two particles. However, TPT2 fails for patch geometries that allow bonding more than two times.

An extreme case of multiple bonding is when the size of the site on solute molecules is such that it covers the whole surface of the molecule hence the association potential is spherically symmetric. Fig. 1.4 shows contributions to the free energy written as a sum over different bonding states of a spherically symmetric solute with a 2-patch solvent molecule. Within an integral equation approach, Kalyuzhnyi and Stell [66] reformulated Wertheim’s multi-density formalism [47] to incorporate spherically symmetric interactions. However, the solution becomes complex for large values of bonding states. For mixtures of spherically symmetric solute in patchy colloids, Marshall and Chapman [3, 67] generalized the single chain approximation of Wertheim [68] and extended Wertheim’s theory/SAFT multi-density formalism to account for multiple bonding of a single site. This theory requires the multi-body correlation function for solvent around the solute in the non-associating reference fluid. These

\[
\Delta c_{\text{sp}}(0) = \Delta c_1^{(0)} + \Delta c_2^{(0)} + \Delta c_3^{(0)} + \Delta c_4^{(0)} + ... \Delta c_n^{(0)}
\]

Figure 1.4 : Bonding states of a spherically symmetric solute in a mixture of 2-patchy solvent molecules.

multi-body correlations for the reference fluid were sought by characterizing the dis-
tribution of gas-phase solute-solvent clusters. The effect of the bulk solvent was subsequently incorporated at the TPT2 level by using the linear superposition of the pair correlation function plus a three body correction. In essence they approximate the integral
\[ \int_v \ldots \int_v d\vec{r}_1 \cdots d\vec{r}_n g_{HS}(\vec{r}_1, \ldots, \vec{r}_n|0), \]

of the \( n \)-particle correlation \( g_{HS}(\vec{r}_1, \ldots, \vec{r}_n|0) \) of the hard sphere solvent given the hard sphere solute at the origin \((\ldots|0)\) by \( y_{HS}(d)\delta^{(n)}\Xi^{(n)} \), where \( y_{HS}(d) \) is the cavity correlation function at contact for particles of diameter \( d \), \( \delta \) is a correction to account for three body interactions, and \( \Xi^{(n)} \) is related to the cluster integral of \( n \)-solvent plus one solute particle within the observation volume \( v \). The cluster integrals are calculated separately \textit{in vacuo} by a Monte Carlo procedure. This TPT2 based approximation works well for systems at low solvent densities or higher concentration of solute, i.e. conditions when low order correlations are important. However, deviations in structural and thermodynamic properties become serious for higher densities and/or bonding strengths.

1.2 A new perturbation approach for associating fluids

In this thesis, we address these limitations of the existing perturbation theories and present a new approach to accurately incorporate multi-body correlations in the hard sphere reference fluid using the statistical associating fluid theory (SAFT) [51] as a foundation. In Wertheim’s thermodynamic perturbation theory, based on the order of correlation function in the reference fluid, TPT1 or TPT2 levels of the theory are defined. In TPT1 only pair correlation information is required and in TPT2 three body information is also required on top of the pair correlation information.
We present a new perturbation approach where the occupancy distribution around a distinguished solute in the reference fluid provides all the multi-body correlation information. Accurate inclusion of the higher order correlation functions in terms of average ‘n-ordered’ cluster does not require any approximation in the estimation of correlation functions. The perturbation represents the associating fluid properties in terms of packing in the hard sphere reference fluid. We focus on a mixture of spheres with directional interactions, the patchy solvent particle, and a sphere with a multi-bonding site, the colloidal solute, that can associate with multiple solvent particles.

Another level of perturbation depends on the inclusion of various graphs in the Wertheim’s theory. The present approach and the approaches that have been implemented in the literature are based on the inclusion of graphs where a single cluster is studied in a monomer fluid ($\Delta c^{(0)}$).

1.3 Overview

For complex associating fluids with larger patch sizes which can bond multiple times, higher order correlations become important. In this work we present insights to accurately incorporate multi-body correlations and extend Wertheim’s theory and SAFT beyond second order perturbation theory.

In chapter 2, a new way of analyzing multi-body correlation information in terms of cluster size distribution in the hard sphere reference fluid is presented. We study different multi-body clusters in the hard sphere systems in terms of occupancy distribution functions around a reference particle. To facilitate the application of our approach, we also present a physically transparent, statistical mechanical model to describe the occupancy probabilities in symmetric and asymmetric hard sphere fluids.
for different packing fractions. A quasichemical [82–84, 106] based analysis is done to study the equilibrium constant for the formation of clusters and study the occupancy distribution in the observation shell around a reference particle. The model corrects multi-body effects obtained for isolated clusters by incorporating the role of the cluster-bulk interface and the bulk medium. Occupancy distribution for symmetric and asymmetric mixtures of hard sphere systems are obtained based on particle simulations and the physical models developed.

In chapter 3 we discuss the association potential for mixtures of patchy and spherically symmetric solute molecules and describe how packing effects are important for the given potential. Based on the average multi-body clusters in hard sphere reference fluid obtained in chapter 2, we find the higher body correlation information required to define the multiple bonding of the spherically symmetric solutes within the framework developed by Marshall-Chapman [3, 67]. We also discuss the Marshall-Chapman [67] theory, their gas-phase cluster with TPT2 approximation and highlight the need for improvement suggested by comparing the results of the theory with Monte Carlo simulations.

In chapter 4 we show that our approach of including multi-body correlations using occupancy statistics in a physically reasonable observation volume accurately captures the multi-bonding effects in symmetric and asymmetric mixtures. For asymmetric mixtures size ratios in the range 0.8 – 1.2 were studied. However, the framework should apply to larger size ratios, and we show this with studies on mixtures with $d_s/d_p$ equal to 0.5 and 2.0. This complete reference approach proved successful in predicting the bonding state and thermodynamics of a colloidal solute in the patchy solvent for a wide range of system conditions. For a solution with just solute-solvent interactions, a chemical potential analysis showed that the new theory is able to
capture the entropic and energetic effects accurately in comparison with simulation as opposed to the Marshall-Chapman TPT2 approximation.

The above development based on a complete reference approach motivated us to reconsider the problem of modeling associating fluids entirely within the quasi-chemical (QC) organization of the potential distribution theorem (PDT) [82–84]. In chapter 5 we consider an infinitely dilute solute with multi-bonding site geometries. Allowing for only solute-solvent interactions we derive an expression for the chemical potential of an associating solute in a solvent relative to the value in a reference fluid using the quasichemical organization of the potential distribution theorem. The fraction of times the solute is not associated with the solvent, the monomer fraction, is expressed in terms of (a) the statistics of occupancy of the solvent around the solute in the reference fluid and (b) the Widom factors that arise because of turning on solute-solvent association. We illustrate the generality of the present approach by considering examples of multiple solvent association to a colloid solute with bonding domains that range from a small patch on the sphere, a Janus particle, and a solute whose entire surface is available for association.

In chapter 6 we extend statistical associating theory (SAFT) beyond second order perturbation to study different multiple bonding of a single site on the solute molecules based on the insights from chapter 5. We study binary mixtures of multi-bonding single site solute molecules in patchy colloid solvent molecules. Solute-solvent and solvent-solvent short-range attractive interactions are studied, where all the sites on the solvent molecules have single bonding condition and the single site on the solute molecules can bond multiple times. For different site geometries of the solute molecules, accurate multi-body correlation information in the hard sphere reference fluid is obtained from chapter 5 on quasi-chemical analysis of association. Detailed
study for Janus solute is presented for 1 and 2 patch solvent molecules, for a range of concentration and association strength. We also study the phase equilibrium for a mixture of 2 patch colloid (with same kind of sites) and different geometries of single site solute for the first time and discover very low density gels for such mixtures.

One of the issues that motivated the current work was our early work on ion-hydration (that we now present in chapter 7). The limited success of that work made us appreciate the multi-bonding effects better. For this reason, and for completeness, we present this early work last (in chapter 7). We present an extension of SAFT model with electrostatic interactions obtained with mean spherical approximation theory to describe electrolyte systems with a new hydration model incorporating multi-body effects based on a TPT2 approach. Sample results for the thermodynamic properties of aqueous alkali halides are presented.

Chapter 8 presents a summary of the work and future applications are also discussed.
Chapter 2

Molecular distribution and average cluster size around a solute in the hard sphere system

The hard sphere fluid exhibits several simplifying features which makes them a convenient starting point for developing a theory for dense fluids. One such feature is that the thermodynamic properties of the hard sphere fluid depends only on the pair correlation function \( g(r) \) at the point of contact, \( r = d \). Simple analytic equations for \( g(d) \) have been developed (for eg. Percus-Yevick, Carnahan-Starling [85], scale particle theories[56]) which are accurate even at high densities. Simple fluids behave as hard sphere fluid in the high temperature limit. Hence, the hard sphere system forms the reference fluid for many perturbation theories that separate attractive and repulsive interactions to model real fluids. Perturbation theories for more complex fluids with non-centric and saturating strong attraction interactions have also been developed with packing information from the hard sphere fluid[45, 51]. For these theories that include attractive forces as perturbation, the pair correlation and higher order correlation functions in the hard sphere reference are needed at separations different than the contact value. The structure and thermodynamics of mixture of hard spheres with different diameters has been studied in detail before [55–60], but a compact form for the multi-body correlations beyond the contact value is still unavailable. Further, for systems with large size asymmetries even the pair-correlation information obtained using the Boublik-Mansoori-Carnahan-Starling-Leland equation is inadequate [61].
In this chapter, we show how coordination distribution around a distinguished solute in the hard sphere fluid obtained from particle simulations can be used to incorporate multi-body correlations in the form of cluster integrals. The link between coordination distribution and multi-body correlations is inspired by quasichemical theory [86, 87] and ultimately draws upon Reiss and coworker’s seminal investigation of hard-sphere packing [56]. Importantly, we also present a physically transparent, statistical mechanical model [86–88] to describe the occupancy probabilities in hard sphere fluids for different packing fractions. This model corrects multi-body effects obtained for isolated clusters by incorporating the role of the cluster-bulk interface and the bulk medium effects. Effect of size asymmetry and the size of the observation volume is studied for various densities.

The rest of the chapter is organized in the following way. In section 2.1.1 we discuss molecular distribution functions and analyze higher order correlations in the hard sphere fluid in terms of average cluster size distribution. In section 2.1.2 we present quasichemical theory to study hard sphere packing around a reference solute particle and develop models based on statistical mechanics [88] and hard sphere simulation data for different densities. In Section 2.3 we present results for the hard sphere reference system (symmetric and asymmetric mixtures) based on the model developed in section 2.1.4. We also provide simulation results for isolated cluster probabilities in asymmetric hard sphere mixtures in the appendix (Section 2.5).
2.1 Theory

2.1.1 Molecular distributions and average n-ordered clusters

Molecular distribution functions express the probabilities of observing different configurations of sets of \( n \) molecules out of the total number of molecules. Because of the presence of interactions between different molecules, no real system exhibits a random distribution in configuration space and correlation functions are defined corresponding to these distribution functions.

\[
\rho(\vec{r}_1 \cdots \vec{r}_n) = \rho^n g(\vec{r}_1 \cdots \vec{r}_n) \tag{2.1}
\]

where \( g(\vec{r}_1 \cdots \vec{r}_n) \) is the \( n \)-body correlation function for the distribution function \( \rho(\vec{r}_1 \cdots \vec{r}_n) \). For this study, we are interested in the distribution of solvent molecules in a defined observation shell around a distinguished solute molecule. Notice that for this system, \( \rho^n g_{HS}(\vec{r}_1 \cdots \vec{r}_n|0) \, d\vec{r}_1 \cdots d\vec{r}_n \) is the probability that the \( n \) volume elements \( d\vec{r}_1 \cdots d\vec{r}_n \) around \( \vec{r}_1 \cdots \vec{r}_n \) simultaneously contain the centers of particles.

The volume integral of this multi-body correlation has a clear physical meaning in terms of average number of \( n \)-solvent clusters \( (F^{(n)}) \) around a distinguished solute. In particular, for the distinguished solute,

\[
F^{(n)} = \frac{\rho_p^n}{n!} \int_v d\vec{r}_1 \cdots \int_v d\vec{r}_n g_{HS}(\vec{r}_1 \cdots \vec{r}_n|0) \tag{2.2}
\]

where \( \rho_p \) is the density of solvent particles, \( v \) is the observation volume of the solute defined by the spherical region of critical radius \( r_c \) and the size of the molecules \( d \), \( g_{HS}(\vec{r}_1 \cdots \vec{r}_n|0) \) is the correlation function of the \( n \)-solvent particles around the solute at the center of the observation volume, indicated by \( (\ldots|0) \). The \( n! \) term is due to the integration over indistinguishable volume elements. This representation
is inspired by the work of Reiss et. al.[56] who studied these clusters in a cavity. Turquato et. al.[89] also studied the nearest neighbor functions and realized such cluster distributions in the expansion of their exclusion probabilities. In the notation used in this thesis, Turquato et. al. [89] expression for the exclusion probability is

\[ x_0 = 1 + \sum_{n \geq 1} (-1)^{(n)} \cdot F^{(n)} \]  

(2.3)

Physically the above expression can be described as follows: the first term in the summation gives the average number of single solvent particles (\(F^{(1)}\)) in the coordination volume of the solute. However this subtraction overestimates the contribution to exclusion probability and hence the term where any two solvent particles (\(F^{(2)}\)) are in the coordination volume should be added. Now the contribution due to any three particles (\(F^{(3)}\)) is over-counted and should be subtracted and so on. Hence the \(n^{th}\) term in this summation is the average number of \(n\) solvent particles in the observation volume. Due to the multi-order integral involved in these \(n\) ordered cluster, analytical expressions for \(F^{(n)}\) were not studied by Torquato et. al.[89]. Notice that the summation in the above expression will be limited by \(n^{\text{max}}\), the maximum number...
of solvent molecules that can occupy the observation volume around the reference solute.

Fig. 2.2: A graphical representation for the distribution \( (x_n) \) around a distinguished solute in the hard sphere system. Left to right: Probability of having no solvent \( (x_0) \), one solvent \( (x_1) \), and two solvent \( (x_2) \) molecules in the coordination volume of the solute.

We focus on a distinguished solute and observe frequencies of the various coordination states \( n \) of this solute in a given observation volume. The coordination/occupancy distribution \( x_n \) gives the probability of having exactly \( n \) solvent molecules in the coordination volume of a solute (See Fig.2.2). We show how coordination distribution around a distinguished solute in the hard sphere fluid can be used to incorporate multi-body correlations in the form of cluster integrals. Fig. 2.1 shows the physical interpretation of our approach to obtain the average cluster size based on the distribution around a solute particle. All the coordination states where at least \( n \) solvent particles are present contribute to the average \( (F^{(n)}) \) and the contribution of a given coordination state \( m \) is augmented by the combinatorial weights of selecting \( n \) particles from the given coordination state \( m \) i.e.

\[
F^{(n)} = \frac{\rho_p^n}{n!} \int_{v} d\vec{r}_1 \cdots \int_{v} d\vec{r}_n g_{HS} (\vec{r}_1 \cdots \vec{r}_n|0) \\
= \sum_{m=n}^{n_{\text{max}}} C_n^m x_m , \tag{2.4}
\]

where \( x_m \) is the probability of observing exactly \( m \) solvent molecules in the observation volume.
shell of the solute in the reference system. $C^n_m \equiv m!/(m-n)! \cdot n!$ is the combinatorial term which defines the weight for a given coordination state.

The coordination distribution functions $x_n$ around a distinguished particle can be obtained from particle simulations for different densities and size ratios of the solute and solvent molecules. We also present a quasichemical theory based analysis to obtain analytical models to describe the distribution functions.

2.1.2 **Quasi-chemical theory for solvation of hard-sphere reference**

Consider a hard sphere fluid with one solute ($\sigma$) and $N$ solvent ($p$) particles in a volume $V$ and temperature $T$. We are interested in the occupancy statistics $\{x_n\}$ of the solvent in the coordination volume around the solute. To this end consider the reaction

$$\sigma + n \cdot P \rightleftharpoons \sigma P_n$$

with the equilibrium constant

$$K_n = \frac{\rho_{\sigma P_n}}{\rho_{\sigma} \rho_p^n}, \quad (2.5)$$

where $\rho_{\sigma P_n}$ is the density of species $\sigma P_n$ and $\rho_p$ is the density of the solvent. Clearly, we have [82, 83, 86]

$$\frac{x_n}{x_0} = K_n \rho_p^n, \quad (2.6)$$

where $x_0$ is the probability that the coordination volume is empty of solvent particles and $x_n$ is the probability that there are exactly $n$ solvent molecules in the coordination volume around the solute. The $x_0$ term is of special interest as $\ln x_0 = - \ln(1 + \sum_{m \geq 1} K_m \rho_p^m)$ is free energy of allowing solvent molecules to populate a formerly empty coordination shell. Observe that the $\ln x_0$ expansion is determined by the various coordination states. In the language of quasichemical theory, $\ln x_0$ is called the
chemical term [70, 82, 83]. Because the bulk medium pushes solvent into the coordi-
nation volume, an effective attraction exists between the solute and solvent even for a
hard-sphere reference. Following earlier work in studying clusters with quasichemical
theory [70, 71, 86, 87], we can show that

\[ K_n = \frac{(e^{\beta \mu_p^{\text{ex}}} n!)}{n!} \int_v d\vec{r}_1 \ldots \int_v d\vec{r}_n e^{-\beta U_{\sigma P_n}(R^n)} e^{-\beta \phi(R^n; \beta)}, \]  

(2.7)

where \( U_{\sigma P_n}(R^n) \) is the potential energy of the \( n \)-solvent cluster (with the solute \( \sigma \) fixed at the center of the cluster), \( \beta = (k_B T)^{-1} \), observation volume \( v \) is defined by

the critical distance \( r_c \) and the particle diameter \( d \). \( \phi(R^n; \beta) \) is the free energy of
interaction of the cluster with the rest of the bulk medium for a given configuration
\( R^n \) of the cluster, and \( \beta \mu_p^{\text{ex}} \) is the excess chemical potential of the solvent particle.

(For completeness, in appendix 2.5.1 we derive the above expression for \( K_n \).) \( \phi(R^n; \beta) \)
can also be thought of as a field imposed by the bulk solvent medium [71, 87] on the
solute-solvent cluster in the observation volume.

### 2.1.3 Self-consistent mean field approach

In the primitive quasichemical approximation [71], the equilibrium constants are eval-
uated by neglecting the effect of the bulk medium, i.e. for an isolated cluster. Thus

\[ K_n \approx K_n^{(0)} \]  

[86], where

\[ n! K_n^{(0)} = \int_v d\vec{r}_1 \ldots \int_v d\vec{r}_n e^{-\beta U_{\sigma P_n}(R^n)}, \]  

(2.8)

for pair wise interactions

\[ n! K_n^{(0)} = \int_v d\vec{r}_1 \ldots \int_v d\vec{r}_n \prod_{j > i=1}^{n} e(i, j) \]  

(2.9)

where \( e(i, j) = \exp(-\beta u_{HS}(r_{ij})) \) are reference system \( e \)-bonds which serve to prevent
hard sphere overlap in the cluster; \( e(i, j) = 0 \) for \( r_{lk} < d \), and the integration is re-
stricted to the coordination volume \((v)\). The hard sphere potential between molecules is given by:

\[
    u_{HS}(r_{ij}) = \begin{cases} 
        \infty, & r_{ij} \leq d \\
        0, & r_{ij} > d 
    \end{cases}
\]

(2.10)

It is known that the primitive approximation leading to Eq. 2.9 introduces errors in the estimation of \(\ln x_0\) [86, 87], especially for systems where the interaction of the solute with the solvent is not sufficiently stronger than the interaction amongst solvent particles [71]. For hard spheres we must then expect the primitive approximation to fail outside the limit of low solvent densities.

One approach to improve the primitive approximation is to include an activity coefficient \(\lambda\), such that the predicted occupancy in the observation volume is equal to average occupancy, \(n_{avg}^{HS}\), expected in the dense reference [86]

\[
    \sum_n nK_n^{(0)} \rho_n^{(0)} \lambda^n = n_{avg}^{HS} \sum_n K_n^{(0)} \rho_n^{(0)} \lambda^n. 
\]

(2.11)

Here the factor \(\lambda\) functions as a Lagrange multiplier to enforce the required occupancy constraint \((n_{avg}^{HS})\). Physically, \(\lambda\) is an activity coefficient that serves to augment the solvent density in the observation volume over that predicted by the gas-phase equilibrium constant \(K_n^{(0)}\). This self-consistent mean field constraint can also be applied by seeking a \(\lambda\) that will reproduce the free energy to evacuate the inner-shell around the reference solute (Eq. 2.12).

In principle, \(\lambda\) should itself be \(n\)-dependent, but here we assume a mean-activity value that is the same for all \(n\) for the given density. With the above consistency requirement, \(x_0\) becomes

\[
    x_0 = \frac{1}{1 + \sum_{m \geq 1} K_m^{(0)} \lambda^m \rho_p^m}. 
\]

(2.12)
In the original implementation of the above idea for the problem of forming a cavity in a hard-sphere fluid, the consistency condition was the average occupancy of the cavity, a quantity that is known given the density of the liquid [86]. While this constraint improves upon the primitive approximation, for high densities this approximation does not predict the correct free energy to open a cavity in the hard-sphere liquid. In a subsequent work [87], in addition to \( \lambda \), a solvent coordinate-dependent molecular field was introduced to enforce the required uniformity of density (for a homogeneous, isotropic system) inside the observation volume. With this additional molecular field, Pratt and Ashbaugh [87] showed that using the few-body cluster integrals (Eq. 2.11), they could predict hard-sphere packing in excellent agreement with the Carnahan-Starling [90] result up to high densities. Both these approaches seek to predict hard-sphere properties from few-body information. However, here we acknowledge the availability of extensive simulation data on hard-spheres, and drawing inspiration from the Pratt and Ashbaugh [87] work, we find that a two-parameter model

\[
x_n = \frac{K_n^{(0)}[\lambda_1, \exp(\lambda_2 n)\rho_p]^n}{1 + \sum_{m \geq 1} K_m^{(0)}[\lambda_1, \exp(\lambda_2 m)\rho_p]^m}
\]  

(2.13)

with parameters reported in Table 2.1 is able to accurately reproduce both the free energy to evacuate the coordination volume around the reference solute and the average occupancy.

Eq. 2.13 can also be derived using a two moment maximum entropy approach, with the mean and variance of the occupancy as constraints and \( K_n^{(0)} \) as the default (See Appendix 2.5.2). Interestingly, Eq. 2.13 is identical in form with the model Reiss et. al.[88] derived to describe the effects of clustering, medium and surface interactions simultaneously in hard-sphere packing in a cavity. Based on this observation,
Table 2.1: Parameters for Eq. 2.12 and Eq. 2.13 for different $\rho d^3$, based on a self-consistent mean field approach.

<table>
<thead>
<tr>
<th>$\rho d^3$</th>
<th>0.2</th>
<th>0.3</th>
<th>0.4</th>
<th>0.5</th>
<th>0.6</th>
<th>0.7</th>
<th>0.8</th>
<th>0.9</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\lambda_1$</td>
<td>1.2991</td>
<td>1.6151</td>
<td>1.9519</td>
<td>2.5269</td>
<td>3.1475</td>
<td>4.1072</td>
<td>5.5875</td>
<td>7.5149</td>
</tr>
<tr>
<td>$\lambda_2$</td>
<td>0.0175</td>
<td>0.015</td>
<td>0.0256</td>
<td>0.023</td>
<td>0.0361</td>
<td>0.0457</td>
<td>0.0609</td>
<td>0.0829</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>1.3347</td>
<td>1.6633</td>
<td>2.0807</td>
<td>2.7198</td>
<td>3.6512</td>
<td>5.2279</td>
<td>8.4893</td>
<td>15.6104</td>
</tr>
</tbody>
</table>

in the next section we develop a more physically transparent representation of the distribution functions by analyzing the field imposed by the solvent.

2.1.4 Physically derived models for coordination distribution functions

We note that without the field term ($-\beta \phi(R_n; \beta)$), the cluster integral presents a simpler $n$-body problem (where $n$ is small, typically less than 20 for systems of interest here). The field is thus an interfacial term that couples the local cluster with the bulk medium. To make this explicit, we can rewrite Eq. 2.7 as

$$K_n = \frac{(e^{\beta \mu_{ex}})^n}{n!} \langle e^{-\beta \phi(R_n; \beta)} \rangle_0 \int_v d\vec{r}_1 \ldots \int_v d\vec{r}_n e^{-\beta U_{\sigma} \nu_n(R_n)}.$$ \hspace{1cm} (2.14)

Here $\langle \ldots \rangle_0$ indicates averaging over the normalized probability density for cluster conformations $R^n$ in the absence of interactions with the rest of the medium, i.e. over the density $e^{-\beta U_{\sigma} \nu_n(R^n)}/(n!K_n^{(0)})$, and the interfacial contribution is $\beta \Omega_n = -\ln \langle e^{-\beta \phi(R_n; \beta)} \rangle_0$.

From analysis of simulation data for different densities, we find that $\Omega_n$ can be described by a two parameter equation as

$$\beta \Omega_n = -\zeta_1 \cdot n^2 + \zeta_2 \cdot n.$$ \hspace{1cm} (2.15)
where the parameters $\zeta_1$ and $\zeta_2$ depend on the density or the packing fraction of the hard sphere system (Table 2.2). For size asymmetric hard sphere mixtures, these parameters will also depend on the size ratio of the solvent and solute molecules. Using this interfacial term we finally obtain

$$x_n = \frac{\exp(\beta \cdot n \cdot \mu_p^{ex})\rho_p^n[\exp((\zeta_1 \cdot n^2 - \zeta_2 \cdot n)]K_n^{(0)}}{1 + \sum_{j \geq 1} \exp(\beta \cdot j \cdot \mu_p^{ex})\rho_p^j[\exp((\zeta_1 \cdot j^2 - \zeta_2 \cdot j)]K_j^{(0)}}$$  \hspace{1cm} (2.16)

This two parameter model of the interfacial term was also anticipated in the previous section with the self-consistent mean field approach. However, in this section we are interested in the physical analysis of the interfacial term. Drawing upon the work of Reiss and Merry [88], we can model the interfacial contribution in terms of surface sites (of the cluster) that are available to interact with the bulk fluid. Realizing that when only one of the surface sites is occupied by a solvent molecule, its interaction with the rest of the medium is not hindered. If $\beta \Omega_1 = \zeta$ is the surface interaction for this occupancy state, then surface interaction for each solvent molecule, due to presence of $k$ solvent molecules on the surface sites is reduced to a factor proportional to the unoccupied surface sites. On the basis of such a mean field approach and guided by Monte Carlo (MC) simulation data for different densities of the symmetric hard sphere systems (with the observation shell defined by $r_c = 1.1d$), we find that

$$\beta \Omega_n = (-0.0109 \cdot n^2 + 1.0109 \cdot n) \cdot \zeta$$  \hspace{1cm} (2.17)

where $\zeta$ is a density dependent parameter (Table 2.2). With the interfacial term given by Eq. (2.17), the $x_n$ distribution can be obtained as

$$x_n = \frac{\exp(\beta \cdot n \cdot \mu_p^{ex})\rho_p^n[\exp(-(-0.0109 \cdot n^2 + 1.0109 \cdot n) \cdot \zeta)]K_n^{(0)}}{1 + \sum_{j \geq 1} \exp(\beta \cdot j \cdot \mu_p^{ex})\rho_p^j[\exp(-(-0.0109 \cdot j^2 + 1.0109 \cdot j) \cdot \zeta)]K_j^{(0)}}$$  \hspace{1cm} (2.18)
Eq. 2.16 and Eq. 2.18 are the 2-parameter and 1-parameter models, respectively, for $x_n$ on the basis of which we obtain $F^{(a)}$ (Eq. 2.4) to describe multi-body correlations in the hard sphere fluid. The parameter values for different densities are given in Table 2.2. These parameters were obtained based on the hard sphere mixtures with all the particles of the same size and the observation volume defined by $r_c = 1.1d$. Similar parameter sets can be obtained for different size ratios for asymmetric hard sphere mixtures, but we realize that the information about size-asymmetry is already contained in the isolated cluster partition function $K_n^{(0)}$. Hence, to provide a simple analytical form, we will use these parameters (obtained based on the symmetric hard sphere mixtures) to study the asymmetric mixtures with the 1-parameter model for $x_n$ (Eq. 2.18). It should be noted that the surface interaction term represented by Eq. 2.17 also depends on the size ratio, hence we will discuss the limitations of the 1-parameter model for the cases with large size asymmetry. Analysis of the interfacial term for different sizes of observation volume will also be made in the result section.

2.2 Methods

2.2.1 Monte Carlo simulations

MC simulations were carried out for symmetric hard sphere mixtures with equal sized solute and solvent molecules to obtain the parameters for models of occupancy distribution. The observation volume is defined by a critical radius $r_c = 1.1d$, where $d$ is the size of the molecules. For occupancy distribution, 255 solvent particles and 1 solute particle were studied in a given simulation cell. Analysis was carried out for different densities. To better reveal the low-$x$ states, we used an ensemble reweighing approach[91]. Essentially biases (calculated iteratively) are used to sample $n$ as
uniformly as possible. The distribution \( \{ x_n \} \) is readily obtained from the reweighed probabilities \( \{ \bar{x}_n \} \) and the biases. The system was equilibrated for 1 million steps with translational factors chosen to yield an acceptance rate of 0.3, and data was collected every 100 sweeps. To analyze the effect of observation volume on these occupancy distributions, we also performed simulations for \( r_c \in (1.1 - 1.5) \) range for these symmetric hard sphere mixtures.

We also performed Monte Carlo simulations to get occupancy distribution in asymmetric hard sphere mixtures. The solute diameter is \( d_\sigma \) and solvent diameter is \( d_p \). The observation volume is defined by a critical radius \( r_c = 1.1 \bar{d} \), where \( \bar{d} = (d_\sigma + d_p)/2 \) is the closest distance of approach. For these mixtures also 255 solvent particles and 1 solute particle were studied in a given simulation cell. Analysis was carried out for different densities and size ratios \( d_\sigma/d_p \) in the range \((0.8 - 1.2)\).

### 2.2.2 Cluster partition function

We also performed Monte Carlo simulations to obtain isolated gas cluster partition functions as follows

\[
n! K_n^{(0)} = \nu^n P^{(n)}
\]  

(2.19)

where \( \nu \) is the observation volume (defined by \( r_c \) and \( d \)) and \( P^{(n)} \) is the probability that there is no hard sphere overlap for randomly generated solvent, \( p \) molecules in the bonding volume (or inner-shell) of solute, \( \sigma \) molecules. A hit-or-miss Monte Carlo [86, 92] approach to calculate \( P^{(n)} \) proves inaccurate for large values of \( n \) (\( n > 8 \)). But since

\[
P^{(n)} = P^{(n)}_{\text{insert}} P^{(n-1)}
\]

(2.20)

where \( P^{(n)}_{\text{insert}} \) is the probability of inserting a single particle given \( n - 1 \) particles are already in the bonding volume, an iterative procedure can be used to build the
higher-order partition function from lower order one [3]. The one-particle insertion probability $P_{\text{insert}}^{(n)}$ is easily evaluated using hit-or-miss Monte Carlo. The maximum number of solvent molecules for which a non-zero insertion probability can be obtained defines $n_{\text{max}}$.

For $P_{\text{insert}}^{(n)}$, with the solute hard sphere at the center of coordinate system, the trial position of the particle in the coordination volume is randomly generated. The position is accepted if there is no overlap with either the solute or the remaining $n - 1$ particles. The insertion probability is based on similar trial placements averaged over $10^8 - 10^9$ insertions. We calculate $P^{(n)}$ (Eq. 2.20) for different size ratios of the solute and solvent molecules. For symmetric mixtures we also calculate $P^n$ for different sizes of the observation volume.

### 2.3 Results

#### 2.3.1 Symmetric hard sphere mixtures

Recall that Eq. 2.18 and Eq. 2.16 are the 1-parameter and 2-parameter models for the occupancy distribution $\{x_n\}$. To obtain the parameters for hard spheres all of the same size, for both the models we use the average occupancy ($n_{\text{avg}}^{\text{HS}} = \sum_n n \cdot x_n$) as a fitting constraint. For the 2-parameter model we additionally use the exclusion probability ($x_0$) — the probability when no hard sphere solvent particle is present in the observation volume — as a constraint. For the 1-parameter model we study the surface interactions based on the mean field approach developed by Reiss and Merry [88]. By analyzing the distribution functions $\{x_n\}$ for different densities, we obtain geometric effects (density independent) that describe the mutual interference of different surface sites (Eq. 2.17). The density (or packing fraction) dependent
Table 2.2: Parameters for Eq. 2.16 ($\zeta_1, \zeta_2$) and Eq. 2.18 ($\zeta$) for different densities $\rho d^3$ and packing fractions ($\eta$). The observation volume is defined by $r_c = 1.1d$ and $d$.

<table>
<thead>
<tr>
<th>$\rho d^3$</th>
<th>$\eta$</th>
<th>$\zeta_1$</th>
<th>$\zeta_2$</th>
<th>$\zeta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2</td>
<td>0.105</td>
<td>0.0175</td>
<td>0.773</td>
<td>0.75</td>
</tr>
<tr>
<td>0.3</td>
<td>0.157</td>
<td>0.015</td>
<td>1.267</td>
<td>1.251</td>
</tr>
<tr>
<td>0.4</td>
<td>0.209</td>
<td>0.0256</td>
<td>1.979</td>
<td>1.947</td>
</tr>
<tr>
<td>0.5</td>
<td>0.262</td>
<td>0.023</td>
<td>2.88</td>
<td>2.876</td>
</tr>
<tr>
<td>0.6</td>
<td>0.314</td>
<td>0.0361</td>
<td>4.179</td>
<td>4.172</td>
</tr>
<tr>
<td>0.7</td>
<td>0.367</td>
<td>0.0457</td>
<td>5.947</td>
<td>5.985</td>
</tr>
<tr>
<td>0.8</td>
<td>0.419</td>
<td>0.0609</td>
<td>8.432</td>
<td>8.562</td>
</tr>
<tr>
<td>0.9</td>
<td>0.471</td>
<td>0.0829</td>
<td>12.088</td>
<td>12.414</td>
</tr>
</tbody>
</table>

parameters for these two models are given in Table 2.2. Fig. 2.3 presents the results

Figure 2.3: Average occupancy $n_{avg}^{HS}$ and exclusion probability $\ln x_0$ for symmetric hard sphere mixture. Model1 (Eq. 2.18) and Model2 (Eq. 2.16) correspond to the 1 and 2-parameter models, respectively. Chang et. al. corresponds to the study in Ref. [1] for $n_{avg}^{HS}$ based on Percus-Yevick approximation. Torquato et. al. corresponds to the study in Ref. [2] for exclusion probabilities based on Carnahan-Starling approximation.
corresponding to the average occupancy \( n_{\text{avg}}^{HS} \) and exclusion probability \( \ln x_0 \) based on the models. We compare these results with the MC simulation values and also include results from literature [1, 2].

Fig. 2.3 makes it clear that 2-parameter model can simultaneously capture both \( n_{\text{avg}}^{HS} \) and \( \ln x_0 \) in excellent agreement with simulation. Importantly, even the 1-parameter model is able to capture most of the details, affirming the physical ideas underlying the models (Eqs. 2.18 and 2.16). The excellent agreement of the correlations based on the literature is due to accurate knowledge of pair correlation \( g(d) \) at the contact even for high densities. However, information about \( g(d) \) is not enough to study the entire occupancy distribution. As shown in Fig. 2.4, the 1 parameter model for occupancy distribution is able to accurately capture the whole distribution and hence we can estimate the cluster size distribution at different densities. With pair correlation information, only \( F^{(1)} \), which is equivalent to \( n_{\text{avg}}^{HS} \) can be obtained. With the entire occupancy distribution, different \( F^{(n)} \) can be obtained which give an estimate of the higher order correlations in the hard sphere fluid (See Eq. 2.5).

Figure 2.4 : Left panel shows the occupancy \( x_n \) distributions for different densities for symmetric hard sphere mixtures. Middle panel shows the average cluster size distributions \( F^{(n)} \) for different densities. Natural logarithm values are plotted in the right panel to clearly show the agreement for higher orders \( (n > 5) \). Solid lines represent results based on 1-parameter model (Eq. 2.18) and symbols represent Monte Carlo simulation results.
2.3.2 Effect of the size asymmetry

Next, using the parameters obtained above for a fluid where both solute and solvent hard-spheres are the same size (a symmetric mixture), we describe the occupancy in a fluid where the solute and solvent are of different sizes (an asymmetric mixture). Our ansatz is that the information about size asymmetry is adequately captured by the isolated cluster partition function $K_n^{(0)}$ (Eq. 2.8). Table 2.6 presents the isolated cluster probabilities ($P^{(n)}$) for different size ratios of solute and solvent molecules. Isolated cluster partition function $K_n^{(0)}$ are obtained from these probabilities by using Eq. 2.19. For an infinitely dilute system comprising one solute in a solvent bath, Fig. 2.5 shows

![Figure 2.5](image)

Figure 2.5: Average occupancy ($n_{avg}^{HS}$) and exclusion probability ($\ln x_0$) for different size ratios and different reduced densities. Symbols represent MC simulation values and lines represent the prediction results based on 1-parameter model (Eq. 2.18).

the predictions of $n_{avg}^{HS}$ and $\ln x_0$ based on the 1-parameter model (Eq. 2.18) for different size ratios and different reduced densities. The level of agreement is encouraging, but perhaps not surprising since the size ratios are not much different from a symmetric case. Thus the geometric effects describing the mutual interference of different surface sites in the packing around the solute will be similar to what is observed in
the symmetric mixture. For high density Fig. 2.5 shows that the 1-parameter model with parameters developed for symmetric mixture, slightly overpredicts the average occupancy for small size ratios and underpredicts the average occupancy for larger size ratios.

For a density of $\rho d^3 = 0.8$, Fig. 2.6 shows the distribution of average cluster size for different size ratios of the solute and solvent molecules. The results show qualitative agreement with the average cluster distribution obtained with the Monte Carlo simulation values for the occupancy distributions. Deviations for different size ratios with 1-parameter model are observed as the parameters were fit for symmetric mixtures. We also present the Monte Carlo simulation results for different size ratios of the solute and solvent molecules at three different densities in the Table 2.4. For asymmetric mixtures, the packing fraction is a better measure of packing in the fluid. Fig. 2.7 presents the variation of average occupancy for different packing fractions for

![Figure 2.6](image-url)

Figure 2.6: Left panel shows the average cluster size distribution $F(n)$ for different size ratios at a density of $\rho d^3 = 0.8$. Corresponding natural logarithm values of average cluster size distribution are plotted in the right panel for higher occupancy states ($n > 5$). Symbols represent MC simulation values and lines represent the prediction results based on 1-parameter model (Eq. 2.18). Solute is infinitely dilute.
three different size ratios for an infinitely dilute solution. The results show that the
1-parameter model is able to predict the average occupancy quite well.

Figure 2.7: Variation of average occupancy ($n_{avg}^{HS}$) for different size ratios with packing
fraction. Symbols represent MC simulation values and curves represent the prediction
results based on 1-parameter model (Eq. 2.18). Solute is infinitely dilute.

2.3.3 Effect of the size of the observation volume

We have developed a model for occupancy distribution in the hard sphere fluid where
various contributions are physically identified and hence the approach can be ex-
tended to different conditions. For example, when the observation volume of the
solute is increased from $r_c = 1.1d$, more number of solvent molecules can occupy the
observation volume. The interfacial interaction can be correspondingly changed by
incorporating the increased maximum number of solvents (or the increased surface
sites) that can occupy the observation volume, $n_{rc}^{max}$, for such cases. i.e.

$$\beta \Omega_n = \left( -0.0109 \cdot \frac{12}{n_{rc}^{max} - 1} \cdot n^2 + 1.0109 \cdot n \right) \cdot \left( \frac{13}{n_{rc}^{max}} \right) \cdot \zeta \quad (2.21)$$

Based on the modified surface interaction (Eq.2.21) for increased observation vol-
umes, 1-parameter model(Eq.2.18) can be used to obtain the occupancy distribution.
Table 2.5 presents the value of isolated cluster probabilities for different observation volumes. Fig. 2.8 shows the variation of mean occupancy $n_{avgs}$ and exclusion probability $ln x_0$ for different size of the observation volume for a symmetric mixture of solute and solvent molecules. 1-parameter model with modified surface interactions presented in Eq.2.21 is able to capture the results from Monte Carlo simulations. Literature models by Chang et. al.[1] and Turquato et. al.[2] show excellent agreement for $n_{avg}$ and $x_0$ values respectively. However, the information about entire occupancy distribution can not be obtained from these models[1, 2]. The 1-parameter model presented in this chapter is able to capture the entire occupancy distribution as shown in Fig. 2.9. Also, the models available in the literature which are based on pair correlation information can be used to guide the parameters for the 1-parameter and 2-parameter physical models developed in this work, without having to do particle simulations.

Figure 2.8 : Average occupancy $n_{avgs}$ and exclusion probability $ln x_0$ for different observation volumes $r_c$ for symmetric hard sphere mixtures, at different densities. Chang et. al. corresponds to the study in Ref. [1] for $n_{avgs}$ based on Percus-Yevick approximation. Torquato et. al. corresponds to the study in Ref. [2] for exclusion probabilities based on Carnahan-Starling approximation. Solid lines represent results based on 1-parameter model (Model1, Eq. 2.18) based on the modified surface interaction(Eq. 2.21) and symbols represent Monte Carlo simulation results.
It can be observed from the modified expression for surface interaction (Eq. 2.21) that as $r_c$ increases, the maximum number of surface sites increases, hence the coefficient corresponding to $n^2$ keeps decreasing and the coordination dependence of the surface interaction becomes less important. Which means that a single parameter model based on a self-consistent mean field would be able to capture the occupancy distribution for larger observation volumes. Physically, this means that a single chemical potential can describe the fluctuations in the occupancy states for the small system which is the cluster around the solute molecules. Such a study of effect of chemical potential on small systems has been recently studied in detail by Dixit et. al [93].

2.4 Conclusions

In this chapter we studied symmetric and asymmetric hard sphere mixtures. We emphasize that the multi-body correlations in the hard sphere fluid can be analyzed through the average cluster size distribution around a distinguished solute. We introduced an approach to represent the multi-body clusters in terms of occupancy distribution to accurately describe the packing in the hard sphere system. These
occupancy distributions were obtained by particle simulations. Based on ideas borrowed from quasichemical theory, we have also developed parametric models to describe occupancy distributions in the hard sphere systems of different densities. These distributions were obtained by describing the effects of clustering, medium and surface interactions simultaneously in the hard sphere packing around a solute. We also extended the parametric models developed for symmetric hard sphere mixtures for large observation volumes. As will be discussed in the next chapters, this cluster size distribution in the hard sphere fluid has broad potential application for perturbation theories of bulk and interfacial properties of fluids as well as predicting adsorption phenomena. With the parametric models developed in this chapter, cluster size distribution in the hard sphere fluid can be incorporated in perturbation theories (for eg. statistical associating fluid theory) without having to perform particle simulations for the hard sphere reference fluid.

2.5 Appendix

2.5.1 Expression for $K_n$

From Eq. 2.6, we find that obtaining an expression for $K_n$ reduces to evaluating the ratio of $x_n/x_0$. The total potential energy of the system when $n$ solvent particles are coordinated with the solute and the remaining $N-n$ solvent particles are outside the observation volume can be formally written as $U = U_{\sigma P_n} + U_{N-n|\sigma P_n} + U_{N-n}$. $U_{\sigma P_n}$ is the potential energy of the solute-$n$-solvent cluster. $U_{N-n|\sigma P_n}$ is the interaction energy of the cluster with the rest of the solvent; specifically $U_{N|\sigma P_0}$ is the interaction energy of the solute with the fluid outside the observation volume. In the particular case of hard-spheres, $U_{N|\sigma P_0} = 0$. Finally, $U_{N-n}$ is the potential energy of the solvent
constituting the bulk.

Since \( x_n \propto Q(n, N - n, V, T) \), where \( Q(n, N - n, V, T) \) is the canonical partition function of the system with \( n \) solvent in the observation volume around the solute and \( N - n \) in the bulk, we immediately have

\[
\frac{x_n}{x_0} = \frac{N!}{(N-n)!n!} \frac{\int_{V-v} d\vec{r}_1 \ldots \int_{V-v} d\vec{r}_n e^{-\beta U_{\sigma P_0}} \cdot \int_{V-v} d\vec{r}_{n+1} \ldots \int_{V-v} d\vec{r}_{N-n} e^{-\beta U_{N-n}|\sigma P_n} e^{-\beta U_{N-n}}}{\int_{V-v} d\vec{r}_1 \ldots \int_{V-v} d\vec{r}_N e^{-\beta U_N}}
\]

(2.22)

where we have implicitly moved the center of the coordinates to the center of the solute and thus canceled a common factor of \( V \) from both the numerator and denominator. Further, since \( U_{\sigma P_0} = 0 \) and \( U_{N|\sigma P_0} = 0 \), the denominator simply depends on the potential energy of the solvent in the bulk. (Of course for a general solute, this restriction is easily removed [70, 71].)

Next consider the ratio

\[
\frac{Q(0, N, V - v)}{Q(0, N - n, V - v)} = \frac{Q(0, N - n + 1, V - v)}{Q(0, N - n, V - v)} \cdot \frac{Q(0, N - n + 2, V - v)}{Q(0, N - n + 1, V - v)} \cdots \frac{Q(0, N, V - v)}{Q(0, N - 1, V - v)}
\]

(2.23)

where we suppress \( T \) for conciseness and the 0 indicates that there is no solute in the system (or as is the case here, \( U_{\sigma P_0} = U_{N|\sigma P_0} = 0 \)). In the thermodynamic limit of large \( V >> v \) and \( N >> n \), from the standard potential distribution relation [82, 83, 94], each of the above factor on the right is simply \( e^{-\beta \mu^e_p / \Lambda_p^3 \rho_p} \), where \( \Lambda_p \) is the thermal de Broglie wavelength of the solvent sphere and \( \mu^e_p \) is its excess chemical potential, and \( \rho_p \) the density of solvent.

Since,

\[
Q(0, N - n, V - v, T) = \frac{1}{\Lambda_p^{3(N-n)}(N-n)!} \int_{V-v} d\vec{r}_1 \ldots \int_{V-v} d\vec{r}_{N-n} e^{-\beta U_{N-n}}
\]

(2.24)

we multiply and divide Eq. 2.22 by the factor \( \int_{V-v} d\vec{r}_1 \ldots \int_{V-v} d\vec{r}_{N-n} e^{-\beta U_{N-n}} \). Rearr
ranging the resulting equation using Eq. 2.23 in the large $V$ and large $N$ limit, and noting that the momentum partition functions (for both solute and solvent) cancel exactly, we obtain Eq. 20 (main text), where

\[
e^{-\beta \phi(R^n; \beta)} = \frac{\int_{V-v} d\vec{r}_{n+1} \ldots \int_{V-v} d\vec{r}_{N-n} e^{-\beta U_{N-n} |\sigma P_n}}{\int_{V-v} d\vec{r}_1 \ldots \int_{V-v} d\vec{r}_{N-n} e^{-\beta U_{N-n}}} = \langle e^{-\beta U_{N-n} |\sigma P_n} \rangle_{N-n} \tag{2.25}
\]

where $\langle \ldots \rangle_{N-n}$ denotes averaging over the configurations of the $N-n$ solvent particles in the volume outside the observation shell.

### 2.5.2 MaxEnt model for $\{x_n\}$

Here we present an alternative derivation of the two parameter model (Eq. 2.13) on the basis of information theoretic modeling of $\{x_n\}$ [95–97]. On the basis of the isolated cluster partition function, we have the distribution of occupancy probabilities $\{x_n^{(0)}\}$ as

\[
x_n^{(0)} = \frac{K_n^{(0)} \rho_p^n}{1 + \sum_{m \geq 1} K_m^{(0)} \rho_p^m} \tag{2.26}
\]

With $\{x_n^{(0)}\}$ as the default model and accepting the availability of the mean (first moment) and variance ($s^2$) of the distribution $\{x_n\}$ from simulation data, by standard maximum entropy arguments, we have

\[
\frac{x_n}{x_n^{(0)}} = e^{-C} e^{-\lambda_1 n} e^{-\lambda_2 n^2} \tag{2.27}
\]

where the Lagrange multipliers $C$, $\lambda_1$, and $\lambda_2$ are, respectively, obtained from enforcing the following constraints

\[
\sum_n x_n = 1 \tag{2.28}
\]
\[\sum_{n} x_n \cdot n = n_{avg} \]  \hspace{1cm} (2.29)

\[\sum_{n} x_n \cdot n^2 = s^2 + n_{avg}^2 \]  \hspace{1cm} (2.30)

We thus obtain

\[x_n = \frac{[e^{-\lambda_1}e^{-\lambda_2\cdot n}]^n K_n^{(0)} \rho_p^n}{1 + \sum_{m \geq 1} [e^{-\lambda_1}e^{-\lambda_2\cdot m}]^m K_m^{(0)} \rho_p^m} \]  \hspace{1cm} (2.31)

Eq. 2.31 is the same form as obtained in section 2.1.3 for a two parameter correlation.

By using \(\lambda' = e^{-\lambda_1}\), we can also represent Eq. 2.31 by

\[x_n = \frac{[\lambda' e^{-\lambda_2\cdot n}]^n K_n^{(0)} \rho_p^n}{1 + \sum_{m \geq 1} [\lambda' e^{-\lambda_2\cdot m}]^m K_m^{(0)} \rho_p^m} \]  \hspace{1cm} (2.32)

Based on this derivation, we can see that \(\lambda_2\) is the term corresponding to surface interactions discussed in section 2.1.4 and constraints the variance of the \(\{x_n\}\) distribution.
Table 2.3: $\ln(x_n)$ in hard sphere reference system obtained by reweighted sampling for different reduced densities ($\rho\sigma^3$). The solute and solvent molecules have the same size ($d$) and the observation shell is defined by $r_c = 1.1d$.

<table>
<thead>
<tr>
<th>$n$</th>
<th>$\rho d^3 = 0.6$</th>
<th>$\rho d^3 = 0.7$</th>
<th>$\rho d^3 = 0.8$</th>
<th>$\rho d^3 = 0.9$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>-2.17</td>
<td>-3.22</td>
<td>-4.74</td>
<td>-6.74</td>
</tr>
<tr>
<td>1</td>
<td>-1.19</td>
<td>-1.78</td>
<td>-2.75</td>
<td>-4.29</td>
</tr>
<tr>
<td>2</td>
<td>-1.15</td>
<td>-1.22</td>
<td>-1.70</td>
<td>-2.75</td>
</tr>
<tr>
<td>3</td>
<td>-1.67</td>
<td>-1.28</td>
<td>-1.27</td>
<td>-1.79</td>
</tr>
<tr>
<td>4</td>
<td>-2.77</td>
<td>-1.87</td>
<td>-1.35</td>
<td>-1.33</td>
</tr>
<tr>
<td>5</td>
<td>-4.44</td>
<td>-2.98</td>
<td>-1.93</td>
<td>-1.35</td>
</tr>
<tr>
<td>6</td>
<td>-6.66</td>
<td>-4.60</td>
<td>-3.05</td>
<td>-1.84</td>
</tr>
<tr>
<td>7</td>
<td>-9.47</td>
<td>-6.85</td>
<td>-4.66</td>
<td>-2.83</td>
</tr>
<tr>
<td>8</td>
<td>-13.20</td>
<td>-9.80</td>
<td>-6.96</td>
<td>-4.39</td>
</tr>
<tr>
<td>9</td>
<td>-17.73</td>
<td>-13.62</td>
<td>-10.06</td>
<td>-6.71</td>
</tr>
<tr>
<td>10</td>
<td>-23.43</td>
<td>-18.64</td>
<td>-14.13</td>
<td>-9.79</td>
</tr>
<tr>
<td>11</td>
<td>-35.23</td>
<td>-25.35</td>
<td>-18.95</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>-47.53</td>
<td>-32.85</td>
<td>-24.88</td>
<td></td>
</tr>
</tbody>
</table>
Table 2.4: $\ln(x_n)$ in asymmetric hard sphere systems obtained by reweighted sampling for different size ratios of the solute and solvent molecules at different reduced densities ($\rho\sigma^3$). The observation shell is defined by $r_c = 1.1\bar{d}$ and $\bar{d} = (d_\sigma + d_p)/2$. Solute is infinitely dilute.

<table>
<thead>
<tr>
<th>$\rho\sigma^3$</th>
<th>$d_\sigma$ = 0.8</th>
<th>$d_\sigma$ = 0.7</th>
<th>$d_\sigma$ = 0.6</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.8</td>
<td>0.9</td>
<td>1.1</td>
</tr>
<tr>
<td>1</td>
<td>-1.66</td>
<td>-2.17</td>
<td>-3.50</td>
</tr>
<tr>
<td>2</td>
<td>-1.13</td>
<td>-1.36</td>
<td>-2.21</td>
</tr>
<tr>
<td>3</td>
<td>-1.29</td>
<td>-1.19</td>
<td>-1.51</td>
</tr>
<tr>
<td>4</td>
<td>-2.05</td>
<td>-1.59</td>
<td>-1.30</td>
</tr>
<tr>
<td>5</td>
<td>-3.44</td>
<td>-2.54</td>
<td>-1.54</td>
</tr>
<tr>
<td>6</td>
<td>-5.51</td>
<td>-4.07</td>
<td>-2.23</td>
</tr>
<tr>
<td>8</td>
<td>-12.53</td>
<td>-9.31</td>
<td>-5.05</td>
</tr>
<tr>
<td>10</td>
<td>-19.49</td>
<td>-10.30</td>
<td>-7.76</td>
</tr>
<tr>
<td>13</td>
<td>-29.48</td>
<td>-19.60</td>
<td>-34.70</td>
</tr>
</tbody>
</table>
Table 2.5: Isolated cluster probabilities $P^{(n)}$ for different observation volumes. The solute and solvent molecules have same size.

<table>
<thead>
<tr>
<th>$r_c/d$</th>
<th>1.1</th>
<th>1.2</th>
<th>1.3</th>
<th>1.4</th>
<th>1.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>2</td>
<td>0.774</td>
<td>0.796</td>
<td>0.816</td>
<td>0.834</td>
<td>0.851</td>
</tr>
<tr>
<td>3</td>
<td>0.444</td>
<td>0.487</td>
<td>0.529</td>
<td>0.569</td>
<td>0.606</td>
</tr>
<tr>
<td>4</td>
<td>0.178</td>
<td>0.220</td>
<td>0.264</td>
<td>0.310</td>
<td>0.355</td>
</tr>
<tr>
<td>5</td>
<td>4.63E-02</td>
<td>6.95E-02</td>
<td>9.79E-02</td>
<td>0.131</td>
<td>0.168</td>
</tr>
<tr>
<td>6</td>
<td>7.11E-03</td>
<td>1.44E-02</td>
<td>2.57E-02</td>
<td>4.18E-02</td>
<td>6.27E-02</td>
</tr>
<tr>
<td>7</td>
<td>5.61E-04</td>
<td>1.79E-03</td>
<td>4.54E-03</td>
<td>9.66E-03</td>
<td>1.80E-02</td>
</tr>
<tr>
<td>8</td>
<td>1.91E-05</td>
<td>1.20E-04</td>
<td>5.04E-04</td>
<td>1.55E-03</td>
<td>3.87E-03</td>
</tr>
<tr>
<td>9</td>
<td>2.12E-07</td>
<td>3.82E-06</td>
<td>3.23E-05</td>
<td>1.65E-04</td>
<td>6.03E-04</td>
</tr>
<tr>
<td>10</td>
<td>1.48E-09</td>
<td>4.66E-08</td>
<td>1.19E-06</td>
<td>1.1E-05</td>
<td>6.53E-05</td>
</tr>
<tr>
<td>11</td>
<td>4.98E-12</td>
<td>2.07E-10</td>
<td>1.88E-08</td>
<td>4.28E-07</td>
<td>4.75E-06</td>
</tr>
<tr>
<td>12</td>
<td>1.11E-15</td>
<td>2.94E-13</td>
<td>1.21E-10</td>
<td>8.97E-09</td>
<td>2.2E-07</td>
</tr>
<tr>
<td>13</td>
<td>5.55E-24</td>
<td>1.76E-16</td>
<td>2.43E-13</td>
<td>9.2E-11</td>
<td>6.21E-09</td>
</tr>
<tr>
<td>14</td>
<td>0</td>
<td>6.44E-20</td>
<td>1.35E-16</td>
<td>4.19E-13</td>
<td>9.96E-11</td>
</tr>
<tr>
<td>15</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>7.47E-16</td>
<td>8.5E-13</td>
</tr>
</tbody>
</table>
Table 2.6: Isolated cluster probabilities $P^{(n)}$ for different relative sizes of the solute as compared to the solvent molecules. The observation shell is defined by $r_c = 1.1 \bar{d}$ and $\bar{d} = (d_\sigma + d_p)/2$.

<table>
<thead>
<tr>
<th>$d_\sigma/d_p$</th>
<th>0.8</th>
<th>0.85</th>
<th>0.9</th>
<th>0.95</th>
<th>1</th>
<th>1.05</th>
<th>1.1</th>
<th>1.15</th>
<th>1.2</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>2</td>
<td>0.7533</td>
<td>0.7586</td>
<td>0.7638</td>
<td>0.7689</td>
<td>0.7740</td>
<td>0.7789</td>
<td>0.7838</td>
<td>0.7887</td>
<td>0.7934</td>
</tr>
<tr>
<td>3</td>
<td>0.4050</td>
<td>0.4147</td>
<td>0.4243</td>
<td>0.4339</td>
<td>0.4435</td>
<td>0.4532</td>
<td>0.4628</td>
<td>0.4724</td>
<td>0.4819</td>
</tr>
<tr>
<td>4</td>
<td>0.1449</td>
<td>0.1527</td>
<td>0.1609</td>
<td>0.1691</td>
<td>0.1778</td>
<td>0.1866</td>
<td>0.1956</td>
<td>0.2048</td>
<td>0.2142</td>
</tr>
<tr>
<td>5</td>
<td>3.15E-02</td>
<td>3.47E-02</td>
<td>3.83E-02</td>
<td>4.22E-02</td>
<td>4.63E-02</td>
<td>5.07E-02</td>
<td>5.55E-02</td>
<td>6.05E-02</td>
<td>6.58E-02</td>
</tr>
<tr>
<td>6</td>
<td>3.67E-03</td>
<td>4.34E-03</td>
<td>5.14E-03</td>
<td>6.05E-03</td>
<td>7.10E-03</td>
<td>8.32E-03</td>
<td>9.69E-03</td>
<td>1.13E-02</td>
<td>1.30E-02</td>
</tr>
<tr>
<td>7</td>
<td>1.94E-04</td>
<td>2.53E-04</td>
<td>3.32E-04</td>
<td>4.32E-04</td>
<td>5.61E-04</td>
<td>7.24E-04</td>
<td>9.28E-04</td>
<td>1.18E-03</td>
<td>1.49E-03</td>
</tr>
<tr>
<td>8</td>
<td>3.76E-06</td>
<td>5.64E-06</td>
<td>8.49E-06</td>
<td>1.27E-05</td>
<td>1.91E-05</td>
<td>2.83E-05</td>
<td>4.17E-05</td>
<td>6.09E-05</td>
<td>8.76E-05</td>
</tr>
<tr>
<td>9</td>
<td>1.98E-08</td>
<td>3.52E-08</td>
<td>6.37E-08</td>
<td>1.16E-07</td>
<td>2.12E-07</td>
<td>3.87E-07</td>
<td>7.00E-07</td>
<td>1.25E-06</td>
<td>2.18E-06</td>
</tr>
<tr>
<td>10</td>
<td>2.29E-11</td>
<td>7.95E-11</td>
<td>8.09E-11</td>
<td>2.86E-10</td>
<td>1.48E-09</td>
<td>1.20E-09</td>
<td>2.98E-09</td>
<td>7.27E-09</td>
<td>1.72E-08</td>
</tr>
<tr>
<td>11</td>
<td>1.89E-15</td>
<td>1.32E-13</td>
<td>3.97E-14</td>
<td>7.02E-14</td>
<td>4.98E-12</td>
<td>1.41E-12</td>
<td>3.11E-12</td>
<td>7.58E-12</td>
<td>2.90E-11</td>
</tr>
<tr>
<td>12</td>
<td>7.85E-20</td>
<td>2.50E-17</td>
<td>1.05E-17</td>
<td>1.35E-18</td>
<td>1.11E-15</td>
<td>1.05E-16</td>
<td>4.51E-16</td>
<td>3.58E-15</td>
<td>2.14E-14</td>
</tr>
<tr>
<td>13</td>
<td>1.73E-25</td>
<td>7.50E-26</td>
<td>2.20E-21</td>
<td>0.00E+00</td>
<td>5.55E-24</td>
<td>2.35E-21</td>
<td>1.39E-21</td>
<td>2.02E-19</td>
<td>1.43E-17</td>
</tr>
</tbody>
</table>
Chapter 3

Symmetric mixtures of patchy and spherically symmetric colloids

In this chapter we study a symmetric mixture of solvent particles with short-range, directional interactions and solute particles with short-range, isotropic interactions. Wertheim’s theory [45, 46] in the form of the statistical associating fluid theory (SAFT) [16, 40, 50–53] has proven effective in describing systems with short range, directional (i.e. specific) interactions and is thus of natural interest in describing patchy colloids. To incorporate multi-body effects in SAFT when the association potential of the solute is such as to allow multiple bonding per site, Marshall and Chapman [3, 67] extended Wertheim’s multi-density [47] formalism to multi-site associating fluids. This theory generalizes the single chain approximation of Wertheim [68] for a site bonding multiple times, but it requires the multi-body correlation function for solvent around the solute in the non-associating reference fluid. These multi-body correlations for the reference fluid were sought by characterizing the distribution of gas-phase solute-solvent clusters. The effect of the bulk solvent is subsequently incorporated at the TPT2 level by using the linear superposition of the pair correlation function plus a three body correction. This approximation works well for systems at low solvent densities or higher concentration of solute, i.e. conditions when low order correlations are important. However, this approach fails at high solvent densities and for low concentrations of solutes. In this chapter, we address these limitations and present a way to accurately incorporate multi-body correlations in the hard sphere
Following Marshall and Chapman [3, 67], we model solute and patchy solvent molecules as hard spheres of equal diameter \((d)\) and short range association sites. For the hard-sphere reference, we show how coordination distribution around a distinguished solute obtained from particle simulations can be used to incorporate multi-body correlations in the cluster integrals that appear in the theory. The link between coordination distribution and multi-body correlations is inspired by quasichemical theory [86, 87] and ultimately draws upon Reiss and coworker’s seminal investigation of hard-sphere packing [56] as shown in chapter 2. In the present framework, all contributions from orientation-dependent attractive interactions are transparently decoupled from multi-body packing effects that are obtained for the reference fluid.

The rest of the chapter is organized in the following way. In Section 3.1.1 we discuss the Marshall-Chapman [67] theory, their gas-phase cluster approximation and highlight the need for improvement suggested by comparing the results of the theory with Monte Carlo simulations. In Section 3.1.2 we discuss our complete reference approach for better describing the multi-body effects in the reference. Section 3.3 collects the results and discussions of this study.

### 3.1 Theory

Consider a mixture of solvent molecules, \(p\), with two directional sites (labeled \(A\) and \(B\)) and isotropically-sticky, solute molecules, \(s\). For solvent-solvent association, only bonding between \(A\) and \(B\) is allowed and the size of sites is such that single bonding condition holds (Fig. 3.1). The solute molecule can bond with site \(A\) of the solvent; the isotropic attraction ensures the solute can bond multiple solvent molecules (Fig. 3.1). We ignore the association between the solutes themselves. The total potential is a
The association potential for solvent-solvent \((p, p)\) and solute-solvent \((s, p)\) molecules is given by:

\[
\begin{align*}
    u_{AB}^{(p,p)}(r) &= \begin{cases} 
    -\epsilon_{AB}^{(p,p)}, & r < r_c \text{ and } \theta_A \leq \theta_c^{(A)} \text{ and } \theta_B \leq \theta_c^{(B)} \\
    0 & \text{otherwise}
    \end{cases} \\
    u_{A}^{(s,p)}(r) &= \begin{cases} 
    -\epsilon_{A}^{(s,p)}, & r < r_c \text{ and } \theta_A \leq \theta_c^{(A)} \\
    0 & \text{otherwise}
    \end{cases}
\end{align*}
\]

Figure 3.1: Association between solute and solvent (left) and solvent molecules (right). \(r\) is the center-to-center distance and \(\theta_A\) and \(\theta_B\) are the orientation of the attractive patches \(A\) and \(B\) relative to line connecting the centers. Note the sticky solute (colored red) can only interact with the patch \(A\) (colored red) on solvent molecules.

In the Wertheim’s multi density formalism [47, 48], the free energy due to association can be expressed as

\[
\frac{A_{AS}}{V k_B T} = \sum \left( \rho^{(k)} \ln \frac{\rho_0^{(k)}}{\rho^{(k)}} + Q^{(k)} + \rho^{(k)} \right) - \Delta c^{(0)}/V
\]
where $k_B$ is the Boltzmann constant, $T$ is the temperature, the summation is over the species ($k = s, p$), $\rho$ is the number density, $\rho_0$ is the monomer density, $Q^{(k)}$ is a factor that follows from Wertheim’s approach [47] (See Appendix 3.5.1) and $\Delta c^{(0)}$ is the contribution to the graph sum due to association between the solvent-solvent ($p, p$) and solute-solvent ($s, p$) molecules, i.e.

$$\Delta c^{(0)} = \Delta c^{(0)}_{pp} + \Delta c^{(0)}_{sp}$$

(3.5)

### 3.1.1 Marshall-Chapman theory

In the Marshall-Chapman [3, 67] work, the role of attractions between solvent, $p,$ molecules is accounted by standard first order thermodynamic perturbation theory [50] (TPT1). For the association contribution to intermolecular interactions between the solute ($s$ molecules) and solvent ($p$ molecules), Marshall and Chapman [3, 67] developed a theory based on generalization of Wertheim’s single chain approximation [47, 68]. By including graph sums for all the possible arrangements of the solvent around the solute i.e. one solvent around solute, two solvents around solute, etc. (Fig. 3.2), Marshall and Chapman obtained the free energy expression for the mixture as:

$$\Delta c^{(0)}_{sp} = \sum_{n=1}^{n_{\text{max}}} \Delta c^{(0)}_{n}$$

(3.6)

where

$$\Delta c^{(0)}_{n} = \frac{\rho_0^{(s)}(\rho^{(p)}) X_A^{(p)}}{\Omega^{n+1} n!} \int d(1) \cdots d(n + 1) g_{HS}(1 \cdots n + 1) \cdot \prod_{k=2}^{n+1} (f_A^{(s,p)}(1, k)).$$

(3.7)
Figure 3.2: Representation of graph sums for all the possible arrangements due to association of the solvent around a solute. Note that, for example, the graph for $\Delta c_3^{(0)}$ will include other higher occupancy states and is thus a measure of the effective association with 3 solvent particles.

In Eq. 3.7, $\rho^{(p)}(= \rho \cdot x^{(p)})$ is the density of solvent molecules obtained from the mole fraction of solvent ($x^{(p)}$) and the total density ($\rho$), $X_A^{(p)}$ is the fraction of solvent molecules not bonded at site $A$, $\tilde{\Omega}(=4\pi)$ is the total number of orientations, $f_A^{(s,p)}(1,k)(=\exp(\varepsilon_{A}^{(s,p)}/k_B T) - 1)$ is the Mayer function for association between $p$ and $s$ molecules corresponding to potential in Eq. 3.3 and the integral is over all the orientations and positions of the $n + 1$ particles. If the spherical particle is fixed at the origin, the above integral can be represented in terms of the distances from the origin

$$\frac{\Delta c_n^{(0)}}{V} = \frac{\rho_0^{(s)} \rho^{(p)} X_A^{(p)}}{\tilde{\Omega}^n n!} \int d\mathbf{r}_1 \cdots d\mathbf{r}_n d\omega_1 \cdots d\omega_n g_{HS}(\mathbf{r}_1 \cdots \mathbf{r}_n|0) \cdot \prod_{k=1}^{n} (f_A^{(s,p)}(0,k)) \quad (3.8)$$

As is usual in SAFT, the contribution due to association is given by an averaged $f$-bond and factored outside the integral. Integrating over the orientations and defining $\sqrt{\kappa_{AA}}(= (1 - \cos(\theta_c))/2)$ as the probability that molecule $p$ is oriented such that patch $A$ on $p$ bonds to $s$, we get

$$\frac{\Delta c_n^{(0)}}{V} = \frac{\rho_0^{(s)} \rho^{(p)} X_A^{(p)} f_A^{(s,p)} \sqrt{\kappa_{AA}}}{n!} \int_v d\mathbf{r}_1 \cdots d\mathbf{r}_n g_{HS}(\mathbf{r}_1 \cdots \mathbf{r}_n|0). \quad (3.9)$$
The limits of the integral in Eq. 3.8 reduce to the volume of the observation shell \((v)\) defined by the region between the diameter of the molecule \((d)\) and \(r_c\), as the Mayer \(f\) function is zero for rest of the positions. Due to the limited knowledge of the \(m^{th}\) order correlation functions for \(m > 2\) \((n = 1\) corresponds to pair correlation), the calculation of the integral in Eq. 3.9 is a daunting numerical challenge.

**Marshall-Chapman approximation (MCA)**

To simplify numerical calculations, Marshall and Chapman [3] developed an approximation for the cavity correlation function, \(y_{HS}(\vec{r}_1 \cdots \vec{r}_n|0)\), defined by

\[
g_{HS}(\vec{r}_1 \cdots \vec{r}_n|0) = y_{HS}(\vec{r}_1 \cdots \vec{r}_n|0) \prod_{\{i,k\}} e_{HS}(r_{ik}). \tag{3.10}
\]

As usual, \(e_{HS}(r_{lk}) = \exp\left(-u_{HS}(r_{lk})/k_B T\right)\) are reference system \(e\)-bonds which serve to prevent hard sphere overlap in the cluster; \(e_{HS}(r_{lk}) = 0\) for \(r_{lk} = |\vec{r}_i - \vec{r}_k| < d\). At the TPT2 level, Marshall-Chapman approximated the cavity correlation function by the first order superposition of pair cavity correlation function at contact corrected by a second order factor \((\delta(n))\) to account for three body interactions [98], i.e.

\[
y_{HS}(\vec{r}_1 \cdots \vec{r}_n|0) \approx y_{HS}^n(d)\delta^{(n)}. \tag{3.11}
\]

This leads to

\[
\int_v d\vec{r}_1 \cdots d\vec{r}_n g_{HS}(\vec{r}_1 \cdots \vec{r}_n|0) \approx y_{HS}^n(d)\delta^{(n)}\Xi^{(n)} \tag{3.12}
\]

where

\[
\Xi^{(n)} = \int_v d\vec{r}_1 \int_v d\vec{r}_2 \ldots \int_v d\vec{r}_n \prod_{j>i=1}^n e_{HS}(r_{ij}) \tag{3.13}
\]

is the partition function for an isolated cluster with \(n\) solvent hard spheres around a hard sphere solute in the bonding volume, i.e. the spherical shell bounded by \(d\) and \(r_c\), within which particles can associate.
\( \Xi^{(n)} \) can be obtained as
\[
\Xi^{(n)} = \nu_b^n P^{(n)}
\]
where \( \nu_b \) is the bonding volume and \( P^{(n)} \) is the probability that there is no hard sphere overlap for randomly generated \( p \) molecules in the bonding volume (or inner-shell) of \( s \) molecules. A hit-or-miss Monte Carlo [86, 92] approach to calculate \( P^{(n)} \) proves inaccurate for large values of \( n \) (\( n > 8 \)). But since
\[
P^{(n)} = P^{(n)}_{\text{insert}} P^{(n-1)},
\]
where \( P^{(n)}_{\text{insert}} \) is the probability of inserting a single particle given \( n - 1 \) particles are already in the bonding volume, an iterative procedure can be used to build the higher-order partition function from lower order one [3]. The one-particle insertion probability \( P^{(n)}_{\text{insert}} \) is easily evaluated using hit-or-miss Monte Carlo. The maximum number of \( p \) molecules for which a non-zero insertion probability can be obtained defines \( n^{\text{max}} \).

With the potential defined by Eq. 3.3 and the approximation made in Eq. 3.11, Eq. 3.9 reduces to
\[
\frac{\Delta c_n^{(0)}}{V} = \frac{1}{n!} \rho_0^{(s)} \Delta^n \Xi^{(n)} \delta^{(n)},
\]
where for a two patch solvent,
\[
\Delta = y_{HS} (d) X_{A}^{(p)} \rho_{A}^{(p)} f_{A}^{(s,p)} \sqrt{\kappa_{AA}}.
\]
The fraction of solute bonded \( n \) times is
\[
X_n^{(s)} = \frac{\frac{1}{n!} \Delta^n \Xi^{(n)} \delta^{(n)}}{1 + \sum_{n=1}^{n^{\text{max}}} \frac{1}{n!} \Delta^n \Xi^{(n)} \delta^{(n)}}, \quad n > 0,
\]
and the fraction bonded zero times is
\[
X_0^{(s)} = \frac{1}{1 + \sum_{n=1}^{n^{\text{max}}} \frac{1}{n!} \Delta^n \Xi^{(n)} \delta^{(n)}}.
\]
Finally, the average number of solvent associated with the solute is given by:

$$n_{\text{avg}} = \sum_n n \cdot X_n^{(s)},$$  \hspace{1cm} (3.20)$$

The fraction of solvent not bonded at site A and site B can be obtained by simultaneous solution of the following equations:

$$X_A^{(p)} = \frac{1}{1 + \xi\kappa_{AB} f_{AB}^{(p,p)} \rho^{(p)} X_B^{(p)} + \rho^{(s)} n_{\text{avg}} / \rho X_A^{(p)}},$$  \hspace{1cm} (3.21)$$

$$X_B^{(p)} = \frac{1}{1 + \xi\kappa_{AB} f_{AB}^{(p,p)} \rho^{(p)} X_A^{(p)}}.$$  \hspace{1cm} (3.22)$$

where

$$\xi = 4\pi d^2 (r_c - d) y_{HS}(d)$$

$$\kappa_{AB} = \frac{[1 - \cos(\theta_c)]^2}{4}$$

$$f_{AB}^{(p,p)} = \exp(\varepsilon_{AB}^{(p,p)} / k_B T) - 1.$$  \hspace{1cm} (3.23)$$

As will be shown below, the approximation Eq. 3.12 works very well for low solvent densities ($\rho d^3 < 0.6$), but is inadequate in modeling a dense system.

### 3.1.2 The complete reference approach

As presented in chapter 2, the integral appearing in Eq. 3.9 has a simple physical interpretation. It is related to the average number of $n$-solvent clusters (around the distinguished solute) in the hard sphere system \cite{56}, $F^{(n)}$, by

$$F^{(n)} = \frac{\rho^n}{n!} \int \nu d\bar{r}_1 \cdots d\bar{r}_n g_{HS} (\bar{r}_1 \cdots \bar{r}_n | 0)$$

$$= \sum_{m=n}^{n_{\text{max}}} C_n^m x_m,$$  \hspace{1cm} (3.23)$$
where $x_n$ is the probability of observing exactly $n$ solvent molecules in the observation shell of the solute in the reference system. $C_n^m = m!/(m-n)! \cdot n!$ is the combinatorial term which defines the weight for a given coordination state. The association contribution (Eq. 3.9) is then simply

$$\frac{\Delta c^{(0)}_n}{V} = \rho_0^{(s)} x^{(p)} A^{(s,p)} f^{(s,p)} \sqrt{K_{AA}} F^{(n)}.$$  

(3.24)

Assuming the availability of $\{x_n\}$, the above approach amounts to including the complete hard-sphere occupancy (packing) information in the Marshall-Chapman framework. Henceforth, we will refer to this as the “complete reference” approach. As figure 3.3 shows for an example of the $\Delta c^{(0)}_3$ term, observe that all occupancy states $m \geq n$ will contribute with combinatorial weights to the bonding state $n$. Thus errors in accounting for the occupancy of the coordination volume will have a substantial impact in capturing the bonding state.

$$\Delta c^{(0)}_3 = x_3 P(X^{(s)}_3 | 3) + x_4 P(X^{(s)}_3 | 4) + x_5 P(X^{(s)}_3 | 5) + x_6 P(X^{(s)}_3 | 6) + \ldots + x_{n_{max}} P(X^{(s)}_3 | n_{max})$$

Figure 3.3: Example graph sum to illustrate the joint role of occupancy and bonding. $x_n$ is the probability of observing $n$-solvent around the solute without regard for their orientation. $P(X^{(s)}_i | n)$ is the conditional probability that given $n$-solvents occupy the bonding volume, $i(\leq n)$ of them are oriented correctly and bond with the solute. Patchy sites for only correctly oriented solvent are shown. Spheres are indicated by a dashed line to differentiate the graph from the effective association indicated in Fig. 3.2.

Eq. 3.24 and the insight derived from it is the central contribution of this work. In support of this, in chapter 2 we presented the results in modeling of $\{x_n\}$ using ensemble-reweighing approaches which are used to obtain $F^{(n)}$ using eq. 3.23 to
calculate associating mixture properties with complete reference theory. We also de-
developed a concise parametric model based on the quasichemical theory of solutions
to represent these \( \{ x_n \} \) distributions. As an aside, note that the Marshall-Chapman
approximation is

\[
F^{(n)}_{\text{MCA}} \approx \frac{\rho^n y_{\text{HS}}^n(d) \delta^{(n)} \Xi^{(n)}}{n!},
\]

(3.25)

Given \( F^{(n)} \), the fraction of solute associated with \( n \) solvent molecules is

\[
X^{(s)}_n = \frac{\left( x^{(p)} X^{(p)} A f^{(s,p)} \sqrt{K AA} \right)^n F^{(n)}}{1 + \sum_{n=1}^{n_{\text{max}}} \left( x^{(p)} X^{(p)} A f^{(s,p)} \sqrt{K AA} \right)^n F^{(n)}},
\]

(3.26)

and the fraction of with not bonded to any solvent molecule is

\[
X^{(s)}_0 = \frac{1}{1 + \sum_{n=1}^{n_{\text{max}}} \left( x^{(p)} X^{(p)} A f^{(s,p)} \sqrt{K AA} \right)^n F^{(n)}}.
\]

(3.27)

Using these distributions for associating mixture, average bonded state and fraction
of solvent not bonded at sites can be obtained from Eq. 3.20 - 3.22.

3.2 Methods

3.2.1 Monte Carlo simulation of associating system

MC simulations were performed to evaluate the Marshall-Chapman approximation
and test the Marshall-Chapman theory with improved representation of the multi-
body cluster integrals (this work). The associating mixture comprises the sticky solute
and the solvent with 2 diagonally opposed bonding sites. For all the simulations, the
solvent-solvent and solute-solvent association is defined by the potentials in Eq. 3.2
and 3.3 respectively, with \( r_c = 1.1d \) and \( \theta^{(A)} = \theta^{(B)} = 27^\circ \). Unless specifically stated
all simulations were based on 255 solvent particles and 1 solute.
The excess chemical potential of coupling the colloid with the solvent was obtained using thermodynamic integration,

$$\beta \mu^{\text{asso}} = \epsilon \int_{0}^{1} \langle \beta \psi \rangle_{\epsilon, \lambda} d\lambda$$

(3.28)

where $\langle \beta \psi \rangle_{\epsilon, \lambda}$ is the average binding energy of solute with the solvent as a function of the solute-solvent interaction strength scaled by $\lambda$ and $\beta = 1/k_{B}T$. The integration was performed using a three-point Gauss-Legendre quadrature [99]. At each coupling strength, the system was equilibrated over 1 million sweeps, where a sweep is an attempted move for every particle. The translation/rotation factor was chosen to yield an acceptance ratio between 0.3 – 0.4. These parameters were kept constant in the production phase which also extended for 1 million sweeps. Binding strength data was collected every 100 sweeps for analysis. Statistical uncertainty in $\mu^{\text{asso}}$ was obtained using the Friedberg-Cameron approach [100, 101]. Simulations were performed at different densities for different interaction schemes and these are specifically noted in the results below. (For $\rho d^{3} = 0.9$, we used 864 particles for better statistics.)

To compare the predictions of the bonding state of the colloid ($X_{i}^{(s)}$) with simulations, from Bayes’ rule we have

$$X_{i}^{(s)} = \sum_{n \geq i} x_{n} P(X_{i}^{(s)} | n) ,$$

(3.29)

where $P(X_{i}^{(s)} | n)$ is the probability of observing the colloid in the $i$-bonded state given precisely $n$ solvent particles are in the coordination volume. Knowing $X_{i}^{(s)}$, the average bonding state of the colloid is then

$$n_{\text{avg}} = \sum_{n} n \cdot X_{n}^{(s)}$$

(3.30)

To better reveal these low-$X$ states, we used an ensemble reweighting approach [91]. Biases are calculated iteratively to sample $n$ as uniformly as possible. The distribution
\( \{ x_n \} \) is readily obtained from the reweighted probabilities \( \{ \bar{p}_n \} \) and the converged biases. For each \( n \) in the biased simulation, the distribution of \( X_i^{(s)} \) is obtained and \( P(X_i^{(s)}|n) \) constructed.

To study the effect of concentration of solute on \( n_{\text{avg}} \), it was necessary to explore system with larger number of particles. Specifically, we performed simulations for various concentrations \( 0 \leq x_s \leq 1 \) by changing the number of solute molecules in a mixture with 864 number of particles. The hard-sphere \( \{ x_n \} \) distribution was obtained using the reweighting approach [91].

### 3.2.2 Cluster partition function

To calculate \( P_{\text{insert}}^n \) (Eq. 3.15), following Refs. [3, 67], with the solute hard sphere at the center of coordinate system, trial position of the (inserted) solvent in the coordination volume is randomly generated. The position is accepted if there is no overlap with either the solute or the remaining \( n - 1 \) particles. The insertion probability is based on similar trial placements averaged over \( 10^8 - 10^9 \) insertions. For the present study involving solute and solvent of equal size, the radius of the coordination volume is the same as the cut-off radius of \( r_c = 1.1d \), where \( d \) is the hard-sphere diameter.

### 3.3 Results and Discussions

#### 3.3.1 Average cluster distribution

Figure 3.4 shows the comparison of the prediction of \( F^{(n)} \) based on the Marshall-Chapman approximation versus molecular simulations. Observe that for higher solvent densities that are of practical interest in modeling a dense solvent, the Marshall-
Chapman approximation overestimates the population of lower n-mers and underestimates that of the higher n-mers, but somewhat fortuitously it captures n-mers in the range (6 – 7). Since the average number of n-mer is augmented by $n^{th}$ power of Mayer $f$-function (Eq. 3.9), the Marshall-Chapman approximation is expected to be progressively inaccurate as the strength of solvent-solute association increases; thus a better account of $F^{(n)}$ is needed in securing quantitative accuracy. We next turn to the study of associating mixtures.

### 3.3.2 Solute-solvent versus solvent-solvent association

Fig. 3.5 shows the distribution of the bonding states $\{X_n^{(n)}\}$ of the solute for a reduced density of $\rho d^3 = 0.8$ for two cases, one with and the other without solvent-solvent interaction. In both cases, only one solute is present in the solvent bath and the solute-solvent interaction is $7 k_B T$.

Fig. 3.5 reveals that for the same interaction energy, higher bonding states are more probable and hence multi-body effects more important in the case when solvent-
Figure 3.5: Distribution of bonding states of the solute when the strength of solvent-solvent interaction is $7k_B T$ (left) and zero (right). The reduced density is $\rho d^3 = 0.8$. $X_n^{(s)}$ is the fraction of solute bonded $n$-times to the patchy solvent molecules. The solute is infinitely dilute and association energy for interaction between solute and solvent is $7k_B T$.

Solvent association is absent. To understand this, note that when both solvent-solvent and solute-solvent interactions are present, there is a competition for patch $A$ on solvent molecule (see Fig. 3.1) to associate with patch $B$ on another solvent molecule or with the sticky solute. This competition is absent in the case when solvent-solvent association is absent and hence effectively more of the solvent patches are available to bond with the solute. Since the Marshall-Chapman approximation has a limitation in capturing the higher $n$-mer state (Fig. 3.4), it is seen that it is unable to capture the distribution of higher bonding states even qualitatively. However, the complete reference approach is able to describe the bonded fraction quite accurately.

3.3.3 $\beta \mu^{asso}$ of solute

The ability of the complete reference approach to capture the distribution of bonded states suggests that it should also better describe the association contribution to the chemical potential. Fig. 3.6 supports this suggestion, but for some densities
deviations as high as $1 \ k_B T$ are found. Somewhat surprisingly, when solvent-solvent interaction energies are comparable with solute-solvent interactions, $\mu^{Asso}$ calculated using the Marshall-Chapman approximation is about as good as the result based with the revised reference (though deviations are larger than the complete reference approach).

Probing the basis for the surprisingly reasonable prediction for $\mu^{Asso}$ based on the Marshall-Chapman approximation reveals the importance of competitive solute-solvent and solvent-solvent interactions. When solute-solvent association is comparable to solute-solvent association, specifically, $\epsilon^{(p,p)} \geq \epsilon^{(s,p)}$, the Marshall-Chapman approximation is able to capture the bonding states up to the most probable bonding state reasonably well (Fig.3.7). However, when solute-solvent association strength is higher than solvent-solvent association, the Marshall-Chapman approximation is unable to capture neither the most probable bonding state nor the lower bonding states. Since in calculating $\mu^{Asso}$ we integrate the mean binding energy (Eq. 3.28) over the regime where $\epsilon^{(p,p)} > \epsilon^{(s,p)}$, and since this is also the regime in which the
Marshall-Chapman approximation is comparable to the revised theory, the final observed differences in the prediction of the chemical potential are not thus substantial.

We suspect that the entropic and enthalpic components of \( \mu^{\text{Asso}} \) will be more sensitive to the description of the reference. However, the chemical potential results do suggest a cautionary note, namely that a metric based on \( \mu^{\text{Asso}} \) may mask differences in underlying approximations.

Figure 3.7: Distribution of bonding states of solute at \( \rho d^3 = 0.8 \) and different association energies between solute-solvent molecules; \( \epsilon^{(s,p)} = 4k_B T \) (left), \( \epsilon^{(s,p)} = 6k_B T \) (middle), \( \epsilon^{(s,p)} = 8k_B T \) (right). Solute is infinitely dilute and association energy for solvent-solvent interactions (\( \epsilon^{(p,p)} \)) is \( 7k_B T \).

3.3.4 Variation of average bonding with association energy

Fig. 3.8 shows the variation of average bonding numbers (\( n_{\text{avg}} \)) for the solute, when the solute-solvent and solvent-solvent association strengths are the same.

It can be observed from Eq. 3.23 that at high densities, the contribution to \( F^{(n)} \) from the higher-occupancy (higher \( x_n \)) state is non-negligible. For the association contribution, recall that \( F^{(n)} \) is multiplied by \( n \)-factors of the Mayer \( f \) function which itself depends exponentially on strength of association. Thus for high density and high association strength, the TPT2 (Marshall-Chapman approximation) prediction
Figure 3.8 : Variation of average bonding number \( (n_{\text{avg}}) \) with the association energy between molecules \( (\epsilon) \) for \( \rho d^3 = 0.8 \). Solute is infinitely dilute.

is expected to underestimate \( n_{\text{avg}} \). We find that this is indeed the case, but using the complete reference approach we can capture \( n_{\text{avg}} \) accurately.

Figure 3.9 : Variation of average bonding number \( (n_{\text{avg}}) \) with the association energy between solute-solvent molecules \( (\epsilon^{(p,p)}) \) (left) and solvent-solvent molecules \( (\epsilon^{(s,p)}) \) (right) for \( \rho d^3 = 0.8 \). Solute is infinitely dilute.

Fig.3.9 further highlights the importance of the relative strengths of solute-solvent and solvent-solvent interactions on multi-body effects. As expected from the foregoing analysis, when the solute-solvent interactions are much stronger than solvent-solvent interactions, \( n_{\text{avg}} \) based on the Marshall-Chapman approximation deviates signifi-
cantly from \( n_{\text{avg}} \) based on simulations.

### 3.3.5 Solute concentration effect

We also study the variation of average bonding number (\( n_{\text{avg}} \)) with the concentration of solute molecules (\( x_s \)) for a reduced density of \( \rho d^3 = 0.8 \). (The solvent-solvent and solute-solvent interactions are all at the same level, \( \epsilon = 7k_B T \)). For low concentration of solute, since more solvent molecules are available to associate with the solute, higher bonding states are more probable. It is precisely in this limit that we expect larger deviations from the Marshall-Chapman approximation. As the concentration of solute is increased, proportionately fewer solvent molecules are available to bond with the colloid. In this limit, the effect of multi-body effects in solvation of the colloid should be tempered and better agreement with the Marshall-Chapman approximation is expected. Fig. 3.10 confirms these expectations.

\[ \rho d^3 = 0.8 \]

\[ \epsilon(s,p) = \epsilon(p,p) = 7k_B T \]

Figure 3.10 : Variation of average bonding number (\( n_{\text{avg}} \)) with the concentration of solute in the solution for \( \rho d^3 = 0.8 \). Energy of association between molecules is \( 7k_B T \).
3.4 Conclusion

In this chapter we have developed a simple and effective way to model multi-body effects in colloidal mixtures. Building on the Marshall and Chapman theory, we show that the challenge in describing the multi-body effects in associating mixtures can be handled by appreciating the importance of packing in the reference system. Importantly, we establish that the complex multi-body effects in the associating mixtures of different association geometries can be accurately determined if correct reference information is used. The present approach can elucidate the structure and thermodynamics of mixtures of patchy-solvent and sticky-solutes with size and interaction asymmetry as well as short-range ion-association phenomena in a dipolar solvent, cases where multi-body effects are potentially important.

In this work, we incorporate complete information from the hard-sphere reference fluid and present a modified expression for calculation of associative contribution to graph sums within the framework provided by Marshall-Chapman theory [3, 67]. This modified expression is based on the analysis of physical clusters in the hard sphere and their representation in terms of occupancy distribution around a distinguished solute in the reference fluid. These occupancy distributions were obtained from enhanced sampling methods for hard sphere systems at different densities. Analysis of a wide range of association and concentration regimes shows that our approach incorporating complete hard sphere information accurately captures the behavior for bonding states, and the prediction of the chemical potential contribution due to association is within $1 \kBT$ of the reference Monte Carlo simulation results.
3.5 Appendix

3.5.1 Expression for $Q^{(k)}$

$$Q^{(k)} = -\rho_k + \sum_{\gamma \subset \Gamma^{(k)}, \gamma \neq \emptyset} c^{(k)}_{\gamma} \sigma^{(k)}_{\Gamma^{(k)}-\gamma}$$  \hfill (3.31)

where $\Gamma^{(k)}$ is the set of all the sites on the species $k$, $\sigma^{(k)}_{\Gamma^{(k)}-\gamma}$ is the sum of the monomer density and the density of molecules at all the combinations of the sites from the set $\Gamma^{(k)} - \gamma$

$$\sigma^{(k)}_{\Gamma^{(k)}-\gamma} = \sum_{\alpha \subset \Gamma^{(k)}-\gamma} \rho^{(\alpha)}_k$$  \hfill (3.32)

with $\sigma^{(k)}_{0} = \rho^{(0)}_k$ and $\sigma^{(k)}_{\Gamma^{(k)}} = \rho_k$, and $c^{(k)}_{\gamma}$ is given by

$$c^{(k)}_{\gamma} = \frac{\partial \Delta c^{(0)}/V}{\partial \sigma^{(k)}_{\Gamma^{(k)}-\gamma}}$$  \hfill (3.33)

As an example, for a two site patchy solvent molecule with sites A and B, $\Gamma^{(p)} = \{A, B\}$

$$c^{(p)}_A = \frac{\partial \Delta c^{(0)}/V}{\partial \sigma^{(p)}_{\Gamma^{(p)}-A}}$$  \hfill (3.34)

the density parameter, $\sigma^{(p)}_{\Gamma^{(p)}-A} = \sigma^{(p)}_B$, will include the monomer density ($\rho^{(0)}_p$) and the density of patchy solvents bonded at the B site ($\rho^{(B)}_p$), i.e.

$$\sigma^{(p)}_{\Gamma^{(p)}-A} = \rho^{(0)}_p + \rho^{(B)}_p$$  \hfill (3.35)

defining $X^{(p)}_A$ and $X^{(p)}_B$ as the fraction of the solvent molecules not bonded at the site $A$ and site $B$ respectively, the density parameter can be obtained as

$$\sigma^{(p)}_{\Gamma^{(p)}-A} = \rho_p \cdot (X^{(p)}_A \cdot X^{(p)}_B) + \rho_p \cdot (X^{(p)}_A \cdot (1 - X^{(p)}_B))$$

$$= \rho_p \cdot X^{(p)}_A$$  \hfill (3.36)
using Eq. 6.24 and Eq. 3.36 we get

\[
Q^{(p)} = -\rho_p + \sum_{A \in \Gamma^{(p)}} c_A^{(p)} \sigma_{\Gamma^{(p)}-A}^{(p)} \\
= -\rho_p + \sum_{A \in \Gamma^{(p)}} c_A^{(p)} X_A^{(p)} \rho_p
\]  

(3.37)

For spherically symmetric solute, there is only one site, covering the whole molecule, which can either be bonded \(\rho_s^{(b)}\) or not bonded \(\rho_s^{(0)}\) i.e.

\[
\sigma_{\Gamma^{(s)}}^{(s)} = \rho_s = \rho_s^{(0)} + \rho_s^{(b)}.
\]  

(3.38)

Using Eq. 6.24 we get

\[
Q^{(s)} = -\rho_s + \frac{\rho_s^{(b)}}{\rho_s^{(0)}} \cdot \rho_s^{(0)} \\
= -\rho_s^{(0)}
\]  

(3.39)
Chapter 4

Asymmetric mixtures of patchy and spherically symmetric colloids

In this chapter we present a theory to predict the structure and thermodynamics of mixtures of colloids of different diameters, building on the previous chapter that considered mixtures with all particles constrained to have the same size. The patchy, solvent particles have short-range directional interactions, while the solute particles have short-range isotropic interactions. The hard-sphere mixture without any association site forms the reference fluid. An important ingredient within the multi-body association theory is the description of clustering of the reference solvent around the reference solute. Here we account for the physical, multi-body clusters of the reference solvent around the reference solute in terms of occupancy statistics in a defined observation volume. The occupancy probabilities are obtained from chapter 2 based on enhanced sampling simulations and also the statistical mechanical models developed in chapter 2 to estimate these probabilities with limited simulation data. Relative to an approach that describes only up to three-body correlations in the reference, incorporating the complete reference information better predicts the bonding state and thermodynamics of the physical solute for a wide range of system conditions. Importantly, analysis of the residual chemical potential of the infinitely dilute solute from molecular simulation and theory shows that whereas the chemical potential is somewhat insensitive to the description of the structure of the reference fluid the energetic and entropic contributions are not, with the results from the complete reference
approach being in better agreement with particle simulations.

4.1 Theory

4.1.1 Asymmetric mixtures with different association geometries

The focus of this chapter is asymmetric mixtures containing molecules with short range attractive interactions. The short range association potential is the same as that in previous chapter [54]: the solute molecule can associate with multiple solvent molecules isotropically and the patchy solvent has directional interactions. The total potential is a sum of hard sphere and association contributions

\[ u(r) = u_{HS}(r) + u_{AS}(r) \]  \hspace{1cm} (4.1)

The association potential for patchy-patchy \((p,p)\) and spherical-patchy \((s,p)\) particles is:

\[ u_{AB}^{(p,p)}(r) = \begin{cases} -\epsilon_{AB}^{(p,p)}, r < r_c \text{ and } \theta_A \leq \theta_{c}^{(A)} \text{ and } \theta_B \leq \theta_{c}^{(B)} \\ 0 \text{ otherwise} \end{cases} \]  \hspace{1cm} (4.2)

\[ u_{A}^{(s,p)}(r) = \begin{cases} -\epsilon_{A}^{(s,p)}, r < r_c \text{ and } \theta_A \leq \theta_{c}^{(A)} \\ 0 \text{ otherwise} \end{cases} \]  \hspace{1cm} (4.3)

where the subscripts \(A\) and \(B\) represent the type of site and \(\epsilon\) is the association energy; \(r\) is the distance between the particles; and \(\theta_A\) is the angle between the vector connecting the centers of two molecules and the vector connecting association site \(A\) to the center of that molecule (Fig. 4.1). The critical distance beyond which particles do not interact is \(r_c\) and \(\theta_{c}\) is the solid angle beyond which sites cannot bond. Fig. 4.1 shows examples of solute-solvent and solvent-solvent short range interaction geometries for different sizes of solute particles.
Figure 4.1: Association between solute and solvent (a) and solvent molecules (b). Different cases with solute larger (middle) and smaller (left) than solvent molecules are studied. $r$ is the center-to-center distance and $\theta_A$ and $\theta_B$ are the orientation of the attractive patches $A$ and $B$ relative to line connecting the centers. The solute (colored red) can only interact with patch $A$ (colored red) on solvent.

Since the solute can associate with multiple solvent molecules (Eq. 4.3), it is important to study the multi-body correlations that determine the packing of solvent particles around the solute in the reference fluid [54]. The difficulty in determining these interactions arises due to the limited knowledge in describing multi-body correlation functions for $n \geq 3$. But the volume integral of the multi-body correlation has a clear physical meaning in terms of average number of $n$-solvent clusters ($F^{(n)}$, Fig. 4.2). In particular, for the distinguished solute,

$$F^{(n)} = \frac{\rho_p^n}{n!} \int_v d\vec{r}_1 \cdots \int_v d\vec{r}_n g_{HS} (\vec{r}_1 \cdots \vec{r}_n|0)$$

$$= \sum_{m=n}^{n_{max}} C_n^m x_m,$$

where $\rho_p$ is the density of solvent particles, $x_m$ is the probability of observing exactly $m$ solvent particles in the observation volume of the solute ($v$) defined by the spherical region of radius $r_c$, $C_n^m (= m!/(m-n)! \cdot n!)$, and $g_{HS}(\vec{r}_1 \cdots \vec{r}_n|0)$ is the distribution function of the $n$-solvent particles around the solute at the center of the observation volume, indicated by ($\ldots |0$). $n_{max}$ is the maximum number of solvent molecules that can occupy the observation volume around the reference solute.

In Wertheim’s multi-density formalism [47, 48], the free energy due to association
Figure 4.2: Schematic of $F^{(3)}$ ($n = 3$ in Eq. 4.4), the average number of $n = 3$-solvent cluster ($n = 3$-mer) around a solute. All the coordination states in the hard sphere reference with at least $n = 3$ solvent molecules in the observation shell of the solute will contribute to this average. $x_m$ ($m \geq 3$) is the probability of observing exactly $m$-solvents in the observation volume around the solute. The bare probability $x_m$ is weighted by the binomial coefficient $C_n^m$ that gives the number of ways of constructing an $n$-solvent cluster from $m \geq n$ solvents in the observation shell. The region between the two concentric dashed circles of radii, $\bar{d}$ (average diameter) and $r_c > \bar{d}$, respectively, represents the bonding volume.

$(A^{AS})$ is expressed as

$$
\frac{A^{AS}}{V k_B T} = \sum \left( \rho_k \ln \frac{\rho_k^{(0)}}{\rho_k} + Q^{(k)} + \rho_k \right) - \frac{\Delta c^{(0)} V}{V}
$$

(4.5)

where $k_B$ is the Boltzmann constant, $T$ is the temperature, the summation is over the species ($k = s, p$), $\rho$ is the number density, $\rho^{(0)}$ is the monomer density, $Q^{(k)}$ is a factor that follows from Wertheim’s approach [47] (Chapter 3 Appendix 3.5.1). $\Delta c^{(0)}$ is the contribution to the graph sum due to association between the solvent-solvent ($p, p$) and solute-solvent ($s, p$) molecules, i.e.

$$
\Delta c^{(0)} = \Delta c_{pp}^{(0)} + \Delta c_{sp}^{(0)}
$$

(4.6)

Marshall and Chapman [3, 67] extended Wertheim’s theory beyond the single bonding condition to incorporate multi-body effects in a solution consisting of an isotropic solute and solvent with directional interactions. The contribution to free
energy due to association between solute and solvent molecules was obtained as

$$\frac{\Delta c^{(0)}_{sp}}{V} = \sum_{n=1}^{n_{\text{max}}} \frac{\Delta c^{(0)}_{n}}{V}$$

(4.7)

where the sum is over different coordination states of the solute and $\Delta c^{(0)}_{n}$ is given by:

$$\Delta c^{(0)}_{n} = \frac{\rho^{(0)}_p (\rho_p X^{(p)}_A)^n}{\Omega^{n+1} n!} \int d(1) \cdots d(n+1) g_{HS}(1 \cdots n+1) \cdot \prod_{k=2}^{n+1} (f^{(s,p)}_A(1,k)).$$

(4.8)

In Eq. 4.8, $\rho_p = \rho \cdot x^{(p)}$ is the density of solvent molecules obtained from the mole fraction of solvent ($x^{(p)}$) and the total density ($\rho$), $X^{(p)}_A$ is the fraction of solvent molecules not bonded at site $A$, $\Omega = 4\pi$ is the total number of orientations, $f^{(s,p)}_A(1,k) = (\exp(\varepsilon^{(s,p)}_A / k_B T) - 1)$ is the Mayer function for association between $p$ and $s$ molecules corresponding to potential in Eq. 4.3 and the integral is over all the orientations and positions of the $n + 1$ particles. By taking the average association strength and acceptable orientations out of the integral and fixing the solute at the origin, the above integral can be rewritten as

$$\frac{\Delta c^{(0)}_{n}}{V} = \rho^{(0)}_s (\rho_p X^{(p)}_A f^{(s,p)}_A \sqrt{KAA})^n \int_v d\vec{r}_1 \cdots \int_v d\vec{r}_n g_{HS}(\vec{r}_1 \cdots \vec{r}_n|0).$$

(4.9)

Marshall and Chapman [3, 67] approximated the integral in Eq. 4.9 as

$$\int_v d\vec{r}_1 \cdots \int_v d\vec{r}_n g_{HS}(\vec{r}_1 \cdots \vec{r}_n|0) \approx y_{HS}^{(n)}(d)\delta^{(n)} \Xi^{(n)},$$

(4.10)

where $\Xi^{(n)}$ is the partition function for an isolated cluster of $n$ solvent hard-spheres around a solute hard-sphere, $y_{HS}(d)$ is (pair) cavity correlation function at contact, and $\delta^{(n)}$ corrects the superposition of cavity correlation functions for three body interactions. We will hereafter refer to Eq. 4.10 as the Marshall-Chapman approximation (MCA).
As shown in the previous chapter [54], MCA fails for high densities and high association energies, conditions where multi-body interactions are important. But recognizing that the integral in Eq. 4.9 is related to \( F(n) \) (Eq. 4.4) we have [54]

\[
\frac{\Delta c_n^{(0)}}{V} = \rho_s^{(0)}(x^{(p)} X_A^{(p)} f^{(s,p)}_{A} \sqrt{\kappa_{AA}})^n F(n). \tag{4.11}
\]

It can be observed that all the multi-body correlation information is subsumed in \( F(n) \) which is obtained from the occupancy distribution \( \{x_m\} \). Finally, with the above information, and based on the Marshall-Chapman theory [67], the fraction of solute associated with \( n \) solvent molecules is

\[
X_n^{(s)} = \frac{(x^{(p)} X_A^{(p)} f^{(s,p)}_{A} \sqrt{\kappa_{AA}})^n F(n)}{1 + \sum_{n=1}^{n_{\text{max}}} (x^{(p)} X_A^{(p)} f^{(s,p)}_{A} \sqrt{\kappa_{AA}})^n F(n)}, \tag{4.12}
\]

and the fraction of solute not bonded to any solvent molecule is

\[
X_0^{(s)} = \frac{1}{1 + \sum_{n=1}^{n_{\text{max}}} (x^{(p)} X_A^{(p)} f^{(s,p)}_{A} \sqrt{\kappa_{AA}})^n F(n)}. \tag{4.13}
\]

Using these distributions for associating mixture, the average number of solvent associated with the solute is given by:

\[
n_{\text{avg}} = \sum_n n \cdot X_n^{(s)}, \tag{4.14}
\]

The fraction of solvent not bonded at site \( A \) and site \( B \) can be obtained by simultaneous solution of the following equations:

\[
X_A^{(p)} = \frac{1}{1 + \xi \kappa_{AB} f_{p}^{(p,p)} \rho_p X_A^{(p)} + \rho_s n_{\text{avg}} X_A^{(p)}}, \tag{4.15}
\]

\[
X_B^{(p)} = \frac{1}{1 + \xi \kappa_{AB} f_{p}^{(p,p)} \rho_p X_A^{(p)}}. \tag{4.16}
\]
where

\[ \begin{align*}
    \xi &= 4\pi d^2 (r_c - d) y_{HS}(d) \\
    \kappa_{AB} &= [1 - \cos(\theta_c)]^2 / 4 \\
    f_{AB}^{(p,p)} &= \exp(\varepsilon_{AB}^{(p,p)}/k_B T) - 1.
\end{align*} \]

### 4.2 Methods

To compare the theory results, we perform Monte-Carlo (MC) simulations for a range of systems. This section presents the details of the MC simulations for different associating mixtures. The Marshall-Chapman approximation (MCA) and the models developed for hard sphere distribution functions require isolated cluster probabilities; these were obtained in chapter 2 for different size ratios of the solute and solvent molecules.

#### 4.2.1 Monte Carlo Simulations

MC simulations were carried out for associating systems to compare the results of Marshall-Chapman theory using MCA and the complete reference approach. The associating mixture contains the patchy solvent particles and the isotropically interacting solute defined by the potentials given by Eq. 4.2 and Eq. 4.3, respectively. The solute diameter is \( d_s \) and solvent diameter is \( d_p \).

For the association contribution, the observation volume should be carefully defined to include only the first shell of the solvent molecules around the distinguished solute. In this work, the observation volume is defined by a critical radius \( r_c = 1.1\bar{d} \), where \( \bar{d} = (d_s + d_p)/2 \) is the closest distance of approach. For cases where \( d_s/d_p \geq 1.5 \), a cutoff of \( 1.1\bar{d} \) can include some of the second-shell solvent. To avoid this and focus
attention to the first observation shell, we set \( r_c = \bar{d} + 0.1d_p \) for these cases. In the associating system (Fig. 4.1 and Eqs. 4.2 and 4.3), the critical angles for interaction are \( \theta_c^{(A)} = \theta_c^{(B)} = 27^\circ \). The maximum angle for which a patch on the solvent molecule can form a single bond is computed using the law of cosines, and hence the critical angle needs to be altered when the solute size is smaller than the solvent. For a size ratio of \( d_s/d_p = 0.8 \), a critical angle \( \theta_c^{(A)} = \theta_c^{(B)} = 20^\circ \) was used to ensure single bonding condition for the \( A \) patch on the solvent molecules which can associate with the solute molecules. The table in Fig. 4.8 Appendix B gives the maximum \( \theta_c \) values for different size ratios.

For associating mixtures bonding distributions and average bonding numbers were studied for mixtures with different sizes and different association strengths for solute-solvent and solvent-solvent interactions. It was established in the previous chapter that the multi-body correlations become important at high association strengths and high densities [54], hence most of the comparisons are done for a packing fraction \( \eta = 0.42 \) and association energy \( \epsilon = 7k_BT \). Most of the analysis was done for the size ratios \( (d_s/d_p) \) in the range 0.8 – 1.2 to restrict the study of \( x_n \) to coordination numbers \( n \leq 20 \). Sample cases with the size ratio of \( d_s/d_p = 0.5 \) and \( d_s/d_p = 2.0 \) were also studied to show the applicability of the theory for large size asymmetry. The excess chemical potential of the coupling of the colloid with solvent was also calculated using thermodynamic integration of average binding energy of solute with solvent as a function of solute-solvent interactions, using the three-point Gauss Legendre quadrature technique [99]. For a symmetric mixture with no solvent-solvent interactions, energetic and entropic contributions for solute chemical potential were also studied at constant volume and temperature.

Concentration effects were also computed considering a total of 864 particles,
with varied number of solute particles. Due to the difference in size of the solute and solvent, the computations were performed keeping the packing fraction constant. Hence, the density of the system changed with respect to the concentration.

### 4.3 Results and discussions

In this section we present results for different associating mixtures. For asymmetric associating mixtures of solute and solvent molecules, we present the results within Marshall-Chapman formalism for our complete reference approach and the Marshall-Chapman approximation. We compare these results with Monte-Carlo simulations to investigate both size and concentration effects.

#### 4.3.1 Infinite Dilution

We first study an infinitely dilute solution and vary the size of solute with respect to a fixed size of solvent particles. In our complete reference theory, the reference fluid \( \{ x_n \} \) distribution is either computed directly from simulations (‘\( x_n \)-Simulation’ in Fig. 4.3) or from the 1-parameter model discussed in Sec. 2.1.4 chapter 2 (‘\( x_n \)-Modell’ in Fig. 4.3). Using \( \{ x_n \} \) we compute \( F^{(n)} \) (Eq. 4.4), and on that basis, the average number of bonds in the associating mixture using Eq. 4.11, Eq. 4.12 and Eq. 4.14. Fig. 4.3 shows the variation of average bonding numbers with size ratio of solute and solvent molecules for a density of 0.8 and association strength of \( 7 \, k_B T \).

As the size of the solute increases with respect to the size of the solvent, more solvent molecules can associate with the solute. With accurate information about the reference fluid \( \{ x_n \} \) (and hence \( F^{(n)} \) from direct simulations, the complete reference theory is able to capture this increase in bonding numbers quite accurately. Interestingly, even \( \{ x_n \} \) obtained using the 1-parameter model (Eq. 2.18) suffices for this
Figure 4.3 : Average bonding numbers $n_{avg}$ in associated mixtures for asymmetric cases with different relative size of solute molecules. Solute is infinitely dilute and density is $\rho d^3 = 0.8$. Symbols represent MC simulation values. ‘$x_n$-Simulation’ corresponds to the complete reference theory results with $\{x_n\}$ distribution computed directly from simulations for calculating $F^{(n)}$ (Eq. 4.4). ‘$x_n$-Model1’ corresponds to the use of 1-parameter model to compute $\{x_n\}$ in our theory. ‘MCA’ corresponds to the second order perturbation approximation used by Marshall-Chapman (Eq. 4.10).

range of size ratios, except for high size ratios. But note that the Marshall-Chapman approximation with only up to 3-body effects incorporated in the theory underestimates the average bonding numbers. These results emphasize the importance of multi-body interactions in describing the association correctly.

As noted in chapter 2 Sec. 2.1.4, the amount of surface exposure (or surface sites) is an important factor in determining the packing effects in the models. For the size ratios considered in Fig. 4.3, the maximum number of surface sites and hence the geometric effects in surface interactions are expected to be similar to the symmetric case, and not surprisingly, the agreement of bonding numbers between simulation and with the 1-parameter model for $x_n$ is very good. For extreme size ratios (Table. 4.1), a high error with the 1-parameter model is expected. This results because
of the disparity in surface sites for these ratios relative to the symmetric mixture within which the density independent geometric effects were obtained (Eq. 2.17). However, even for these extreme size ratios, with information for reference hard sphere distribution functions \( (x_n) \) from simulation, the complete reference theory is able to capture the average bonding numbers for these extreme size ratios quite well.

Table 4.1: Comparison of average bonding numbers \( (n_{avg}) \) of solute for extreme size ratios.

<table>
<thead>
<tr>
<th>( d_s/d_p )</th>
<th>MC</th>
<th>( x_n )-Simulation</th>
<th>( x_n )-Model1</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>3.61</td>
<td>3.55</td>
<td>4.50</td>
</tr>
<tr>
<td>2</td>
<td>15.84</td>
<td>15.04</td>
<td>17.66</td>
</tr>
</tbody>
</table>

4.3.2 Varying association strengths

To understand the effect of varying association strengths between solute-solvent and solvent-solvent particles, we studied a case with a fixed size ratio of \( d_s/d_p = 0.8 \) and for varying association strengths (Fig. 4.4).

As the strength of solute-solvent association is increased as compared to solvent-solvent interactions, multi-body effects become important. It was observed that higher deviations are observed with TPT2-based Marshall-Chapman approximation, especially for increasing strength of solute-solvent association. Importantly, excellent agreement with the complete reference theory is observed for all cases noted in the figure.
Figure 4.4: Variation of average bonding numbers \((n_{\text{avg}})\) with the relative strengths of solute-solvent and solvent-solvent association strengths. Left: solute-solvent association strength is varied with solvent-solvent association fixed at \(\epsilon(p,p) = 7k_B T\). Right: solvent-solvent association strength is varied with solute-solvent association fixed at \(\epsilon(s,p) = 7k_B T\). Solute is infinitely dilute and density is \(\rho d^3 = 0.8\). Rest of the representation is the same as Fig. 4.3.

### 4.3.3 Chemical potential and energy entropy contributions

Fig. 4.5 shows the chemical potential of the solute for two limiting cases: one where the solvent-solvent association is present and one where it is absent, for two size ratios. The results indicate that despite the large deviations in \(n_{\text{avg}}\) (Fig. 4.3) noted above, the deviations using the Marshall-Chapman approximation are not as high relative to the complete reference approach.

To better understand this result, we consider a symmetric system where there is no association between solvent particles. For this case, the partial molar energy is the energy of the system with solute-solvent association and there is no contribution for change in solvent-solvent association due to inclusion of an ideal solute at infinite dilution. We decompose the residual chemical potential of the solute \((\mu_s^{\text{asso}})\) into its energetic and entropic contributions [102, 103]:

\[
\mu_s^{\text{asso}} = \mu_s^{\text{energic}} + \mu_s^{\text{entropic}}
\]
Figure 4.5: Chemical potential for charging a solute molecule in a patchy solvent environment for different reduced densities and different size ratios. The solute is infinitely dilute and association energy for interactions between solute-solvent molecules is $7k_B T$. Solvent-solvent interaction energy is $7k_B T$ (left) and zero (right). Symbols represent simulation values, solid curves are complete reference theory results with $x_n$ from simulations and dotted curves corresponds to results with ‘MCA’.

\[
\beta \mu_{Asso} = \beta E_{Asso} - T \cdot \beta S_{Asso,V} \tag{4.17}
\]

where $E_{Asso} = \left( \frac{\partial \mu_{Asso}}{\partial T} \right)_{\rho_s, \rho_p}$ is the partial molar energy and $S_{Asso,V} = -\left( \frac{\partial \mu_{Asso}}{\partial T} \right)_{\rho_s, \rho_p}$ is the partial molar entropy contribution. The entropy and energy values can be obtained with MCA and complete reference approach based on the corresponding temperature derivatives of the chemical potential of solute.

Fig. 4.6 shows that energy and entropy contributions are not captured accurately by MCA, but the chemical potential is in relatively better agreement because of cancellation of the errors between the entropy and energy contributions. However, the complete reference approach correctly captures the energy, entropy, and the chemical potential. These results suggest that in comparing perturbation theories, it could be useful and prudent to study chemical potential and also its energy and entropy contributions.
4.3.4 Concentrated systems

We also study the variation of average bonding number of the solute for different concentration of the solute in the asymmetric mixtures. As the concentration of the solute increases, the system becomes limited in the number of solvent molecules that can bond to the solute molecules and hence TPT2 approximation used in MCA becomes more accurate. For low concentrations, multi-body correlations are important and hence deviations are observed with MCA. Fig. 4.7 shows the results for two different size ratios. The theory with the complete reference is able to capture the average bonding numbers for the whole concentration range.

4.4 Concluding discussions

We have studied asymmetric mixtures having strong short-range association between differently sized solute and solvent molecules. The solute molecules have isotropic interactions and the solvent molecules have directional interactions. Such systems are archetypes of colloidal mixtures that are being actively studied in designing materials.
Figure 4.7: Variation of average bonding number of solute ($n_{avg}$) with the concentration of solute for size ratio, $d_s/d_p$, 1.1 (left) and 0.8 (right). Note that to ensure the single bonding condition for solvent sites, the critical angle has been reduced to $\theta_c = 20^\circ$ for 0.8 size ratio.

from the nanoscale level. These systems can also describe the short range ion-solvation and ion-pairing effects in electrolyte systems which is another focus of our research.

The isotropic interactions of the solute can allow multiple solvent molecules to associate and hence multi-body effects become important for these systems. Previously [54], we discussed that the development of an accurate perturbation theory for these systems is hindered by the difficulty in obtaining the multi-body correlations in the reference system (typically hard sphere). We discussed the limitation of an approach based on obtaining the multi-body correlations for the hard sphere system in the gas phase and approximating the bulk solvent effect with a linear superposition of the pair correlation (together with a term to account for the three body correction). It was observed that this second order perturbation method fails at high association strengths and high densities. We introduced an approach to represent the multi-body clusters in terms of the occupancy distribution to accurately describe the packing in the hard sphere system. Excellent agreement with MC simulation for a range of con-
ditions of association and concentrations were obtained with this *complete reference* approach for the symmetric mixtures.

In this chapter, we have built upon the earlier work and study systems with size asymmetry. Our study shows that the multi-body correlations for the asymmetric hard sphere mixtures can be accurately studied in terms of occupancy distributions. With these accurate packing effects, our approach gives excellent agreement with MC simulation for the asymmetric associating mixtures. These occupancy distributions were obtained by particle simulations. We validate this complete reference theory (using particle simulation results for the reference distribution) against several simulations. A critical test was in analyzing the energy and entropy contributions to the chemical potential of the solute. For a system where solvent-solvent association is not present, such a decomposition of chemical potential in energy and entropy contributions with complete reference theory showed excellent agreement with MC simulations. The apparently reasonable agreement of the second order perturbation approach is shown to arise from the balancing of errors in the energy and entropy contributions. This important finding suggests the need to study different properties while validating perturbative theories for fluids. This present framework can prove useful in modeling real solutions where concentration of solute is low and its size is different from the solvent molecules.

4.5 Appendix

To find the maximum number of solvent molecules that can occupy the observation volume for different sizes of th solute molecules, we use spherical code [104, 105].
4.5.1 Spherical Code

The spherical code provides information to place \( n \) points optimally across a sphere. It gives the optimal angle between the points, considering the center of the sphere as the origin. This is extended to place solvent particles across the solute surface, point of contact between the sphere serving as the optimizing points. The angle between the two contact points, \( \theta \), is determined as given in the fig. 4.8. The number of solvent molecules that can be tightly packed is obtained from the data [104]. The sphere onto which the points are optimally placed is an imaginary sphere which includes the critical radius as shown in the dashed lines. It is to be noted that this is still a theoretical estimate for contact packing on the imaginary larger sphere, and due to higher freedom of packing in our case, coordination states can be marginally higher for very large size ratios, \( d_s/d_p \geq 5 \). Table in fig. 4.8 also gives the maximum angle for which single bonding condition holds for a given size ratio (\( \theta_{c,max} \)) and specified critical distance (\( r_c \)).
\[
\begin{array}{cccc}
\frac{d_s}{d_p} & r_c & n^{\text{max}} & \theta_{c,\text{max}} \\
0.5 & 0.80 & 8 & 17.64 \\
0.8 & 0.99 & 12 & 23.83 \\
0.9 & 1.05 & 12 & 25.51 \\
1.0 & 1.10 & 14 & 27.04 \\
1.1 & 1.16 & 16 & 28.44 \\
1.2 & 1.21 & 18 & 29.73 \\
2.0 & 1.55 & 31 & 40.18 \\
3.0 & 2.10 & 58 & 45.58 \\
4.0 & 2.60 & 89 & 50.28 \\
5.0 & 3.10 & 128 & 53.75 \\
\end{array}
\]

Figure 4.8 : Left: Maximum number of coordination states possible and their respective maximum permissible patch angle for different size ratios \(\frac{d_s}{d_p}\). Right: Diagram to compute the angle between two solvent particles to get the maximum number of coordination states
Chapter 5

Quasichemical theory and the description of associating fluids relative to a reference: Multiple bonding of a single site solute

The “complete reference” approach introduced in the previous chapters motivated us to reconsider the problem of modeling associating fluids entirely within the quasichemical (QC) organization of the potential distribution theorem (PDT) [82–84]. As has been emphasized earlier [82, 83], the potential distribution theorem provides a general basis for the theory of solutions and a tool to develop physically motivated approximate models of solution thermodynamics. The potential distribution theorem presents a local partition function to be evaluated for the excess chemical potential of the defined component. Importantly, this partition function can be recast as a summation over physical clusters within the defined observation volume, leading to the quasichemical organization of the potential distribution theorem. The equilibrium constant for forming the clusters then plays an important role in the theory. While the calculation of the equilibrium constant is not trivial for most problems of interest, a definite virtue of the approach is its rather clear physical underpinnings. Importantly, the many-body aspect of clustering is built into the very foundations of the theory.

It is helpful to contrast the QC/PDT approach with the Wertheim/SAFT approach. The latter rests on an expansion of the grand-potential of the entire system in terms of physically bonded components, but to discover the physically bonded
clusters requires use of subtle graph-theoretic ideas. A virtue of the Wertheim/SAFT approach is that it makes available the excess Helmholtz free energy of the system, making its use in applications easier. But, as noted above, incorporating many-body correlations in Wertheim/SAFT is not as transparent as in QC/PDT. For problems requiring attention to many-body correlations, QC/PDT may helpfully complement Wertheim/SAFT. With this broader goal, in this chapter we present the key steps for describing associating fluids within QC/PDT.

In this chapter we explore a range of bonding configurations from a solute that can bond only once, to a solute that can bond multiple solvents but only on one-hemisphere of its surface, i.e. a Janus particle [19, 20], and to a solute with a sticky patch that covers its entire surface. We derive an expression for the chemical potential of an associating solute in a solvent relative to the value in a reference fluid using the quasichemical organization of the potential distribution theorem. The fraction of times the solute is not associated with the solvent, the monomer fraction, is expressed in terms of (a) the statistics of occupancy of the solvent around the solute in the reference fluid and (b) the Widom factors that arise because of turning on solute-solvent association. Assuming pair-additivity, we expand the Widom factor into a product of Mayer $f$-functions and the resulting expression is rearranged to reveal a form of the monomer fraction that is analogous to that used within the statistical associating fluid theory (SAFT). The present formulation avoids all graph-theoretic arguments and provides a fresh, more intuitive, perspective on Wertheim’s theory and SAFT. Importantly, multi-body effects are transparently incorporated into the very foundations of the theory. Quasichemical theory leads to the identification of the occupancy of a patch conditional on the total occupancy of the observation volume, all in the reference fluid, as an important quantity within the theory. We suggest
a Monte Carlo procedure to calculate this for general cases and provide analytical models for limiting cases of a patch that can bond only once or a patch that covers the entire surface of the solute. For simplicity, in the present chapter we consider a system where only solute-solvent bonding is allowed. Studies in the next chapter will ease this requirement.

The rest of the chapter is organized as follows. In Section 5.1 we sketch the quasichemical approach and then develop the idea of association relative to a non-associating reference. In Section 5.2 we present the methods, and in Section 5.3 we present the results from several model systems.

5.1 Quasichemical theory

The excess chemical potential, $\mu^{ex}$, of a solute in a solvent is that part of the Gibbs free energy of solvation that arises due to intermolecular interactions; $\mu^{ex}$ is defined relative to the ideal gas at the same density and temperature. Formally, $\mu^{ex}$ is given by the potential distribution relation

$$\beta \mu^{ex} = \ln \int e^{\beta \varepsilon} P(\varepsilon) d\varepsilon,$$

(5.1)

where $P(\varepsilon)$ is the probability density distribution of the solute-solvent binding energies, and as usual, $\beta = 1/k_B T$.

A direct application of Eq. 5.1 is almost never satisfactory because the high-\(\varepsilon\) tail of the probability distribution, which reflects short-range repulsive interactions, is usually difficult to characterize [106]. In the quasichemical (QC) approach [82–84, 106], we separate the short-range and long-range contributions and include the contribution from the short-range solute-solvent interactions within a chemical equilibrium framework. To this end we demarcate a domain, the observation volume or
inner-shell, around the solute (Fig. 5.1). The observation volume is usually restricted
to the first solvation shell of the solute. The probability of observing \( n \)-solvent par-
ticles within the observation volume is denoted as \( x_n \). The reversible work to empty
the observation volume is \(-\beta^{-1} \ln x_0\). The solute with an empty observation shell,
the conditioned solute, interacts with the bulk fluid solely through long-range inter-
actions. In particular, for a sufficiently large inner-shell radius, the solute-solvent
binding energy of the conditioned solute is Gaussian [107]. To complete the ther-
modynamic description of solvation, we also need to account for the free energy to
create a bare cavity of the size and shape of the observation volume. This free energy
is denoted as \(-\beta^{-1} \ln p_0\), where \( p_0 \) is the probability to form an empty cavity in the
bulk fluid. Thus the excess chemical potential is written as

\[
\beta \mu^{ex} = \ln x_0 - \ln p_0 + \ln \langle e^{\beta \varepsilon |n = 0} \rangle.
\]

(5.2)

Fig. 5.1 provides a schematic of the quasichemical organization. As discussed next,
the appellation quasichemical derives from the chemical organization of \( x_0 \) and \( p_0 \).

Consider the chemical equilibrium between the solute (\( \sigma \)) and solvent (\( p \)) to form
an \( n \)-solvent cluster,

\[
\sigma + n \cdot p \rightleftharpoons \sigma p_n
\]
The usual products-over-reactants equilibrium constant is given by \( K_n = \frac{x_n}{x_0 \rho_p^n} \), where \( \rho_p \) is the density of the solvent. A mass balance \([70, 82, 83]\) then gives

\[
\ln x_0 = -\ln \left[ 1 + \sum_{n \geq 1} K_n \rho_p^n \right].
\] (5.3)

A similar equation can be written for \( p_0 \),

\[
\ln p_0 = -\ln \left[ 1 + \sum_{n \geq 1} \tilde{K}_n \rho_p^n \right].
\] (5.4)

where \( \tilde{K}_n \) is the equilibrium constant for the association between a bare cavity and \( n \)-solvent particles.

\( K_n \) is related to configurational integrals by

\[
K_n = \frac{(e^{\beta \mu_p^c})^n}{n!} e^{-\beta w(R^n)} \int_v d\vec{r}_1 \ldots \int_v d\vec{r}_n e^{-\beta U_{\sigma p n}(R^n)},
\] (5.5)

where \( v \) is the volume of the inner-shell, \( U_{\sigma p n}(R^n) \) is the potential energy of the solute-\( n \)-solvent cluster, \( \mu_p^c \) is the excess chemical potential of the solvent, and \( e^{-\beta w(R^n)} = \langle e^{-\beta \phi(R^n; \beta)} | R^n \rangle_0 \) is the average of the interaction free energy, \( \phi(R^n; \beta) \), between the cluster and the bulk. Here \( \langle \ldots | R^n \rangle_0 \) indicates averaging over the normalized probability density for cluster conformations \( R^n \) in the absence of interactions with the rest of the medium.

### 5.1.1 Quasichemical perspective of associating fluids

Associating fluids are characterized by short range, directional interactions. In SAFT and in Wertheim’s theory \([45, 46, 50, 51, 108]\), we assume the availability of a well-characterized reference and the role of association is considered relative to the reference. For definiteness, we assume the reference is a hard-sphere fluid. The above quasichemical organization can be used for the reference as well, and we distinguish all the reference properties with the subscript \( r \).
We first focus on $x_0$ and rewrite this in terms of the properties of the reference. From Eqs. 5.3 and 5.5 and the corresponding relations for the reference, we can re-express the chemistry contribution relative to the reference as

$$\ln x_0 = - \ln \left[ 1 + \sum_{n \geq 1} \frac{K_n}{K_{n,r}} K_{n,r} \rho_p^n \right] = \ln x_{0,r} = \ln x_{0,r} - \ln \left[ x_{0,r} + \sum_{n \geq 1} \frac{K_n}{K_{n,r}} x_{n,r} \right]$$

(5.6)

Let us next examine the ratio of the equilibrium constants. We have

$$\frac{K_n}{K_{n,r}} = e^{n \cdot \beta \Delta \mu_p^{ex}} \cdot e^{\beta \Delta \mu^{ex}_p} \cdot \langle e^{-\beta \Delta U_{\sigma p n}(R^n)} \rangle_{R^n}$$

(5.7)

where $\Delta U_{\sigma p n}(R^n)$ is the potential energy of the $n$-solvent plus solute cluster in the physical system relative to the reference. Likewise, $\Delta \mu_p^{ex}$ and $\Delta \mu^{ex}$ are the corresponding properties relative to the reference. The factor $e^{n \cdot \beta \Delta \mu_p^{ex}} \cdot e^{\beta \Delta \mu^{ex}_p}$ accounts for the entropic effects in sequestering the solvent within the observation volume above the effect in the reference system. The factor $\langle e^{-\beta \Delta U_{\sigma p n}(R^n)} \rangle_{R^n}$ are Widom-factors, but now relative to a reference and in the volume $v$. The above relations are exact within classical statistical mechanics for any arbitrary forcefield. Appendix (Section 5.5) provides a concise derivation of Eq. 5.7.

The potential energy $\Delta U_{\sigma p n}$ can be partitioned into solvent-solvent ($\Delta U_{pp}$) and solute-solvent ($\Delta U_{\sigma p n}$) contributions. The presence of solvent-solvent short-range interaction can be incorporated by factoring the Widom factor as $\langle e^{-\beta \Delta U_{pp}} \rangle_{R^n} \cdot \langle e^{-\beta \Delta U_{\sigma p n}(R^n)} \rangle_{R^n} + \langle e^{-\beta \Delta U_{\sigma p n}} \rangle_{R^n r+pp}$, where $\langle \ldots \rangle_{r+pp}$ indicates averaging over the case where solute-solvent interactions are reference interactions and solvent-solvent interactions including short-range bonding. (There are other ways to incorporate solvent-solvent association effects, but we will not consider those in the present chapter.)

We consider solvent bonding configurations such that solvent-solvent bonding within the solute’s inner-shell is avoided. In this case, $\langle e^{-\beta \Delta U_{pp}} \rangle_{R^n} = 1$ and
\( \langle e^{-\beta \Delta U_{\sigma p}} | R^n \rangle_{r+pp} = \langle e^{-\beta \Delta U_{\sigma p}} | R^n \rangle_r \). Further, for a pair additive forcefield, \( \Delta U_{\sigma p}(R^n) = \sum_{i=1}^n \Delta U_{\sigma p} \). Thus

\[ e^{-\beta \Delta U_{\sigma p}(R^n)} = \prod_{i=1}^n (1 + f_{\sigma i}) = 1 + \sum_i f_{\sigma i} + \sum_{1 \leq i < j \leq n} f_{\sigma i} f_{\sigma j} + \ldots, \quad (5.8) \]

where \( f_{\sigma i} = e^{-\beta \Delta U_{\sigma i}} - 1 \) is the Mayer \( f \)-function for association between the solute and the \( i \)th solvent within the observation volume. Each term in the above expansion is a contribution due to association when one, two, \ldots, \( n \) solvent particles bond with the solute, given that \( n \) solvent particles are in the inner shell of the solute. As is typically assumed in SAFT and Wertheim’s approach, we assume the association strength is the same for all the solvent-solute pairs. The association potential \[109\] for the solute-solvent pair \((\sigma, p)\) is given by:

\[ \Delta u_{AB}^{\sigma p}(r) = \begin{cases} -\epsilon, & r < r_c \text{ and } \theta_A \leq \theta_{c,\sigma}^{(A)} \text{ and } \theta_B \leq \theta_{c,p}^{(B)} \\ 0, & \text{otherwise} \end{cases} \quad (5.9) \]

where the superscripts \( A \) and \( B \) represent the type of site on, respectively, the solute and the solvent, and \( \epsilon \) is the association energy; \( f_{\sigma} = e^{-\beta \epsilon} - 1 \) is the corresponding Mayer \( f \) function. \( r \) is the distance between the particles and \( \theta_A \) is the angle between the vector connecting the centers of two molecules and the vector connecting association site \( A \) to the center of that molecule (Fig. 5.2). The critical distance beyond which particles do not interact is \( r_c \). The angular extents of the patch for the solute and the solvent molecules are, respectively, \( \theta_{c,\sigma}^{(A)} \) and \( \theta_{c,p}^{(B)} \); if the inter-particle vector falls outside a patch, the particles cannot bond. The angular span of the patch \( \theta_{c,\sigma}^{(A)} \) on the solute molecule determines whether the solute can bond one or more solvent particles (Fig. 5.2).
Denoting the Mayer $f$-functions as $f_\sigma$, we thus find

$$
\langle e^{-\beta U_{\text{exp}}(R^n)}|R^n\rangle_r = 1 + \sum_{1 \leq i \leq n} \langle f_\sigma|R^n\rangle_r + \sum_{1 \leq i < j \leq n} \langle f^2_\sigma|R^n\rangle_r + \ldots \quad (5.10)
$$

Consider the term $\langle f_\sigma|R^n\rangle_r$. This is the average Mayer $f$-function for a single solvent particle bonded with the solute. There are $n \geq 1$-solvent particles in the observation volume, leading to the summation $\sum_{1 \leq i \leq n}$. Now, consider the term $\sum_{1 \leq i < j \leq n} \langle f^2_\sigma|R^n\rangle_r$, here $n \geq 2$ particles are in the inner shell of the solute ($\sigma$). The attractive patch on the solute covers only part of the solute, hence for a given $i^{th}$ bonding state of the solute represented by the $(i+1)^{th}$ term in the above summation, there are $(i \leq k \leq n)$ choices of particles to occupy the bonding patch (solid bond angle) on the solute. It proves helpful to codify the combinatorics by means of an indicator function. Specifically, we define $\theta(k,n)$ as an indicator function which is
equal to 1 when exactly $k$ particles are over the patch and zero otherwise.

$$
\theta(k, n) = \begin{cases} 
1, & \text{if exactly } k \leq n \text{ solvent occupy the bonding patch} \\
0, & \text{otherwise}
\end{cases}
$$

(5.11)

With this definition we find that

$$
\sum_{1 \leq i < j \leq n} \langle f_{\sigma i} f_{\sigma j} \rangle_r = \sum_{2 \leq k \leq n} \langle f_{\sigma}^2 \cdot \theta(k, n)|R^n\rangle_r \cdot \binom{k}{2}
$$

(5.12)

Physically, $f_{\sigma}^2$ can have a non-zero contribution only when at least two particles are above the bonding patch. Of the $k$ particles above the patch, we can choose any two in $kC_2$ ways to bond with the patch. We can rewrite the right hand side of Eq. 5.12 as

$$
\sum_{2 \leq k \leq n} \frac{\langle f_{\sigma}^2 \cdot \theta(k, n)|R^n\rangle_r \cdot \langle \theta(k, n)|R^n\rangle_r \cdot \binom{k}{2}}{\langle \theta(k, n)|R^n\rangle_r} = \\
\sum_{2 \leq k \leq n} \langle f_{\sigma}^2[k \cdot R^n]_r \cdot \langle \theta(k, n)|R^n\rangle_r \cdot \binom{k}{2}
$$

(5.13)

where $\langle f_{\sigma}^2[k \cdot R^n]\rangle_r$ is the average given that $n$ particles are in the inner shell and exactly $k(\geq 2)$ are positioned over the bonding patch of the solute. $\langle \theta(k, n)|R^n\rangle_r$ is the probability that given $n$ molecules in the spherical shell, exactly $k$ molecules are in the patch region. In deriving the last term in Eq. 5.13 we have used the rule-of-averages [82–84], and $\langle \ldots |k \cdot R^n\rangle_r$ indicates that (a) $n$-solvent particles are in the inner shell and (b) $k$ of the $n$ solvent particles are over the bonding patch. The other terms in the expansion can be given a similar meaning. For any bonding state $i$, when $k(\geq i)$ solvent molecules are present in the patch region, there are $\binom{k}{i}$ ways to choose exactly $i$ from the $k$ molecules. When the association strength is the same for all the solute-solvent pairs, as in the usual cases in Wertheim/SAFT, the solvent on the
solute patch bonds independently of the bonding state of the other solvent particles, we find

\[ \langle f^i_\sigma | R^n \rangle_r = \bar{f}^i_\sigma \cdot \kappa_p^i, \]  

(5.14)

where \( \kappa_p = \frac{1 - \cos(\theta_{c,p})}{2} \) is the probability that the solvent molecule is oriented such that it can bond with the solute and \( \bar{f} \) accounts for averaging over the radial coordinate. For a square-well potential (Eq. 5.9), we simply have \( f = \bar{f} = e^{-\beta \varepsilon} - 1 \).

Putting all of the above together, we have

\[ \langle e^{-\beta \Delta U_{\sigma pn}} | R^n \rangle_r = 1 + \sum_{1 \leq i \leq n} \bar{f}^i_\sigma \kappa_p^i \sum_{i \leq k \leq n} \binom{k}{i} \cdot \Theta(k|n) \]  

(5.15)

or

\[ \langle e^{-\beta \Delta U_{\sigma pn}} | R^n \rangle_r = 1 + \sum_{1 \leq i \leq n} \bar{f}^i_\sigma \cdot \kappa_p^i \cdot Q(i|n) \]  

(5.16)

where

\[ Q(i|n) = \sum_{i \leq k \leq n} \binom{k}{i} \cdot \Theta(k|n) \]  

(5.17)

The factor \( Q(i|n) \) is the average that given \( n \)-solvent particles in the inner-shell, at least \( i \leq n \) occupy the patch region, and for the occupancy of \( k \geq i \) over the patch region, weights corresponding to choosing \( i \) out of \( k \) molecules are applied to the exact probabilities \( \Theta(k|n) \). Fig. 5.3 shows an example of average factors \( Q(2|3) \) for a Janus particle.

Going back to Eq. 5.7, we provisionally assume that the surface term is also pair-decomposable, with each pair-wise contribution the same. (We emphasize that pair decomposability is assumed for a free energy rather than an interaction potential, but this assumption can be relaxed.) Thus, provisionally we set \( \beta \Delta w(R^n) = n \cdot \beta \Delta w \).

For convenience we write \( \xi_p = \exp(\beta \mu_{p}^{ex}) \exp(\beta \Delta w) \).
\[ Q(2\mid 3) = C_2^2 \cdot \Theta(2\mid 3) + C_3^2 \cdot \Theta(3\mid 3) \]

Figure 5.3: Average factors \((Q(2\mid 3))\) of observing at least two molecules in the patch region for a Janus particle, when there are three molecules in the observation shell.

Thus we finally obtain

\[
\frac{K_n}{K_{n,r}} = \xi^n_p \cdot \left[ 1 + \sum_{1 \leq i \leq n} \bar{f}_\sigma^i \cdot \kappa^i_p \cdot Q(i\mid n) \right]
\]  
(5.18)

Substituting the above ratio in Eq. 5.6, we find

\[
\ln x_0 = \ln x_{0,r} - \ln \left[ x_{0,r} + \sum_{n \geq 1} \xi^n_p \cdot \left[ 1 + \sum_{1 \leq i \leq n} \bar{f}_\sigma^i \cdot \kappa^i_p \cdot Q(i\mid n) \right] \cdot x_{n,r} \right]
\]

\[
= \ln x_{0,r} + \ln X_\sigma .
\]  
(5.19)

The physical meaning of the above equation is the following. The chemical work (Fig. 5.1) is composed in two steps: (1) the free energy \(\ln x_{0,r}\) to populate the observation shell with reference solvent particles, and (2) the free energy \(\ln X_\sigma\) to turn on solute-solvent and solvent-solvent association. Eq. 5.19 is the principal contribution of this work.

We can pursue a similar development for the packing contribution (Fig. 5.1). The final form of the association contribution to the excess chemical potential of the solute is thus

\[
\mu^\text{ex}_{\text{asso}} = \ln \frac{x_0}{x_{0,r}} - \ln \frac{p_0}{p_{0,r}}
\]

\[
= \ln X_\sigma - \ln P_\sigma .
\]  
(5.20)
where the \( \ln P_{\sigma} \) term arises solely from association contribution to solvent reorganization.

Given the ratio of the equilibrium constants \((K_n/K_{n,r})\) and \(X_{\sigma}\), the occupancy distribution of solvent molecules around the associating solute is

\[
x_n = K_n \cdot \rho_p^n \cdot x_0
\]

\[
= \frac{K_n}{K_{n,r}} \cdot x_{n,r} \cdot X_{\sigma}
\]  

(5.21)

The bonding distribution can be obtained from this occupancy distribution using standard rules of probability

\[
X_i = \sum_{n \geq i} x_n \cdot P(X_i|n), \ \forall \ n \geq 0,
\]

(5.22)

where \( P(X_i|n) \) is the conditional probability of having \( i \) bonded solvents when \( n \) solvent molecules are present in the observation volume. Note that

\[
\sum_{i \leq n} P(X_i|n) = 1, \ \forall \ n \geq 0
\]

(5.23)

### 5.1.2 Single site solute

To maximize clarity and simplify the analysis of the association contribution, in this article we consider the case of an infinitely dilute solute in a solvent which can not associate with other solvent molecules, i.e. only solute-solvent association is allowed. For this case \( \xi_p = 1 \); please note that there will also be some contribution to the chemical potential of the solvent due to solute-solvent association, but for an infinitely dilute case this can be neglected. The equilibrium ratio simplifies to

\[
\frac{K_n}{K_{n,r}} = \left[ 1 + \sum_{1 \leq i \leq n} \bar{f}_i^\sigma \cdot \kappa_p^i \cdot Q(i|n) \right].
\]

(5.24)

For this system, \( X_{\sigma} \) is equal to \( X_0 \), the fraction of times the solute is not bonded, i.e. the monomer fraction, a quantity that plays a central role in Wertheim/SAFT.
the chemical contribution, expanding and rearranging the order of summation in the second term on the right hand side of Eq. 5.19, we have
\[
x_{0,r} + \sum_{n \geq 1} \left[ 1 + \sum_{1 \leq i \leq n} \bar{f}^i_s \cdot \kappa^i_p \cdot Q(i|n) \right] \cdot x_{n,r} = x_{0,r} + \sum_{n \geq 1} x_{n,r} + \sum_{i \geq 1} \bar{f}^i_s \cdot \kappa^i_p \cdot \left[ \sum_{n \geq i} Q(i|n) \cdot x_{n,r} \right]
\]

Eq. 5.19 simplifies to:
\[
\ln x_0 = \ln x_{0,r} - \ln \left[ 1 + \sum_{i \geq 1} \bar{f}^i_s \cdot \kappa^i_p \cdot \left[ \sum_{n \geq i} Q(i|n) \cdot x_{n,r} \right] \right] = \ln x_{0,r} + \ln X_0
\]

\[\text{(5.26)}\]

Note that the summation \(\sum_{n \geq i} Q(i|n) \cdot x_{n,r}\) contains all of the multi-body information in the reference fluid for a given patch geometry of the solute, at the density of the solution. This approach of representing the multi-body information can also be incorporated within SAFT and Wertheim’s approach [54] for different patch geometries.

Eqs. 5.21 and 5.22 can be used to obtain the occupancy and bonding distributions, respectively, with \(P(X_i|n)\) given by
\[
P(X_i|n) = \frac{\bar{f}^i_s \cdot \kappa^i_p \cdot Q(i|n)}{K_n/K_{n,r}}, \quad \text{(5.27)}
\]

the bonded fractions in Eq. 5.22 are
\[
X_i = \bar{f}^i_s \cdot \kappa^i_p \cdot X_0 \left[ \sum_{n \geq i} Q(i|n) \cdot x_{n,r} \right]
\]

\[\text{(5.28)}\]

As there is no association between the solvent molecules, the excess chemical potential of the solute due to association is reduced to
\[
\mu_{\text{asso}}^{\text{ex}} = \ln X_0
\]

\[\text{(5.29)}\]
We consider several cases of solute patch geometry to test and illustrate the generality of the present approach. Please note that as the patch size increases, as illustrated by Fig. 5.2, we should expect multi-body interactions to become more important, making the analysis of association interactions more challenging.

5.2 Methods

5.2.1 Monte Carlo Simulations

Monte Carlo simulations were carried out for the reference hard sphere systems and associating systems to validate the theory. The associating system contains a single solute and 255 solvent particles [54]. Solute-solvent association is allowed, but the solvent-solvent association is absent. The system was equilibrated for 1 million steps with translational factors chosen to yield an acceptance rate of 0.3, and data was collected every 100 sweeps, where a sweep is an attempted move of all the particles in the system. Analysis was carried out for different densities. As discussed before [54], we use ensemble reweighting [91] to map $\{x_n\}$.

For associating systems, bonding $(X_n)$ and occupancy $(x_n)$ distributions were studied for a range of critical angles for the solute and solvent molecules. The inner-shell radius (Fig. 5.1) is $r_c = 1.1d$, where $d$ is the diameter of the solute and solvent molecules. Since we are only exploring solute-solvent association in this work, from here onwards for notational simplicity we dispense with the super-script (A or B) that classifies the patch according to its type. For association, Table 5.1 gives the different solute patch sizes $(\theta_{c,\sigma})$ along with the corresponding maximum bonding numbers $(N_{\text{max}})$, studied in this work.

For most systems, a single bonding condition i.e. $\theta_{c,p} = 27^\circ$ was used for the
Table 5.1: Patch size of the solute (θ_{c,σ}) studied in the present work and the corresponding maximum bonding number (N^{max}).

<table>
<thead>
<tr>
<th>θ_{c,σ}</th>
<th>27°</th>
<th>35°</th>
<th>40°</th>
<th>50°</th>
<th>60°</th>
<th>90°</th>
<th>180°</th>
</tr>
</thead>
<tbody>
<tr>
<td>N^{max}</td>
<td>1</td>
<td>2</td>
<td>3</td>
<td>4</td>
<td>5</td>
<td>7</td>
<td>12</td>
</tr>
</tbody>
</table>

Some cases with the same critical angle for the solute and solvent molecules, i.e. θ_{c,σ} = θ_{c,p}, were studied to compare QC results with the TPT2 framework developed earlier by Marshall et al. [63]. For the spherically symmetric solute (θ_{c,σ} = 180°), the excess chemical potential of coupling the solute with solvent was also calculated using thermodynamic integration using a three-point Gauss Legendre quadrature rule [54, 99]. We analyzed cases of different densities and different association strengths between the solute and solvent molecules.

5.2.2 Calculation of Θ(k|n)

Recall that Θ(k|n) = ⟨θ(k, n)|R^n⟩_r is the probability that for n-solvent particles in the spherical inner-shell, exactly k of those occupy the bonding patch and are available to bond with the solute. For a defined solute patch geometry and occupancy n, we first obtain a viable n-solvent structure by adapting a method that we formerly used to compute the n-solvent cluster integral [54]. Then we generate new configurations by a Monte Carlo procedure. The Monte Carlo moves comprise a radial displacement that is restricted to be within [d, r_c] and an orientational move over the surface of the sphere. The latter is performed by first picking at random one of three orthogonal axes, then choosing at random an angle by which to move around that axis. The maximum angular move is adjusted to target 30 percent acceptance. After every 100th sweep, we analyze the configuration to compose Θ(k|n). We discretize the spherical
polar coordinates $\cos \theta \in [-1, 1]$ and $\phi \in [0, 2\pi]$ into a grid of dimension $400 \times 8000$. Then we sweep through the grid treating each grid site as a candidate direction for the bonding patch (Fig. 5.2). As we sweep through the grid sites, we collect statistics on how many of the $n$ particles in the cluster occupy the patch. From this information, we construct $\Theta(k|n)$. The factors $Q(i|n)$ are obtained from the values of $\Theta(k|n)$ by applying appropriate combinatorial weights as given by Eq.5.17.

5.3 Results and Discussions

As discussed above, the present approach is general and can be applied to any geometry of the patch on the solute molecule. The factors $Q(i|n)$ discussed above play an important role in the theory. As we will also show below, a simple representation of $Q(i|n)$ can be obtained for the solute patch geometries that allow the separation of orientation dependence from occupancy, as happens for a patch that can bond only once or a spherically symmetric patch. For all other cases, we need to explicitly calculate the probabilities $\Theta(k|n)$ to obtain $Q(i|n)$. Appendix 5.5.2 gives the values of $\Theta(k|n)$, using which $Q(i|n)$ can be calculated, for different patch geometries studied in this work. Throughout, we compare our results with Monte Carlo simulations, and where possible, with available SAFT models.

5.3.1 Patch geometries for the solute

We first consider a case where the solute can bond between 2 to 7 particles (Table 5.1), i.e. $\theta_{c,\sigma} \in [35, 90]$, and the solvent bonds only once, $\theta_{(c,p)} = 27^\circ$. Fig. 5.4 (Left panel) shows the occupancy distribution for different patch geometries of the solute for a reduced density of 0.8. Observe that when the patch size is increased from $35^\circ$ to $90^\circ$, the distribution moves towards higher occupancy states. The hard sphere distribution
Figure 5.4: Left panel: Comparison of the occupancy distribution for different patch geometries on the solute. The hard sphere reference distribution is also shown using black dashed line. Right panel: Average occupancy for an associating solute for a range of patch geometries and for different reduced densities. The solvent molecules can bond only once to the solute molecule ($\theta_{c,p} = 27^\circ$) and $\epsilon = 7k_B T$. Solid lines are QC predictions and symbols are Monte Carlo simulation results.

Fig. 5.4 (Right panel), shows the average occupancy for a range of patch sizes on the solute and for different reduced densities of the solvent. We find that the QC based approach is able to capture accurately the average occupancy for the entire range of densities.

Fig. 5.5 shows the bonding distribution for the solute patch sizes of 35° to 90°. The QC theory is able to describe adequately the bonding distribution for all these patch sizes. Deviations for the highest bonded state were observed and are ultimately traced to numerical limitations in estimating $Q(i|n)$ accurately. For high association strengths (such as $\epsilon = 7k_B T$), due to the higher powers of Mayer $f$ function (Eq. 5.27), even slight errors in the magnitude of $Q(i|n)$ will have considerable impact on the bonding state.
Figure 5.5: Comparison of the bonding distribution for a solute with 40°, 50°, 60° (Left panel), and 90° patch (Middle panel). Observe that the bonding fraction for the highest bonding state is invariably less well described by the theory. Right panel: Variation of different bonding fractions with association strength for a patch size of 35° at a density of 0.8. Rest as in Fig. 5.4.

Fig. 5.5 (Right panel) shows the variation in the bonding fractions with association strength for the case with $\theta_{c,\sigma} = 35^\circ$. As the solute-solvent association strength is increased, the fraction of times the solute is non-bonded, the monomer fraction ($X_0$), decreases. The fraction bonded once ($X_1$) first increases and then decreases after a certain association threshold that starts favoring the double bonded fractions. This variation highlights the competition between the entropic effects that would favor the reference state, and the energetic effect, which favors higher bonding, of association. The QC theory is able to capture this behavior rather well.

The decrease in the value of $X_1$ after a certain association strength as shown in Fig. 5.5 cannot be captured within the TPT1 framework as the doubly bonded fractions are ignored. Marshall et.al. [63] extended SAFT beyond first order perturbation to include the double bonding condition. Their approach was based on a second order perturbation, but terms beyond second bonding were left out. They studied mixtures of solvent and solute having the same bonding angles and allowed only solute-solvent association. As is clear from Fig. 5.5, as the bond angle increases beyond 35°, the
solute can bond more than two times and the second order perturbation is also inadequate.

In Fig. 5.6 (left panel), we compare the results of Marshall et. al. [63] for a 40° patch at a density of $\rho d^3 = 0.6$ and for different association strengths. We find that for lower association strengths ($\epsilon/k_B T < 6$), the second order perturbation is able to capture the bonding fractions. When the association strength is increased, fractions that are bonded three times increase and become more dominant. Necessarily, the second order perturbation is not adequate for these cases. The QC approach is able to capture accurately all the bonding fractions across the association energy range. Fig. 5.6 (right panel) shows the excellent agreement for higher bonding fractions as the patch size on the solute is increased to 90° to model a Janus particle (Fig. 5.2).

![Graphs showing bonding fractions](image)

**Figure 5.6**: Left panel: Comparison of the variation of different bonding fractions with the association strength, for a patch size of 40° at a density of 0.6. Right panel: Comparison of bonding fractions for different patch sizes at a density of 0.6 and association strength of $\epsilon = 7k_B T$. For clarity, the bonding distribution for a 90° patch are shown in the inset figure in the right panel. The solvent molecules and solute molecule have same patch size ($\theta_{c,p} = \theta_{c,\sigma} = \theta_c$). Solute is infinitely dilute. Dotted lines are based on the approach by Marshall et.al.[63], solid lines are QC predictions and symbols are Monte Carlo simulation results.
5.3.2 Simplifications — Single bonding patch

In Wertheim’s theory [45, 46] and SAFT [51], a single bonding condition is assumed for the association sites. Thus $Q(i|n) = 0$ for $i > 1$. This assumption is valid only for a patch size $\theta_c = 27^\circ$ or less (Fig. 5.2). For this case, bonding and occupancy can be separated, and in particular, we have

$$Q(1|n) = \kappa_\sigma \cdot C_1^n$$

(5.30)

where $C_1^n$ is a combinatorial factor accounting for the freedom to choose 1 solvent molecule from $n$ solvent molecules in the observation volume and $\kappa_\sigma = (1 - \cos(\theta_{c,\sigma})) / 2$ is the probability that a solute molecule is oriented such that it can bond with the solvent. The equilibrium constant ratio (Eq. 5.24) simplifies to

$$\frac{K_n}{K_{n,r}} = \left[1 + \bar{f}_\sigma \cdot \kappa_p \kappa_\sigma \cdot C_1^n\right]$$

(5.31)

$$= \left[1 + \bar{f}_\sigma \cdot \kappa \cdot n\right]$$

where $\kappa = \kappa_p \kappa_\sigma$. The monomer fraction is then

$$\ln X_0 = -\ln \left[x_{0,r} + \sum_{n \geq 1} \left[1 + \bar{f}_\sigma \cdot \kappa \cdot n\right] \cdot x_{n,r}\right]$$

$$= -\ln \left[1 + \bar{f}_\sigma \cdot \kappa \cdot \sum_{n \geq 1} n \cdot x_{n,r}\right]$$

(5.32)

In our previous work [54], we identified the sum in Eq. 5.32 as

$$F^{(1)} = \sum_{n \geq 1} n \cdot x_{n,r} = n_{avg}^{hs} = \rho_p \int d\vec{r}_1 g_r \ (\vec{r}_1|0)$$

(5.33)

where $n_{avg}^{hs}$ is the average occupancy in the hard sphere reference, $\rho_p$ is the density of the solvent and $g_r$ is the pair correlation in the reference hard sphere system. Substituting the pair correlation form for the summation in Eq. 5.32, we recover the
SAFT representation [51] for the monomer fraction

\[
X_0 = \left[ 1 + \mathbf{f}_\sigma \cdot \kappa \cdot \rho_p \int_{v} d\mathbf{r}_1 g_r (\mathbf{r}_1 | 0) \right]^{-1}, \quad (5.34)
\]

and the excess chemical potential of the solute due to association is

\[
\mu_{\text{asso}}^{\text{ex}} = \ln X_0, \quad (5.35)
\]

again a well-known result within SAFT.

Figure 5.7: Comparison of the occupancy distribution (Left panel) and chemical potential (Right panel) of an infinitely dilute solute with single bonding condition (\(\theta_{c,\sigma} = 27^\circ\)) for solute. Middle panel: the average occupancy of associating solute for different association strengths.

Fig. 5.7 (Right) compares SAFT [51] and QC estimates for the residual chemical potential of the solute due to association. At higher densities, the SAFT approach is in error, whereas the QC approach describes the simulation results accurately. The deviation in the SAFT-based prediction ultimately arises from the approximation

\[
r^2 \cdot g_r (r) \approx d^2 \cdot g_r (d) \quad (5.36)
\]

that is made within SAFT. It was observed [110, 111] that this approximation is most accurate at a reduced density of 0.5. This approximation under-predicts bonding at
the lower densities and over-predicts bonding at the higher densities, leading to a much too negative chemical potential at higher densities. We observe that, when accurate \( n_{avg}^{hs} \) values are provided in SAFT from Monte Carlo simulations [54] (represented by SAFT MC in Fig. 5.7 (Right)), excellent agreement with the QC estimate is obtained.

The occupancy distribution can be obtained from Eq. 5.21 by using equilibrium constant ratio from Eq. 5.32

\[
x_n = \frac{K_n}{K_{n,r}} \cdot x_{n,r} \cdot X_0 \quad (5.37)
\]

For a reduced density of 0.8 and an association strength of \( 7k_B T \), Fig. 5.7 (Left) shows that excellent agreement with Monte Carlo results is obtained with the QC theory for the entire distribution. The average occupancy for an associating solute can be obtained from the above distribution

\[
n_{avg}^{asso} = \sum_{n \geq 1} n \cdot x_n
\]

\[
= n_{avg}^{hs} + \Delta n_{asso}
\]

where \( n_{avg}^{hs} = \sum_{n \geq 1} n \cdot x_{n,r} \). Fig. 5.7 (Middle panel) gives the results for a single bonding solute for different association strengths.

### 5.3.3 Simplifications — Spherically symmetric patch

When the solute has a spherically symmetric patch \( \theta_{c,\sigma} = 180^\circ \) (Fig. 5.2), all the orientations of the solute are favorable for bonding and hence the isolated cluster probabilities \( Q(i|n) \), reduce to just choosing \( i \) solvent molecules from the \( n \) solvent molecules in the cluster, i.e. \( Q(i|n) = C_i^n \).

\[
Q(i|n) = C_i^n = \binom{n}{i}, \forall i \leq n \quad (5.39)
\]
Substituting Eq. 5.39 in Eq. 5.24, we have

\[
\frac{K_n}{K_{n,r}} = \left[ 1 + \sum_{1 \leq i \leq n} \bar{f}_i \cdot \kappa^i_p \cdot \binom{n}{i} \right] \tag{5.40}
\]

The chemical contribution is obtained as

\[
\ln x_0 = \ln x_{0,r} - \ln \left[ 1 + \sum_{n \geq 1} \bar{f}_n \cdot \kappa^n_p \cdot \sum_{i \geq n} \binom{i}{n} \cdot x_{i,r} \right] = \ln x_{0,r} + \ln X_0 \tag{5.41}
\]

Recognizing that in the reference fluid, the average number of clusters with \( n \) solvent molecules in the observation volume [54, 56, 112] is given by

\[
F^{(n)} = \sum_{i \geq n} \binom{i}{n} \cdot x_{i,r} = \frac{\rho^n_p}{n!} \int_v d\vec{r}_1 \cdots \int_v d\vec{r}_n g_r (\vec{r}_1 \cdots \vec{r}_n | 0) , \tag{5.42}
\]

we find that monomer fraction is

\[
X_0 = \left[ 1 + \sum_{n \geq 1} \bar{f}_n \cdot \kappa^n_p \cdot F^{(n)} \right]^{-1} \tag{5.43}
\]

and the chemical potential of the solute is

\[
\mu^{ex}_{asso} = \ln X_0 = -\ln \left[ 1 + \sum_{n \geq 1} \bar{f}_n \cdot \kappa^n_p \cdot F^{(n)} \right] , \tag{5.44}
\]

expressions that were derived earlier within SAFT using the complete reference approach [54, 112].

Fig. 5.8 shows the comparison with Monte Carlo simulation for the occupancy distribution (Eq. 5.21), bonding distribution (Eq. 5.22), and the chemical potential (Eq. 5.44) of an infinitely dilute solute with spherically symmetric association. The QC theory is able to capture the distribution accurately for a high density and high association strength where multi-body correlations are important [54].
Figure 5.8: Comparison of the occupancy distribution (Left panel), bonding fractions (Middle panel), and chemical potential (Right panel) of an infinitely dilute solute with spherically symmetric association ($\theta_{c,\sigma} = 180^\circ$)

5.4 Conclusions

The quasichemical (QC) approach offers a physically transparent and intuitive way to model the physics of association given the properties of a reference fluid. In particular, the approach provides a simple path to incorporate the physics of multi-body correlations. In the context of such multi-body correlations, the QC approach leads to the identification of a term, $Q(i|n)$, that plays a central role in the theory. $Q(i|n)$ is a reference fluid property and average factors when at least $i$ particles are present over the association patch given that $n$ particles are in the observation volume. These factors are obtained from the conditional probabilities ($\Theta(k|n)$) of observing exactly $k$ particles in the patch region given $n$ particles in the spherical observation shell around the solute molecule. For a generic bonding patch we develop a Monte Carlo procedure for estimating $Q(i|n)$; for limiting cases where the orientation of the solvent can be decoupled from occupancy in the solute’s inner-shell, we develop analytical expressions for $Q(i|n)$.

In this chapter, for simplicity we study a mixture where solvent-solvent bonding is absent but the solvent can bond with the solute. Further, the solute is infinitely
dilute. For such a mixture and for solutes with varying patch sizes, ranging from a solute that bonds only once, to solutes with larger patch sizes including a Janus particle, and a particle whose entire surface is available for bonding, the theory leads to predictions of bonding and occupancy that agree very well with results based on particle simulations. The quasichemical approach directly provides the excess chemical potential of the solute, which is expressed in terms of three contributions: the work to create a cavity the size of the solute’s inner-solvation shell to accommodate the solute, the long-range work to couple the solute with the solvent when the inner-shell is empty of solvent, and the work to allow short-range association within the inner-shell. By construction, in the present study, the first two contributions are zero and the chemistry contribution simplifies to the logarithm of the monomer fraction of the solute molecule. For limiting cases, the expression for the nonbonded fraction of the solute is the same as the expression based on Wertheim’s theory/SAFT.

We note that the restriction of no solvent-solvent association is easily relaxed, potentially allowing us to model more complex mixtures. Further, our work hints at the possibility of readily modeling multi-body association within Wertheim/SAFT by using the $Q(i|n)$ factors identified by quasichemical theory. Results from these investigations will be presented in the next chapter.

5.5 Appendix

5.5.1 Equilibrium constant

The equilibrium constant for the associating system can be expressed as [112]

$$K_n = \frac{(e^{\beta \mu_{ip}^n})^n}{n!} e^{-\beta w(R^n)} \int_v d\vec{r}_1 \cdots \int_v d\vec{r}_n e^{-\beta \sigma_{pn}(R^n)}, \quad (5.45)$$
and for the hard sphere reference as

\[ K_{n,r} = \frac{(e^{\beta p_n})^n}{n!} e^{-\beta w_{hs}(R^n)} \int_v d\mathbf{r}_1 \ldots \int_v d\mathbf{r}_n e^{-\beta U_{sph}^{bs}(R^n)}, \]  

(5.46)

Taking ratio of the above two equations, we get

\[ \frac{K_n}{K_{n,r}} = e^{n \beta \Delta \mu_{ps}} \cdot e^{\beta \Delta w(R^n)} \cdot \frac{\int_v d\mathbf{r}_1 \ldots \int_v d\mathbf{r}_n e^{-\beta U_{sph}^{bs}(R^n)}}{\int_v d\mathbf{r}_1 \ldots \int_v d\mathbf{r}_n e^{-\beta U_{sph}^{bs}(R^n)}} \]  

(5.47)

we define

\[ Z_0 = \int_v d\mathbf{r}_1 \ldots \int_v d\mathbf{r}_n e^{-\beta U_{sph}^{bs}(R^n)} \]  

(5.48)

Factoring \( e^{-\beta U_{sph}^{bs}(R^n)} \), we get

\[ \frac{K_n}{K_{n,r}} = e^{n \beta \Delta \mu_{ps}} \cdot e^{\beta \Delta w(R^n)} \cdot \frac{\int_v d\mathbf{r}_1 \ldots \int_v d\mathbf{r}_n e^{-\beta \Delta \tilde{U}_{sph}(R^n)} e^{-\beta U_{sph}^{bs}(R^n)}}{Z_0} \]  

(5.49)

which reduces to Eq. 5.7.

### 5.5.2 \( \Theta(k|n) \) - Conditional isolated cluster probabilities

As explained in section 5.2, \( \Theta(k|n) \) gives the probability of having exactly \( k \) molecules in the patch region given \( n \) molecules in the spherical shell of the solute. We calculated \( \Theta(k|n) \) for different patch sizes (\( \theta_{(c, \sigma)} \)) of the solute molecule. The values for different patch sizes studied in this work are presented in Tables 5.2 and 5.3. It should be noted that for all the patch sizes, the maximum bonding numbers \( N^{max} \) (see Table 5.1) also give the maximum number that can be occupied in the patch region and hence, \( \Theta(k|n) = 0, \forall k > N^{max} \). For different patch sizes, \( \Theta(1|1) \) can be physically interpreted as the probability that the solvent molecule is in the patch region of
the solute. The numerical values of $\Theta(1|1)$ obtained in this work agree with $k_\sigma = [1 - \cos(\theta_{c,\sigma})]/2$, the probability that a solute molecule is oriented such that it can bond with the solvent.

Table 5.2 : Conditional isolated cluster probabilities, $\Theta(k|n)$ of having exactly $k$ molecules in the patch region given $n$ molecules in the spherical shell around the solute, for the critical angle on the solute, $\theta_{(c,\sigma)} = 35^\circ, 40^\circ$ and $50^\circ$. The spherical observation shell is defined by $r_c = 1.1d$ and $d$.

<table>
<thead>
<tr>
<th>$\theta_{(c,\sigma)} = 35^\circ$</th>
<th>$\theta_{(c,\sigma)} = 40^\circ$</th>
<th>$\theta_{(c,\sigma)} = 50^\circ$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Theta(1</td>
<td>n)$</td>
<td>$\Theta(2</td>
</tr>
<tr>
<td>n</td>
<td>$\Theta(1</td>
<td>n)$</td>
</tr>
<tr>
<td>1</td>
<td>0.0904</td>
<td>0.1170</td>
</tr>
<tr>
<td>2</td>
<td>0.1799</td>
<td>0.0005</td>
</tr>
<tr>
<td>3</td>
<td>0.2679</td>
<td>0.0017</td>
</tr>
<tr>
<td>4</td>
<td>0.3543</td>
<td>0.0037</td>
</tr>
<tr>
<td>5</td>
<td>0.4384</td>
<td>0.0069</td>
</tr>
<tr>
<td>6</td>
<td>0.5188</td>
<td>0.0118</td>
</tr>
<tr>
<td>7</td>
<td>0.5949</td>
<td>0.0190</td>
</tr>
<tr>
<td>8</td>
<td>0.6649</td>
<td>0.0292</td>
</tr>
<tr>
<td>9</td>
<td>0.7260</td>
<td>0.0439</td>
</tr>
<tr>
<td>10</td>
<td>0.7724</td>
<td>0.0659</td>
</tr>
<tr>
<td>11</td>
<td>0.7923</td>
<td>0.1011</td>
</tr>
<tr>
<td>12</td>
<td>0.8280</td>
<td>0.1282</td>
</tr>
</tbody>
</table>
Table 5.3 : Conditional isolated cluster probabilities, $\Theta(k|n)$ of having exactly $k$ molecules in the patch region given $n$ molecules in the spherical shell around the solute, for the critical angle on the solute, $\theta_{(c,\sigma)} = 60^\circ$ and $90^\circ$. The spherical observation shell is defined by $r_c = 1.1d$ and d.

<table>
<thead>
<tr>
<th>$\theta_{(c,\sigma)} = 60^\circ$</th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th>$\theta_{(c,\sigma)} = 90^\circ$</th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$n$</td>
<td>$\Theta(1</td>
<td>n)$</td>
<td>$\Theta(2</td>
<td>n)$</td>
<td>$\Theta(3</td>
<td>n)$</td>
<td>$\Theta(4</td>
<td>n)$</td>
<td>$\Theta(5</td>
<td>n)$</td>
<td>$\Theta(6</td>
<td>n)$</td>
<td>$\Theta(1</td>
</tr>
<tr>
<td>1</td>
<td>0.2500</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.5000</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>0.4334</td>
<td>0.033</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.5849</td>
<td>0.2075</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>0.5456</td>
<td>0.0995</td>
<td>0.0018</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.4329</td>
<td>0.4329</td>
<td>0.0671</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>0.5790</td>
<td>0.1970</td>
<td>0.0090</td>
<td>1.30E-05</td>
<td>0</td>
<td>0</td>
<td>0.2277</td>
<td>0.5145</td>
<td>0.2277</td>
<td>0.0150</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>5</td>
<td>0.5434</td>
<td>0.3119</td>
<td>0.0275</td>
<td>1.04E-04</td>
<td>0</td>
<td>0</td>
<td>0.0809</td>
<td>0.4170</td>
<td>0.4170</td>
<td>0.0809</td>
<td>0.0020</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>6</td>
<td>0.4567</td>
<td>0.4256</td>
<td>0.0633</td>
<td>5.43E-04</td>
<td>5.00E-10</td>
<td>0</td>
<td>0.0177</td>
<td>0.2256</td>
<td>0.5133</td>
<td>0.2256</td>
<td>0.0177</td>
<td>9.39E-05</td>
<td>0</td>
</tr>
<tr>
<td>7</td>
<td>0.3402</td>
<td>0.5167</td>
<td>0.1228</td>
<td>0.0020</td>
<td>3.34E-08</td>
<td>1.89E-03</td>
<td>0.0778</td>
<td>0.4203</td>
<td>0.4203</td>
<td>0.0778</td>
<td>1.89E-03</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>0.2207</td>
<td>0.5499</td>
<td>0.2184</td>
<td>0.0061</td>
<td>4.69E-07</td>
<td>2.33E-05</td>
<td>0.0154</td>
<td>0.2278</td>
<td>0.5137</td>
<td>0.2278</td>
<td>0.0154</td>
<td>2.33E-05</td>
<td>0</td>
</tr>
<tr>
<td>9</td>
<td>0.1230</td>
<td>0.5182</td>
<td>0.3420</td>
<td>0.0162</td>
<td>3.42E-06</td>
<td>0</td>
<td>4.97E-04</td>
<td>0.0764</td>
<td>0.4231</td>
<td>0.4231</td>
<td>0.0764</td>
<td>4.97E-04</td>
<td>0</td>
</tr>
<tr>
<td>10</td>
<td>0.0559</td>
<td>0.4301</td>
<td>0.4719</td>
<td>0.0420</td>
<td>2.31E-05</td>
<td>0</td>
<td>5.24E-06</td>
<td>0.0072</td>
<td>0.2360</td>
<td>0.5134</td>
<td>0.2360</td>
<td>7.23E-03</td>
<td>0</td>
</tr>
<tr>
<td>11</td>
<td>0.0179</td>
<td>0.2945</td>
<td>0.6073</td>
<td>0.0801</td>
<td>1.83E-04</td>
<td>0</td>
<td>0</td>
<td>0.30E-04</td>
<td>0.0480</td>
<td>0.4514</td>
<td>0.4514</td>
<td>0.0480</td>
<td>0</td>
</tr>
<tr>
<td>12</td>
<td>0.0090</td>
<td>0.1164</td>
<td>0.7406</td>
<td>0.1355</td>
<td>4.91E-04</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>2.60E-07</td>
<td>7.26E-03</td>
<td>0.1334</td>
<td>0.7187</td>
<td>0.1334</td>
</tr>
</tbody>
</table>
Chapter 6

Cluster size distribution theory for associating fluids

In this chapter we present a new perturbation theory to study the structure and phase equilibrium in the mixtures of multi-bonding single site solutes in patchy colloid solvent. The size of the site on the solute molecules can be varied to allow for different bonding conditions ranging from single bonding, to Janus, to a spherically symmetric patch. Only solute-solvent and solvent-solvent interactions are allowed. Ring formations is not present with these interactions.

For multiple bonding of single site solutes, based on the quasichemical analysis of the association developed in the previous chapter, we study multi-body correlations in the hard sphere reference fluid using the isolated cluster information around a solute of given site geometry. This isolated cluster information is complemented by the occupancy distributions around a solute in the hard sphere reference at the density of interest to get the multi-body correlations at the density of the system. This cluster size distribution for a distinguished solute provides the accurate multi-body correlations necessary to describe association interactions for different multi-bonding geometries of single site solutes. We extend the framework developed by Marshall and Chapman [3, 67] for spherically symmetric solute molecules, to different multi-bonding site geometries of solute molecules. Our approach [113] of obtaining multi-body information can be extended to study much complex ternary geometries of solute, such as “saturn rings” [27]. Our theory extends SAFT beyond second order
perturbation to study multiple bonding of a single site on the solute molecules. As the patch size on the solute molecules increases, higher bonding states become more probable and our theory is able to predict different bonding states for a range of solute site geometry. Detailed study for Janus solute is presented for 1 and 2 patch solvent molecules, for a range of concentration and association strength. We also study different self-assembled geometries by changing the relative strength between solute-solvent and solvent-solvent attractions.

Equilibrium phase studies on limited valency patchy colloids show that the reduction of valency reduces the density of the coexisting liquid phase, giving rise to empty liquids (low density liquids) at low valencies [39, 114, 115]. This empty liquid behavior is due to the networks formed in the liquid state due to bonding between limited valencies. For isotropic molecules, such networks are absent and instead the structure is dominated by maximum packing of nearest neighbors which increases the density. For anisotropic patchy particles as the valency decreases to 2, the liquid density vanishes to zero or no phase separation can be observed [39, 116]. Wertheim’s theory has been used to predict the phase behavior for mixtures of patchy colloid for different valencies [52, 114, 117]. In this chapter we also study the equilibrium phase behavior of a mixture of 2 patch (patches are of same kind) solvent with a multi-bonding single site solute. Since there are no solute-solute attractions and the patchy colloid has only 2 patches, neither the solute nor the solvent molecules can phase separate in the pure form. We study the concentrations of the solute (in liquid phase) where equilibrium phase behavior can be observed for these mixtures due to network formation at suitable association strengths. Our theory predictions for phase equilibrium for a mixture of 2 patch colloid and different geometries of single multi-bonding site solute suggest very low density gel formation for such mixtures. The
multi-bonding site on the solutes acts as a linker for the chains of solvent molecules forming networks in the liquid state. For the relative association strength studied in this chapter, we observe that the vapor-liquid coexistence curve broadens as the concentration of the patchy solvent molecule is increased. We also observe that as the size of the patch on the solute molecules is decreased, the critical temperature and the critical packing fraction decreases. This reduction in the critical temperature is due to the decrease in the total number of bonds and has also been observed by simulation studies in literature for cluster forming one-patch colloids [36, 37].

This extension of Wertheim’s theory/SAFT to mixtures of different multi-bonding geometries of single site solutes in patchy colloid solvents provides an excellent framework for advances in the study of mixtures of these solutes with patchy particles in the bulk and at interfaces. The rest of the chapter is organized as follows. In Section 6.1 we sketch the association theory for multi-bonding solutes and provide information about the multi-body correlations in the hard sphere reference fluid for various site geometries on the solute. In Section 6.2 we present the methods, and in Section 6.3 we present the results for structure and phase equilibrium from several model systems. A general thermodynamic framework for mixtures of multi-patch solvent molecules with single, multiple bonding site solute is presented in Appendix 6.5.

6.1 Theory

We study thermodynamics of a mixture of single site solute molecules, $\sigma$, and patchy solvent molecules, $p$. The $B$ site on the solute molecule can bond with the sites $A$ of the solvent; the size of the site on the solute determines the extent of multiple bonding of solvent molecules, Fig. 6.1 shows the range of site geometries of solute studied in this work. The solvent molecule can have one or two directional sites (labeled $A$ and
and the size of the sites is such that single bonding condition holds (See Fig.6.2). We ignore the association between the solutes themselves, only AB bonding is allowed between different solvent molecules.

Figure 6.1: Different patch geometries ($\theta_{c,\sigma}^{(B)}$) of the solute molecule. Note that the critical angle for the solvent molecules $\theta_{c,p}^{(A)} = 27^\circ$, so that the patch A (colored green) on the solvent can only interact once with the multi-bonding patch B (colored red) on the solute molecule. It should be noted that due to the 2-D nature of the graph, all the possible bonding conditions can not be represented. Table 6.1 gives the maximum bonding numbers for different patch sizes on the solute molecule. The solvent can have one or two patches as shown in Fig.6.2.

Figure 6.2: Association between B patch on solute and patch A on solvent (left). For a solute with ($\theta_{c,\sigma}^{(B)} = 180^\circ$), the attractive patch B can be approached from any direction. Right panel shows the association between two solvent molecules when the solvent has two patches. $r$ is the center-to-center distance and $\theta_A$ and $\theta_B$ are the orientation of the attractive patches A and B relative to line connecting the centers. A sample sticky solute (colored red) interacting with the patch A (colored green) is shown and Fig. 6.1 shows the range of solute geometries studied in this work.

The total potential is a sum of hard sphere and association contributions

$$u(r) = u_{HS}(r) + u_{AS}(r)$$

(6.1)
The association potential for solvent-solvent \((p,p)\) and solute-solvent \((\sigma,p)\) molecules is modeled as square well sites \([109]\) as:

\[
\begin{align*}
u^{(p,p)}_{AB}(r) &= \begin{cases} 
-\epsilon^{(p,p)}_{AB}, & r < r_c \text{ and } \theta_A \leq \theta_{c,p}^{(A)} \text{ and } \theta_B \leq \theta_{c,p}^{(B)} \\
0 & \text{otherwise}
\end{cases} \\
u^{(\sigma,p)}_{BA}(r) &= \begin{cases} 
-\epsilon^{(\sigma,p)}_{BA}, & r < r_c \text{ and } \theta_A \leq \theta_{c,\sigma}^{(A)} \text{ and } \theta_B \leq \theta_{c,\sigma}^{(B)} \\
0 & \text{otherwise}
\end{cases}
\end{align*}
\]

(6.2) (6.3)

where subscripts \(A\) and \(B\) represent the type of site and \(\epsilon\) is the association energy.

For different molecules, bonding between \(A\) and \(B\) type of sites is allowed. \(r\) is the distance between the particles and \(\theta_A\) is the angle between the vector connecting the centers of two molecules and the vector connecting association site \(A\) to the center of that molecule. The critical distance beyond which particles do not interact is \(r_c\) and \(\theta_c\) is the solid angle beyond which sites cannot bond. For the sites on the solvent molecules, a single bonding condition holds \(\theta_{c,p} = 27^\circ\) and Fig. 6.1 shows the range of site geometries \(\theta_{c,\sigma}\) for solute molecules.

### 6.1.1 Multiple bonding of a single site on solute

As can be seen from the potentials of Eqs. 6.2 and 6.3, for association to occur between molecules, the orientation and the radial distance must be correct. To describe these anisotropic short range interactions between molecules, in Wertheim’s theory \([45, 46]\) and SAFT \([50, 51]\), a single bonding condition is assumed for the association sites. This assumption is valid only for a patch size \(\theta_c = 27^\circ\) or less. When the patch size increases, the site on solute can bond multiple times (Fig. 6.1). Table 6.1 gives the range of patch sizes studied in this work and the corresponding maximum bonding numbers. It should be noted that these maximum bonding numbers also depend on
the size of the molecules and the critical distance for association. In this study we consider equal diameters \(d\) for solute and solvent molecules and critical distance for association is defined as \(r_c = 1.1d\).

Table 6.1: Patch size of the solute \((\theta_{c,\sigma})\) and the corresponding maximum bonding number \((N_{\text{bond}}^{\text{max}}})\). The solute and solvent molecules have the same size \(d\) and the critical distance for association is \(r_c = 1.1d\).

<table>
<thead>
<tr>
<th>(\theta_{c,\sigma})</th>
<th>27°</th>
<th>35°</th>
<th>40°</th>
<th>50°</th>
<th>60°</th>
<th>90°</th>
<th>180°</th>
</tr>
</thead>
<tbody>
<tr>
<td>(N_{\text{bond}}^{\text{max}})</td>
<td>1</td>
<td>2</td>
<td>3</td>
<td>4</td>
<td>5</td>
<td>7</td>
<td>12</td>
</tr>
</tbody>
</table>

For a patch that can bond multiple times, multi-body correlation information in the reference fluid is required [113] in our perturbation theory. The study in the previous chapter on quasichemical theory [113] led to the identification of a physical representation of these multi-body effects. For a solute patch bonded \(i\) times, the average number of clusters with \(i\) molecules in the patch region of the solute in the reference fluid \((F_{\theta_{c,\sigma}}^{(i)})\), contains all of the multi-body information. This average number of clusters for different patch geometries \((\theta_{(c,\sigma)})\) is obtained as

\[
F_{\theta_{(c,\sigma)}}^{(i)} = \sum_{n \geq i} Q(i|n) \cdot x_{n,r} \tag{6.4}
\]

where \(x_{n,r}\) is the occupancy distribution in the hard sphere reference fluid in the observation shell of the solute, at the density of the solution. The spherical observation shell is defined by the critical distance for bonding \((r_c)\) and the particle diameter \((d)\). We obtained \(Q(i|n)\) in the isolated clusters, from the exact conditional probabilities, \(\Theta(k|n)\), of having exactly \(k\) particles being over the association patch given that \(n\) particles are in the spherical observation volume as,

\[
Q(i|n) = \sum_{i \leq k \leq n} \binom{k}{i} \cdot \Theta(k|n) \tag{6.5}
\]
The factor $Q(i|n)$ is the weighted average that given $n$-solvent particles in the spherical observation shell, at least $i \leq n$ occupy the patch region, and for the occupancy of $k \geq i$ over the patch region, weights corresponding to choosing $i$ out of $k$ molecules are applied to the exact probabilities $\Theta(k|n)$. Fig. 5.3 shows an example of average factors $Q(2|3)$ for a Janus particle.

It should be noted that for all the patch sizes, the maximum bonding number $N_{\text{bond}}^{\text{max}}$ (see Table 6.1) also gives the maximum number that can be occupied in the patch region and hence, $Q(i|n) = 0, \forall i > N_{\text{bond}}^{\text{max}}$. When the solute has a spherically symmetric patch $\theta_{c,\sigma} = 180^\circ$ (Fig. 6.2), all the orientations of the solute are favorable for bonding and hence the average factors $Q(i|n)$, reduce to just choosing $i$ solvent molecules from the $n$ solvent molecules in the cluster, i.e. $Q(i|n) = C^n_i$. Also for a single bonding condition, $Q(1|n) = \kappa_{\sigma} \cdot C^n_1$, where $C^n_1$ is a combinatorial factor accounting for the freedom to choose one solvent molecule from $n$ solvent molecules in the observation volume and $\kappa_{\sigma} = (1 - \cos(\theta_{c,\sigma}))/2$ is the probability that a solute molecule is oriented such that it can bond with the solvent.

Total configurations in the reference fluid where $i$ solvent molecules are available to bond with the central molecule is obtained by accounting for the favorable orientations of the solvent molecules present over the solute patch, as

$$\Phi_{\theta_{c,\sigma}}^{(i)} = \kappa_p^i \cdot F_{\theta_{c,\sigma}}^{(i)}$$

(6.6)

where $\kappa_p = (1 - \cos(\theta_{c,p}))/2$ is the probability that a solvent molecule is oriented such that it can bond with the solute. In obtaining Eq. 6.6 we consider that all the bonds between the solute and solvent molecules have the same strength and hence the orientation information for the solvent can be extracted out of the multi body clusters.
\( F^{(i)}_{\theta_{(c,a)}} \). With this approach, multi-body effects in the dense fluids can be obtained for any patch geometry of the solute. Information only in isolated clusters in the form of exact probabilities \( \Theta(k|n) \) is required to obtain the average factors \( Q(i|n) \), which are complemented with the occupancy distributions in the hard sphere reference fluid, at the density of the solution.

### 6.1.2 Thermodynamic perturbation theory

Wertheim’s multi-density approach provides an excellent way to model short range interactions. In the Wertheim’s multi density formalism [47, 48], the free energy due to association can be expressed as

\[
\frac{A^{AS}}{V k_B T} = \sum \left( \rho^{(k)} \ln \frac{\rho_0^{(k)}}{\rho^{(k)}} + Q^{(k)} + \rho^{(k)} \right) - \Delta c^{(0)} / V \tag{6.7}
\]

where \( k_B \) is the Boltzmann constant, \( T \) is the temperature, the summation is over the species \( (k = \sigma, p) \), \( \rho \) is the number density, \( \rho_0 \) is the monomer density, \( Q^{(k)} \) is obtained from Marshall-Chapman [67] work and \( \Delta c^{(0)} \) is the contribution to the graph sum due to association between the solvent-solvent \( (p,p) \) and solute-solvent \( (\sigma,p) \) molecules, i.e.

\[
\Delta c^{(0)} = \Delta c_{pp}^{(0)} + \Delta c_{\sigma p}^{(0)} \tag{6.8}
\]

Since the sites on solvent molecules can bond only once, the first order perturbation theory can be used to obtain this contribution to free energy [51]. For solute-solvent association, extensions beyond first order perturbation theory are needed to account for all possible bonding contributions beyond single bonding. We extend the framework developed by Marshall and Chapman [3, 67] and incorporate accurate multi-body correlations necessary to describe association interactions for different
multi-bonding geometries of single site solutes. For a given patch geometry of solute, the solute-solvent contribution to free energy can be expressed as a sum of all the bonding states i.e.

\[ \Delta c_{\sigma p}^{(0)} = \sum_{i=1}^{N_{\text{max}}^{\text{bond}}} \Delta c_i^{(0)} \]  

(6.9)

where \( N_{\text{max}}^{\text{bond}} \) is the maximum bonding of the site on solute molecules for different patch sizes (See Table 6.1). When the \( B \) patch on the solute can bond with the \( A \) patch on the solvent, for a given bonding state of the solute, the contribution to free energy is

\[ \frac{\Delta c_i^{(0)}}{V} = \frac{\rho_0^{(\sigma)}(\rho^{(p)} X_A^{(p)})^i}{\Omega_i} \int d\vec{r}_1 \cdots d\vec{r}_i d\omega_1 \cdots d\omega_i g_r(\vec{r}_1 \cdots \vec{r}_i|0) \prod_{k=1}^i (f^{(\sigma,p)}_{BA}(0,k)) \]  

(6.10)

In Eq. 6.10, \( \rho^{(p)}(= \rho \cdot x^{(p)}) \) is the density of solvent molecules obtained from the mole fraction of solvent \( x^{(p)} \) and the total density \( \rho \), \( X_A^{(p)} \) is the fraction of solvent molecules not bonded at site \( A \), \( \Omega(= 4\pi) \) is the total number of orientations, \( f^{(\sigma,p)}_{BA}(0,k)(= \exp(\zeta_{BA}^{(\sigma,p)}/k_B T) - 1) \) is the Mayer function for association between solute \( \sigma \) and solvent \( p \) molecules corresponding to potential in Eq. 6.3. \( g_r(\vec{r}_1 \cdots \vec{r}_i|0) \) is the multi-body correlation function in the hard sphere reference fluid and the integral is over all the orientations \( (\omega_i) \) and positions \( (r_i) \) of the \( i \) solvent particles when the solute particle is fixed at the origin. We consider same strength of association for different solute-solvent bonds and represent it by an average Mayer f function, \( f^{(\sigma,p)}_{BA} = \bar{f}_\sigma \). The magnitude of \( \bar{f}_\sigma \) can be extracted out of the integral by applying an indicator function \( \chi(i) \) which checks for the orientation and radial information of the solute and \( i \) solvent molecules for possible bonding i.e.
\[ \Delta c_i^{(0)} \frac{V}{V} = \rho_0^{(\sigma)} (x^{(p)} X_A^{(p)})^i \cdot \bar{f}_\sigma^i \cdot \frac{\rho^i}{\Omega_{\sigma}^i!} \int d\vec{r}_1 \cdots d\vec{r}_i d\omega_1 \cdots d\omega_i \, g_r(\vec{r}_1 \cdots \vec{r}_i|0) \cdot \chi(i) \] (6.11)

where,

\[ \chi(i) = \begin{cases} 
1, & \text{if at least } i \text{ solvent occupy the bonding patch} \\
0, & \text{otherwise} 
\end{cases} \] (6.12)

We identify the integral in Eq. 6.11 as the total configurations in the hard sphere reference fluid where \( i \) solvent molecules are available to bond with the solute molecule i.e.

\[ \frac{\rho^i}{\Omega_{\sigma}^i!} \int d\vec{r}_1 \cdots d\vec{r}_i d\omega_1 \cdots d\omega_i \, g_r(\vec{r}_1 \cdots \vec{r}_i|0) \cdot \chi(i) = \Phi^{(i)}_{\theta_{(c,\sigma)}} \] (6.13)

With this multi-body information (See Eq.6.6), the free energy contribution in Eq. 6.10 can be simplified as

\[ \Delta c_i^{(0)} \frac{V}{V} = \rho_0^{(\sigma)} (x^{(p)} \cdot X_A^{(p)} \cdot \bar{f}_\sigma^i)^i \cdot \Phi^{(i)}_{\theta_{(c,\sigma)}} = \rho_0^{(\sigma)} (x^{(p)} \cdot X_A^{(p)} \cdot \bar{f}_\sigma \cdot \kappa_p)^i \cdot F^{(i)}_{\theta_{(c,\sigma)}} \] (6.14)

where \( F^{(i)}_{\theta_{(c,\sigma)}} \) (See Eq. 6.4) is the average number of clusters where \( i \) solvent molecules are in the patch region of the central solute molecule.

The fraction of solute bonded \( i \) times can then be obtained as

\[ X_i^{(\sigma)} = X_0^{(\sigma)} (x^{(p)} \cdot X_A^{(p)} \cdot \bar{f}_\sigma \cdot \kappa_p)^i \cdot F^{(i)}_{\theta_{(c,\sigma)}} \] (6.15)

where

\[ X_0^{(\sigma)} + \sum_{i=1}^{N_{\text{max}}^{\text{bond}}} X_i^{(\sigma)} = 1 \] (6.16)
for a given patch size \( \theta_{(c,\sigma)} \) on the solute molecule, the average bonding number can be obtained as

\[
n_{\text{bond}}^{\text{avg}} = \sum_{i=1}^{N_{\text{max}}^{\text{bond}}} i \cdot X_i^{(\sigma)}
\]  

(6.17)

Once the multiple bonding information is available for the solute, solvent bonding information can be obtained based on first order perturbation theory [51]. The expressions developed by Marshall and Chapman [67] for \( M \) site patchy solvent molecules with spherically symmetric solute molecules can be implemented here for different multiple bonding geometries of the solute molecules. Here we will show detailed equations for one and two patch solvent molecules.

With this multiple bonding information for the solute, Marshall-Chapman theory [67], which was originally developed for spherically symmetric solute molecules with a second order perturbation, has been extended to study different multiple bonding geometries of the solute beyond second order perturbation. The solvent bonding information can be obtained based on the first order perturbation theory [51, 67]. Appendix 6.5 presents the general thermodynamic framework for mixtures of multi-patch solvent molecules and solutes with single multiple bonding patch. Detailed equations for one and two patch solvent molecules, analyzed in this work, are also shown in Appendix 6.5.

6.1.3 Analytical model for hard sphere distribution

The occupancy distribution in a spherical shell around a solute in the reference hard sphere fluid \( (x_{n,r}) \) plays an important role in determining multi-body effects in the associating mixture (Eq. 6.4). Previously in chapter 2, we developed analytical models for the hard sphere distribution [112]. In this chapter we will use the one parameter model for hard sphere distribution developed in our previous work [112].
\[ x_{n,r} = \frac{\exp(\beta \cdot n \cdot \mu^e_r)\rho^n[\exp (-\beta \Omega_n)]K_n^{(0)}}{1 + \sum_{n=1}^{n_{\text{max}}} \exp(\beta \cdot n \cdot \mu^e_r)\rho^n[\exp (-\beta \Omega_n)]K_n^{(0)}} \]  
(6.18)

where \( n_{\text{max}} \) is the maximum number of particles that can be occupied in the observation shell defined by \( r_c \) and \( d, \beta \mu^e_r \) is the excess chemical potential of the hard sphere solvent particle when the solute is infinitely dilute. The isolated cluster partition function is given by

\[ n!K_n^{(0)} = v_b^n \cdot P^{(n)} \]  
(6.19)

where \( v_b = \frac{4}{3} \pi \cdot (r_c^3 - d^3) \) and \( P^{(n)} \) are the isolated cluster probabilities\[3\]. The interfacial contribution, \( \beta \Omega_n \), is given by \[112\]

\[ \beta \Omega_n = (-0.0109 \cdot n^2 + 1.0109 \cdot n) \cdot \zeta \]  
(6.20)

where we find the density dependence of the \( \zeta \) factor based on MC simulation data \[54, 112\] as

\[ \zeta = \frac{a_1 \eta - a_2 \eta^2 + a_3 \eta^3}{(1 - \eta)^3} \]  
(6.21)

where \( a_1 = 5.393568939, a_2 = 4.225324689, a_3 = 2.216387922 \) and \( \eta = \pi/6\rho \) is the packing fraction. The average occupancy of the spherical shell around the solute in the hard sphere reference can be obtained as

\[ n_{\text{avg}}^{(HS)} = \sum_{n=1}^{n_{\text{max}}} n \cdot x_{n,r} \]  
(6.22)

6.2 Methods

6.2.1 Monte Carlo Simulations

Monte Carlo simulations were carried out for the associating systems to validate the theory. The associating system contains a mixture of solute and solvent particles with
equal diameters $d$. A total number of 864 molecules were considered in the simulation and the number of solute particles was changed for different concentrations. Solvent with one and two patches were studied. A single bonding condition i.e. $\theta_{c,p} = 27^\circ$ was used for the solvent molecules. Table 6.1 gives the different solute patch sizes ($\theta_{c,\sigma}$) along with the corresponding maximum bonding numbers ($N_{\text{bond}}^\text{max}$), studied in this work. The observation volume is defined by $d$ and $r_c = 1.1d$, where $d$ is the diameter of the solute and solvent molecules. The system was equilibrated for 1 million steps with translational factors chosen to yield an acceptance rate of 0.3, and data was collected every 100 sweeps, where a sweep is an attempted move of all the particles in the system.

Bonding ($X_n$) distributions were studied for a range of critical angles for the solute molecules. We analyzed cases of different concentrations and association strengths between the solute and solvent molecules. Detailed analysis for Janus particles ($\theta_{c,\sigma} = 90^\circ$) was done.

Isolated cluster probabilities, $\Theta(k|n)$, of finding exactly $k$ particles in the patch region given $n$ particles in the spherical observation volume of the solute, were also obtained for different patch geometries of the solute molecule with a Monte Carlo procedure, explained in detail in the previous chapter [113]. Factors $Q(i|n)$ were calculated from $\Theta(k|n)$ using Eq. 6.5. Recall that $Q(i|n)$ gives the average that for $n$-solvent particles in the inner-shell, at least $i$ of those occupy the bonding patch and are available to bond with the solute (if oriented correctly).

### 6.3 Results and Discussions

We have extended Wertheim’s theory/SAFT beyond second order perturbation to incorporate multiple bonding of different geometries of a single site on solute molecules.
The patches on the solvent molecules have single bonding condition. Different site geometries of solute molecules studied in this work are given in Table 6.1. A detailed study for multiple bonding of spherically symmetric solute has been showed by us previously [54, 112]. Hence, in this work we focus on Janus and other multi-bonding site geometries on solute. We present results for one patch and two patch solvent molecules. Throughout theory results are compared with Monte Carlo simulations.

6.3.1 Janus solute particles

For Janus particles, the patch geometry on the solute molecule is such that the attractive patch covers half of the molecule i.e. $\theta_{(c,\sigma)} = 90^\circ$. Due to their interesting geometry with half the surface attractive to solvent and other half being only repulsive, they find enormous application in the study of colloidal self assembly. We first study the effect of concentration on the association of Janus solute molecules in patchy solvents, at a density of $\rho d^3 = 0.8$. The association strength is $\epsilon = 7k_BT$ for solute-solvent and solvent-solvent association. For 1-patch solvent molecules, only solute-solvent association is present. At infinite dilution of the solute, maximum average bonding is observed for the solute molecules which decreases as the concentration of the solute increases (Fig. 6.3 Left panel), since the system becomes limited in the number of solvent molecules. Fig. 6.4 Left panel shows a corresponding sharp decrease in the monomer fraction of the solvent molecules as most of the solvent molecules are engaged in bonding with solutes for $x^{(\sigma)} \geq 0.3$. However, the average bonding of solutes is low for these concentrations of the solute. This analysis shows that multi-body effects are more important at low concentrations of the solute. Internal energy due to association (Fig. 6.4 Right panel) for this mixture shows a minimum at a concentration of $x^{(\sigma)} = 0.2$ showing that the average bonds per molecule is maximum.
Figure 6.3: Effect of concentration of the solute \( x(\sigma) \) on the association for solute molecules. Solute is a Janus particle \( \theta_{(c,\sigma)} = 90^\circ \). (Left panel) shows the average bonding numbers of the solute \( n_{\text{avg}}^{\text{bond}} \). (Right panel) shows the comparison of the bonding distribution for an infinitely dilute solute with 90° patch. Two cases with solvent having 1-patch and 2-patch are presented. Density is \( \rho d^3 = 0.8 \) and association strength is \( \epsilon = 7k_B T \) for solute-solvent and solvent-solvent interactions. Solid (red) and dashed (blue) lines are theory predictions based on this work for 2-patch and 1-patch solvent case respectively. Symbols are Monte Carlo simulation results.

For this concentration.

For 2-patch solvent molecules, solute-solvent and solvent-solvent bonding is present. When the concentration of solute is low, there is enough solvent to associate with the solute and hence high average bonding numbers are observed for solute molecules (Fig. 6.3 Left Panel) for both one patch and two patch solvent cases. For the same concentration, presence of solvent-solvent bonding provides competition for solute-solvent bonding for a two patch solvent case and hence low bonding is observed as compared to one patch solvent. For an infinitely dilute solute, where the bonding is maximum for solute, Fig. 6.3 right panel shows the bonding distribution of solute for 1-patch and 2-patch solvent cases. It can be observed that the distribution shifts to higher bonding numbers for 1-patch case due to absence of solvent-solvent bonding.
Figure 6.4: (Left panel) shows the effect of concentration of solute on the bonding fractions of the solvent molecule, only monomer fractions are plotted for the 1 patch solvent case. (Right panel) shows the variation of the internal energy per particle due to association $E_{\text{AS}}/Nk_BT$, with the concentration of the solute. Rest is same as Fig. 6.3.

For the bonding distribution of 2-Patch solvent molecules, the monomer fractions are always low due to presence of solute-solvent and solvent-solvent association (Fig. 6.4 Left Panel). A solvent is bonded twice when the $A$ site is bonded either to another $B$ site on solvent or solute molecule and $B$ site is bonded to $A$ site on another solvent molecule. As the concentration of the solute is increased, the fraction of the solvent that is bonded twice decreases due to decrease in the concentration of the solvent molecules. As the concentration of the solute increases, most of the solvent is bonded once. The internal energy (Fig. 6.4 Right Panel) shows a minimum for a concentration of $x^{(\sigma)} \approx 0.1$ showing maximum bonding per molecule for this concentration. Theory prediction are in excellent agreement with the simulation results. Deviation at the highest state in the bonding distribution (and hence for average bonding) for infinite dilution are due to numerical limitations in estimating $Q(i|n)$ using Monte Carlo Simulations [113].
The above analysis was done for the same strength of association between solute-solvent and solvent-solvent molecules. Different structures can be obtained in the mixture by changing the relative strength of solute-solvent and solvent-solvent association. Fig. 6.5 shows the effect of increase in the solvent-solvent association strength, when the solute-solvent association is fixed at $\epsilon^{(\sigma,p)} = 7k_B T$. The concentration of the solute is $x^{(\sigma)} = 0.1$ and density is $\rho d^3 = 0.8$. Fig. 6.5 shows the average bonding numbers of the solute molecules (left panel) and the corresponding bonding fractions for the solvent molecules (right panel). When the solvent-solvent association strength is low as compared to the solute-solvent association, the $A$ site on a solvent molecule prefers bonding to the $B$ site on the solute molecules as compared to $B$ site on other solvent and hence solvent-solvent association is minimal. This is shown by the negligible fraction of solvent bonded twice $X_2^{(p)}$. For the given concentration ($x^{(\sigma)} = 0.1$), the fraction of solvent bonded once $X_1^{(p)}$ is less than one, as there are not enough solute molecules. When the solvent-solvent association strength is increased, the $A$ site on the solvent starts to bond with the $B$ site on another solvent molecule as well and prefers to bond to $B$ site on another solvent when the solvent-solvent association strength is higher than solute-solvent interactions. At a fixed concentration, the increase in the fraction of solvent bonded twice $X_2^{(p)}$ and the simultaneous decrease in average bonding numbers of the solute shows this effect clearly. For these high solvent-solvent association cases, higher lengths of the chains originating from the solute molecules will be observed, the length of the free chains of solvent molecules will also increase. As shown in the left panel of Fig. 6.5, the average length of the arms originating from the Janus particles ($L_{arm}$) increases with the increase in the solvent-solvent association strength. The fraction of chains that originate from the patch on solute molecules ($\Psi$) also increases. Theory is able to capture accurately
Figure 6.5: Effect of strength of solvent-solvent association $\epsilon^{(p,p)}$, when the solute-solvent association strength is fixed at $\epsilon^{(\sigma,p)} = 7k_B T$. Left Panel: Average bonding numbers for the solute molecules ($n_{\text{bond}}$); average length of arms ($L_{\text{arm}}$) and fraction of chains originating from the patch on solute molecules ($\Psi$). Right Panel: Bonding fractions of the solvent molecules. Solute is a Janus particle with concentration of $x^{(\sigma)} = 0.1$ and the solvent has two patches. Solid lines are theory prediction based on this work and symbols represent simulation results.

6.3.2 Other multi-bonding geometries for solute

Similar studies for concentration and association strength effects can be done for other site geometries on the solute molecules. To study the effect of size of the patch we show the bonding distributions and average bonding for solutes at a concentration of $x^{(\sigma)} = 0.1$. Structure analysis in terms of average length of arms and the fraction of chains originating from the multi-bonding patch on the solute molecules is also done for various patch geometries.

For a given concentration of solute molecules, and same strength of association for solute-solvent and solvent-solvent interactions, Fig. 6.6 shows the increase in the average bonding number (right panel) as the size of the patch on solute molecules is
increased. The structure analysis shows that for a given concentration and for the same strength of interaction between solute-solvent and solvent-solvent molecules, more number of smaller chains originate from the solute with increasing patch size. This is evident from the increasing average bonding numbers and the fraction of chains originating from solute, with a simultaneous decrease in the average length of the arm originating from the solute molecules. Corresponding bonding distributions of solutes are shown in the left panel for different site geometries. Theory is able to capture accurately the shift in the bonding distributions towards higher bonding states, as the size of the patch on the solute molecules is increased.
6.3.3 Phase equilibrium

We also study the equilibrium phase diagram for binary mixtures of multi-bonding single site solutes with solvent molecules containing two $A$ sites (See Fig. 6.7). The $A$ patches on the solvent molecules can bond with the $B$ patch on solute molecules or to the $A$ patch on other solvent molecules i.e. AA and AB bonding is allowed for these calculations. The multi-bonding solute molecules with a $B$ patch act as linkers for the associated chains of solvent molecules. It has been studied that phase separation for mixtures of patchy particles occurs in the limit of large connected networks in the system. To ensure enough bonding, we study the phase behavior for a solute-solvent association strength of three times stronger than the solvent-solvent association strength i.e. $\epsilon^{(\sigma,p)} = 3 \cdot \epsilon^{(p,p)}$. Since there are no solute-solute interactions and the patchy colloid only has 2 patches, neither the solute nor the solvent molecules can phase separate in the pure form. We study the concentrations of the solute where equilibrium phase behavior can be observed for these mixtures due to connected network formation at higher association strength for solute-solvent interactions i.e. $\epsilon^{(\sigma,p)} = 3 \cdot \epsilon^{(p,p)}$.

![Figure 6.7](image)

Figure 6.7 : Patchy solvent molecules with two $A$ sites are considered to study the equilibrium phase behavior.

We first study mixtures with a spherically symmetric solute and observe an empty fluid (liquid at very low density) regime for such mixtures. For the relative association strength studied in this work, we observe that the vapor-liquid coexistence curve
Figure 6.8: Vapor-liquid coexistence curves for three different concentrations of patchy solvent molecules. The solute has a spherically symmetric $B$ site and solvent molecules have two $A$ patches. AA, AB association is allowed and $\epsilon^{(\sigma,p)} = 3 \cdot \epsilon^{(p,p)}$. Symbols represent critical point.

broadens as the concentration of the patchy solvent molecule in the liquid phase ($x^{(p)}$) is increased. As the strength of solute-solvent is higher than solvent-solvent interactions, an increase in solvent concentration in the liquid phase increases the nearest neighbors around the spherically symmetric solute hence increasing the liquid density. We also study binary mixtures of multi-boding solute and 2 similar patch solvent, for three different geometries of site on the solutes. We observe that as the size of the patch on the solute molecules is decreased, the critical temperature and the critical packing fraction decreases. This reduction in the critical temperature is due to the decrease in the bonding energy of the system as the patch size limits the maximum number of bonds. Similar observations have been made by simulation studies in literature for cluster forming one-patch colloids [36, 37].
Figure 6.9: Vapor-liquid coexistence curves for three different size geometries of solute molecules in 2A patch solvent. Solute size of $\theta_{(c,\sigma)} = 60^\circ, 90^\circ, 180^\circ$ (bottom to top) are presented. Concentration of the solvent is $x^{(p)} = 0.65$. Symbols represent critical point.

### 6.4 Conclusions

We present a molecular theory to study structure and phase behavior of mixtures of multi-bonding single site solutes in patchy colloid solvents. Marshall-Chapman theory, which was originally developed for spherically symmetric solute molecules with a second order perturbation, has been extended to study different multiple bonding geometries of the solute beyond second order perturbation. The key contribution of our work is the incorporation of accurate multi-body information in the hard sphere reference fluid for different site geometries of the solute, which is based on a quasi-chemical perspective of association [113]. Within this quasichemical approach, occupancy information in the patch region for different site geometries of the solute are required only in the isolated clusters. This isolated cluster information is complemented by the occupancy distributions around a solute in the hard sphere reference to get the multi-body correlations at the density of the system. This method [113] of obtaining multi-body information is unique and can be extended to study much complex...
ternary geometries of solute, such as “saturn rings” [27].

We study the effect of concentration and association strength on the thermodynamics of these mixtures. A detailed study for Janus particles is presented due to their application in physical systems. Theory is accurately able to capture the behavior for different site geometries over a range of concentrations and association strengths. Theory predicts that different structure in terms of clusters of solute and chains of solvent molecules can be obtained by changing the relative strength of solute-solvent and solvent solvent association strengths. The equilibrium phase studies also show the importance of these mixtures in obtaining very low density gels. A detailed phase equilibrium study for these binary mixtures can be done in future.

This extension of Wertheim’s theory/SAFT to mixtures of different multi-bonding geometries of single site solutes in patchy colloid solvents, provides an excellent framework for advances in the study of mixtures of these solutes with patchy particles in the bulk and at interfaces.

6.5 Appendix

6.5.1 Thermodynamic framework

In this section we present a general thermodynamic framework for a mixture of multi-patch solvent molecules and single, multi-bonding patch on solute molecules. The patches on solvent molecules have single bonding condition and the extent of multiple bonding on the solute patch is determined by the patch size (See Table 6.1). Based on the Wertheim’s multi density formalism [47, 48], the Helmholtz free energy due to association is

$$\frac{A_{AS}}{V k_B T} = \sum_k \left( \rho^{(k)} \ln \frac{\rho^{(k)}}{\rho_{0}^{(k)}} + Q^{(k)} + \rho^{(k)} \right) - \Delta c^{(0)}/V$$  \hspace{1cm} (6.23)
where $Q^{(k)}$ is a combinatorial term given by

$$
Q^{(k)} = -\rho^{(k)} + \sum_{\gamma \subset \Gamma^{(k)}} c^{(k)}_{\gamma} \sigma^{(k)}_{\Gamma^{(k)} - \gamma}
$$

(6.24)

where $\Gamma^{(k)}$ is the set of all the sites on the species $k$, $\sigma^{(k)}_{\Gamma^{(k)} - \gamma}$ is the sum of the monomer density and the density of molecules at all the combinations of the sites from the set $\Gamma^{(k)} - \gamma$

$$
\sigma^{(k)}_{\Gamma^{(k)} - \gamma} = \sum_{\alpha \subset \Gamma^{(k)} - \gamma} \rho^{(\alpha)}_{k}
$$

(6.25)

with $\sigma^{(k)}_0 = \rho^{(0)}_k$ and $\sigma^{(k)}_{\Gamma^{(k)}} = \rho_k$, and $c^{(k)}_{\gamma}$ is given by

$$
c^{(k)}_{\gamma} = \frac{\partial \Delta c^{(0)}}{\partial \sigma^{(k)}_{\Gamma^{(k)} - \gamma}} / V
$$

(6.26)

For multi-patch solvent and single patch solute molecules, $Q^{(k)}$ can be simplified as

$$
Q^{(p)} = -\rho^{(p)} + \sum_{A \in \Gamma^{(p)}} c^{(p)}_A X_A^{(p)} \rho^{(p)}
$$

(6.27)

$$
Q^{(\sigma)} = -\rho^{(\sigma)} \cdot X_0^{(\sigma)}
$$

(6.28)

In the free energy expression given by Eq. 6.23, the graph sum due to association has contributions from solvent-solvent and solute-solvent association

$$
\Delta c^{(0)} = \Delta c^{(0)}_{pp} + \Delta c^{(0)}_{\sigma p}
$$

(6.29)

The solute-solvent association contribution is a sum of different bonding states of the solute molecules

$$
\Delta c^{(0)}_{\sigma p} = \sum_{n=1}^{N_{\text{bond}}^{\text{max}}} \Delta c^{(0)}_n
$$

(6.30)
where based on the multi-body information identified in this work \( F^{(n)}_{\theta_{(c,\sigma)}} \), the contribution for a given bonding state is obtained as

\[
\frac{\Delta c^{(0)}_n}{V} = \rho_0^{(\sigma)} \left( \sum_{A \in \Gamma(p)} x^{(p)} \cdot X^{(p)}_A \cdot f^{(\sigma,p)}_{BA} \cdot \kappa_p \right)^n \cdot F^{(n)}_{\theta_{(c,\sigma)}}
\]

(6.31)

The bonding distribution for solute can be obtained from this contribution as,

\[
\frac{\Delta c^{(0)}_n}{V} = \rho^{(\sigma)} X^{(\sigma)}
\]

(6.32)

the monomer fraction \( X^{(\sigma)}_0 \) and the average bonding numbers \( n^{\text{bond}}_{\text{avg}} \) for the solute molecules can be obtained from Eq. 6.16 and Eq. 6.17 respectively.

The patches on the solvent molecules can bond only once, hence based on the first order perturbation theory \([51]\), the solvent-solvent association contribution is obtained \([67]\) as

\[
\frac{\Delta c^{(0)}_{pp}}{V} = \frac{1}{2} \sum_{L \in \Gamma(p)} \sigma^{(p)}_{\Gamma(p) - L} \sum_{M \in \Gamma(p)} \sigma^{(p)}_{\Gamma(p) - M} \cdot \kappa_{LM} \cdot f^{(p,p)}_{LM} \]  

(6.33)

For a given patch on the solvent molecules, the fraction not bonded is given by

\[
X^{(p)}_A = \frac{1}{1 + c^{(p)}_A}
\]

(6.34)

where \( c^{(p)}_A \) is obtained from the derivative of associative contribution to the fundamental graph sum with respect to the density parameter (See Eq. 6.26) as

\[
c^{(p)}_A = \sum_{M \in \Gamma(p)} \kappa_{AM} f^{(p,p)}_{AM} \rho^{(p)}(p) X^{(p)}_M + \sum_{n=1}^{N^{\text{max}}_{\text{bond}}} \rho^{(\sigma)}(\sigma) \sum_{A \in \Gamma(p)} \rho^{(p)}(p) X^{(p)}_A
\]

(6.35)

Multiplying the above equation by \( \rho^{(p)}(p) X^{(p)}_A \) both sides and taking the sum over all the sites \( \sum_{A \in \Gamma(p)} \) after rearranging we get

\[
\frac{\Delta c^{(0)}_{pp}}{V} = \frac{1}{2} \sum_{A \in \Gamma(p)} \rho^{(p)}(p) X^{(p)}_A c^{(p)}_A - \sum_{n=1}^{N^{\text{max}}_{\text{bond}}} \rho^{(\sigma)}(\sigma) \frac{n \cdot X^{(\sigma)}_n}{2}
\]

(6.36)
With the contributions due to solvent-solvent and solute-solvent association defined, the free energy can be minimized with respect to the monomer densities to get the bonding fractions. Detailed bonding fractions for one patch and two patch solvent molecules are presented next.

### 6.5.2 One patch solvent molecule

For one patch solvent there is no association between the solvent molecules i.e. $\Delta e_{pp}^{(0)} = 0$. By minimizing the free energy with respect to the monomer fractions mass action equations can be obtained to solve for the monomer fractions of the solute and solvent molecules. For solute, Eq. 6.16 is obtained by minimizing the free energy and for the solvent molecules following equation is obtained [3]

$$X_A^{(p)} = 1 - \frac{x^{(\sigma)}}{x^{(p)}} \cdot \sum_{i=1}^{X_i^{(\sigma)}} i \cdot X_i^{(\sigma)}$$

(6.37)

Eqs. 6.15, 6.16 and 6.37 can be solved simultaneously to obtain the monomer and bonded fractions of the solute and solvent molecules.

### 6.5.3 Two patch solvent molecule

**Distinct (A,B) patches**

When there are two patches on the solvent molecules, where the $A$ patch on a solvent can bond with the $B$ patch on a solute or the $B$ patch on other solvent molecule. The free energy contribution due to solute-solvent association, for different patch geometries of the solute molecules has been developed in this work as given by Eq. 6.14. The free energy contribution due to solvent-solvent association is
\[ \frac{\Delta c^{(0)}_{pp}}{V} = \rho^2 \cdot x^{(p)} A \cdot x^{(p)} B \cdot \Delta^{(p,p)}_{AB} \] (6.38)

where for the single bonding condition of sites on the solvent molecules, the association contribution is

\[ \Delta^{(p,p)}_{AB} = \kappa^2_{p} \cdot f^{(p,p)}_{AB} \int_v g_r(r_1) d(r_1) \]

\[ = \kappa_{AB} \cdot f^{(p,p)}_{AB} \int_v g_r(r_1) d(r_1) \] (6.39)

where the integration is now over the observation volume defined by the diameter of molecules \( d \) and the critical distance \( r_c \),

\[ \kappa_{AB} = \kappa^2_{p} = \left[ 1 - \cos(\theta_{c,p}) \right]^2 / 4 \] (6.40)

\[ f^{(p,p)}_{AB} = \exp(\varepsilon^{(p,p)}_{AB} / k_B T) - 1. \] (6.41)

The contribution to free energy becomes

\[ \frac{\Delta c^{(0)}_{pp}}{V} = \rho^{(p)} X^{(p)} A \cdot x^{(p)} B \cdot \kappa_{AB} \cdot f^{(p,p)}_{AB} \cdot \rho \int_v g_r(r_1) d(r_1) \] (6.42)

Instead of using the approximation of \( r^2_1 \cdot g_r(r_1) = d^2 \cdot g_r(d) \) [51], we identify \( \rho \int_v g_r(r_1) d(r_1) \) as the average number of molecules in the observation shell defined by \( r_c \) and \( d \) around a central molecule in the hard sphere reference system, i.e. \( n_{HS}^{avg} \).

\[ \frac{\Delta c^{(0)}_{pp}}{V} = \rho^{(p)} X^{(p)} A \cdot x^{(p)} B \cdot \kappa_{AB} \cdot f^{(p,p)}_{AB} \cdot n_{HS}^{avg} \] (6.43)

Following the work by Marshall et. al. [67], the fraction of solvent not bonded at site \( A \) and site \( B \) can be obtained by simultaneous solution of the following equations:

\[ \left( 1 + \kappa_{AB} f^{(p,p)}_{AB} x^{(p)} B \cdot n_{HS}^{avg} \right) X^{(p)} A = \frac{1}{1 + \kappa_{AB} f^{(p,p)}_{AB} x^{(p)} B \cdot n_{HS}^{avg} + \frac{\rho^{(p)} n_{bond}^{avg}}{\rho^{(p)} X^{(p)} A}}, \] (6.44)

\[ \left( 1 + \kappa_{AB} f^{(p,p)}_{AB} x^{(p)} B \cdot n_{HS}^{avg} \right) X^{(p)} B = \frac{1}{1 + \kappa_{AB} f^{(p,p)}_{AB} x^{(p)} B \cdot n_{HS}^{avg} + \frac{\rho^{(p)} n_{bond}^{avg}}{\rho^{(p)} X^{(p)} B}}. \] (6.45)
With these fractions for the solvent molecules, the bonding distribution and the monomer fraction for the solute molecules can be obtained by Eqs. 6.15 and 6.16. The average bonding numbers for solute are obtained by using Eq. 6.17. The fraction of solvent not bonded, bonded once and bonded twice can be obtained as

\[
X_0^{(p)} = X_A^{(p)} \cdot X_B^{(p)}, \quad (6.46)
\]

\[
X_1^{(p)} = X_0^{(p)} \left( \frac{1}{X_A^{(p)}} + \frac{1}{X_B^{(p)}} - 2 \right), \quad (6.47)
\]

\[
X_2^{(p)} = X_0^{(p)} \left( \frac{1}{X_A^{(p)}} - 1 \right) \cdot \left( \frac{1}{X_B^{(p)}} - 1 \right). \quad (6.48)
\]

For a 2-patch solvent, since the A site on a solvent can bond with the B site on the solute or the B site on another solvent molecule, different structures can be analyzed by varying the association strength, concentration and the patch size of the solute molecules. For a spherically symmetric solute, Marshall and Chapman [67] analyzed the structure in the mixture with 2 patch solvent molecules in terms of average length of the arms originating from the patch on the solute molecules \(L_{arm}\) and the fraction of the chains that originate from the multi-bonding patch on solute \(\Psi\) molecules. Total number of chains is given by the free chains of the solvent molecules including the monomers and the chains originating from the solute molecules. We extend this structure analysis to different patch sizes on the solute molecules. Following Marshall and Chapman [67] these structural properties are obtained as,

\[
L_{arm} \approx \frac{1}{X_B} \quad (6.49)
\]

\[
\Psi = \frac{n_{avg}^{bond} \cdot \rho^{(\sigma)}}{n_{avg}^{bond} \cdot \rho^{(\sigma)} + \rho^{(p)} \cdot X_A^{(p)}} \quad (6.50)
\]
Same kind (2A) patches

When the two patches on the solvent molecules are of the same kind, both the A type patch on solvent molecules can bond with the B site on the solute or A patch on other solvent molecule. The bonding distribution for solute molecules is given by

\[ X_i^{(\sigma)} = X_0^{(\sigma)} (2 \cdot x^{(p)} \cdot X_A^{(p)} \cdot f_{BA}^{(\sigma,p)} \cdot \kappa_p)^i \cdot F_{\theta(c,\sigma)}^{(i)} \]  

(6.51)

The fraction of solvent molecules not bonded at patch A is given by

\[ X_A^{(p)} = \frac{1}{1 + 2 \kappa_{AA} f_{AA}^{(p,p)} x^{(p)} X_A^{(p)} \cdot n_{\text{avg}}^H + \frac{\rho^{(p)} n_{\text{bond}}^A}{\rho^{(p)} 2 X_A^{(p)}}} \]  

(6.52)

The fraction of solvent not bonded, bonded once and bonded twice can be obtained as

\[ X_0^{(p)} = \left( X_A^{(p)} \right)^2, \]  

(6.53)

\[ X_1^{(p)} = X_0^{(p)} \left( \frac{1}{X_A^{(p)}} + \frac{1}{X_A^{(p)}} - 2 \right), \]  

(6.54)

\[ X_2^{(p)} = X_0^{(p)} \left( \frac{1}{X_A^{(p)}} - 1 \right)^2. \]  

(6.55)

6.5.4 Thermodynamic properties in associating mixtures

With the contributions to free energy defined, other thermodynamic properties can be obtained by taking appropriate derivative of the free energy.

\[ \frac{A_{AS}^{\text{ads}}}{N k_B T} = x^{(\sigma)} \left( \ln X_0^{(\sigma)} + \frac{n_{\text{avg}}^{\text{bond}}}{2} \right) + x^{(p)} \sum_{A \in \Gamma^{(p)}} \left( \ln X_A^{(p)} - \frac{X_A^{(p)}}{2} + \frac{1}{2} \right) \]  

(6.56)
The chemical potential of solute molecules due to association is

$$
\Delta \mu^{AS}_{(\sigma)} = \ln X_0^{(\sigma)} - \sum_{i=1}^{N_{\text{max}}^{\text{bond}}}(\rho^{(\sigma)} \cdot X_0^{(\sigma)} \left( \sum_{A \in \Gamma(p)} x^{(p)} X_A^{(p)} f_{BA}^{(\sigma,p)} \kappa_{p} \right)^i \left( \frac{\partial F_{\theta(c,\sigma)}^{(i)}}{\partial \rho(\sigma)} - \frac{F_{\theta(c,\sigma)}^{(i)}}{\rho} \right)) - \frac{1}{2} \left[ \sum_{A \in \Gamma(p)} \rho^{(p)} \cdot X_A^{(p)} \sum_{B \in \Gamma(p)} x^{(p)} \cdot X_B^{(p)} \left( f_{AB}^{(p,p)} \kappa_{AB} \right) \cdot \left( \frac{\partial n_{\text{HS}}^{\text{avg}}}{\partial \rho^{(p)}} - \frac{n_{\text{HS}}^{\text{avg}}}{\rho} \right) \right]
$$

(6.57)

and for solvent molecules

$$
\Delta \mu^{AS}_{(p)} = \ln X_0^{(p)} - \sum_{i=1}^{N_{\text{max}}^{\text{bond}}}(\rho^{(\sigma)} \cdot X_0^{(\sigma)} \left( \sum_{A \in \Gamma(p)} x^{(p)} X_A^{(p)} f_{BA}^{(\sigma,p)} \kappa_{p} \right)^i \left( \frac{\partial F_{\theta(c,\sigma)}^{(i)}}{\partial \rho(\sigma)} - \frac{F_{\theta(c,\sigma)}^{(i)}}{\rho} \right)) - \frac{1}{2} \left[ \sum_{A \in \Gamma(p)} \rho^{(p)} \cdot X_A^{(p)} \sum_{B \in \Gamma(p)} x^{(p)} \cdot X_B^{(p)} \left( f_{AB}^{(p,p)} \kappa_{AB} \right) \cdot \left( \frac{\partial n_{\text{HS}}^{\text{avg}}}{\partial \rho^{(p)}} - \frac{n_{\text{HS}}^{\text{avg}}}{\rho} \right) \right]
$$

(6.58)

The internal energy can be obtained from the Helmholtz free energy as

$$
\frac{E^{AS}}{Nk_B T} = \frac{\partial}{\partial \beta} \left( \frac{A^{AS}}{Nk_B T} \right) = x^{(\sigma)} \left( \frac{\partial \log X_0^{(\sigma)}}{\partial \beta} + \frac{1}{2} \frac{\partial n_{\text{avg}}^{\text{bond}}}{\partial \beta} \right) + x^{(p)} \sum_{A \in \Gamma(p)} \frac{\partial X_A^{(p)}}{\partial \beta} \left( \frac{1}{X_A^{(p)}} - \frac{1}{2} \right)
$$

(6.59)

The contribution to compressibilty factor due to association can be obtained from the chemical potential and Helmholtz free energy as

$$
Z^{AS} = \frac{P^{AS}}{\rho k_B T} = \sum_k \Delta \mu^{AS}_{(k)} \cdot x^{(k)} - \frac{A^{AS}}{Nk_B T}
$$

(6.60)

### 6.5.5 Analytical expressions for density derivatives of hard sphere distribution

For the chemical potential expressions in Eqs.6.57 and 6.58, the density derivative of average number of clusters with $i$ solvents in the patch region of the solute molecules are required. In this section we present analytical expressions for the derivative terms.
The average number of clusters is given by

$$F_{\theta(c, \sigma)}^{(i)} = \sum_{n \geq i} Q(i|n) \cdot x_{n,r}$$  \hspace{1cm} (6.61)$$

As explained in the theory section, the distributions in the reference fluid are given by

$$x_{n,r} = \frac{\Delta^{(n,r)}}{[1 + \sum_{n \geq 1} \Delta^{(n,r)}]}$$  \hspace{1cm} (6.62)$$

$$x_{0,r} = \left[ 1 + \sum_{n \geq 1} \Delta^{(n,r)} \right]^{-1}$$  \hspace{1cm} (6.63)$$

where

$$\Delta^{(n,r)} = \exp(\beta \cdot n \cdot \Delta \mu_{ex}^{(r)}) \rho^n \left[ \exp \left( -(-0.0109 \cdot n^2 + 1.0109 \cdot n) \cdot \zeta \right) \right] K_n^{(0)}$$  \hspace{1cm} (6.64)$$

The excess chemical potential in a hard sphere reference fluid is based on the Carnahan Starling equation

$$\Delta \mu_{ex}^{(r)} = \frac{8 \eta - 9 \eta^2 + 3 \eta^3}{(1 - \eta)^3}$$  \hspace{1cm} (6.65)$$

Taking logarithm on both sides of Eq. 6.62 and then taking derivative of both sides with respect to the packing fraction \( \eta \), we get

$$\frac{\partial \ln(x_{n,r})}{\partial \eta} = \frac{\partial \ln \Delta^{(n,r)}}{\partial \eta} - x_{0,r} \cdot \sum_{n \geq 1} \frac{\partial \Delta^{(n,r)}}{\partial \eta}$$  \hspace{1cm} (6.66)$$

where

$$\frac{\partial \ln \Delta^{(n,r)}}{\partial \eta} = n \cdot \frac{\partial \Delta \mu_{ex}^{(r)}}{\partial \eta} + n \cdot \frac{\partial \ln \rho}{\partial \eta} - \left[ (-0.0109 \cdot n^2 + 1.0109 \cdot n) \cdot \frac{\partial \zeta}{\partial \eta} \right]$$  \hspace{1cm} (6.67)$$

hence we get

$$\frac{\partial F_{\theta(c, \sigma)}^{(i)}}{\partial \eta} = \sum_{n \geq i} Q(i|n) \cdot \frac{\partial x_{n,r}}{\partial \eta}$$  \hspace{1cm} (6.68)$$
also for single bonding condition, derivative of average occupancy in reference fluid is required, which is obtained as

\[
\frac{\partial n_{\text{avg}}^{HS}}{\partial \eta} = \sum_{n \geq 1} n \cdot \frac{\partial r_{n,r}}{\partial \eta}
\]  

(6.69)
Chapter 7

New ion-hydration model for electrolyte systems

Various versions of SAFT which have been used to model electrolyte systems, both primitive and non-primitive, use ion-solvent association to describe ion-solvation. More recently, such ion-solvent association has been used to inform dielectric constant calculations in salt solutions [118]. In the SAFT association [51], used with different versions of SAFT and CPA [119], the ions are modeled as segments with directional sites. For ions where charge is uniform over the molecule, such a representation may not be able to give the true picture. In SAFT association term, the sites on a segment are independent of each other, meaning, the bonding on one site does not affect the bonding at other site. When this association is used to describe solvation of ions, unphysical behavior might be present for the systems where the ratio of sizes of ion and solvent molecule are very low. Fixed number of sites may allow overlapping of solvent molecules present around an ion.

In this chapter, a new statistical mechanics based model has been implemented to describe molecular aspects of ion solvation. This novel ion-solvation model is based on the theory developed by Marshall and Chapman [3, 67] for self-assembling mixtures of patchy colloids and colloids with spherically symmetric attractions. This theory is applied to electrolyte solution when association potential of the ion is assumed to be spherically symmetric, as opposed to patchy. The spherically symmetric association scheme for ions calculates the number of solvent bonded by the successive insertion probabilities and hence prevents any overlapping between solvent molecules.
Other advantage of using this modified association with spherically symmetric association sites for ions, is that characteristic information can be retrieved such as the hydration number variation with concentration/temperature and distribution of ions bonded with n number of water molecules (speciation). Also for primitive models to incorporate the dielectric constant variation, changes in hydration numbers, which are input to the model, with concentration are inherently accounted in the theory. Hydration shell structure with the new approach agrees well with Monte Carlo and molecular dynamic simulation results. A study is done to show that this novel approach can represent the hydration behavior in electrolyte systems better and with guidance from molecular simulation can better predict properties at high temperature high pressure (HTHP).

7.1 Theory

In SAFT framework, the Helmholtz free energy for an electrolyte system can be written as the sum of contributions from the following components

$$A = A^{id} + A^{hs} + A^{disp} + A^{AS} + A^{npMSA}$$  \hspace{1cm} (7.1)

The first term in the Helmholtz free energy equation is the ideal gas interaction which is known from thermodynamics. The hard sphere contribution $A^{hs}$ is obtained from the Carnahan Starling [85] equation of state. Perturbation to hard sphere reference fluid is used to get the dispersion interaction $A^{disp}$ terms [120]. $A^{AS}$ is the association contribution for solvent-solvent and solute solvent association and is presented in detail in the following section. $A^{npMSA}$ is the free energy contribution due to electrostatic interactions calculated using a semi-restricted non primitive mean spherical approximation (MSA) model developed by Blum et. al [121]. Herzog et. al. [122]
developed a model in the SAFT framework using semi restricted non-primitive MSA i.e. incorporating solvent molecules explicitly. Herzog et. al [122] modeled ion-water association based on a fixed number of sites for ions and hence the behavior of the free energy of hydration was not captured correctly, here we present a modified approach for ion-solvent interactions.

7.1.1 Association with spherically symmetric and patchy colloid model

In the ion-solvation theory, the system is described as a mixture of patchy molecules, denoted as \( p \), and spherically symmetrical molecules \( s \). For the scope of this work, two patch water model with \( A \) type and \( B \) type patch is used. There are no \( AA \) or \( BB \) attractions, \( s \) colloids are attracted to type \( A \) patch on \( p \) colloid and also no association between \( s \) colloids (no ion pairing) is present. The patch size on \( p \) colloid is such that the single bonding condition holds and the single uniform patch on \( s \) colloid can bond multiple times (See Fig. 7.1).

![Figure 7.1: Association between patchy-spherical and patchy-patchy colloids.](image)

The treatment of attractions between \( p \) molecules is accounted by standard TPT1 [46] and for attractions between \( p \) and \( s \) molecules, we implement the theory developed by Marshall and Chapman [3, 67]. The association potential for patchy-patchy and patchy-spherically symmetric association can be represented as:
\[ u_{AB}^{(p,p)}(r) = \begin{cases} -\epsilon_{AB}^{(p,p)}, & r < r_c \text{and} \beta_A \leq \beta_c^{(A)} \text{and} \beta_B \leq \beta_c^{(B)} \\ 0, & \text{otherwise} \end{cases} \] (7.2)

\[ u_A^{(s,p)}(r) = \begin{cases} -\epsilon_A^{(s,p)}, & r < r_c \text{and} \beta_A \leq \beta_c^{(A)} \\ 0, & \text{otherwise} \end{cases} \] (7.3)

where superscript \((p,p)\) represents association between two patchy molecules and \((s,p)\) represents association between patchy and spherically symmetric molecules; subscripts \(A\) and \(B\) represent the type of site, \(c\) subscript represents critical value, \(\beta\) is the solid angle of a patch and \(\epsilon\) is the association energy.

According to Marshall and Chapman, the free energy contribution due to association \((A^{AS})\) between 2 patch \(p\) molecule and spherically symmetric \(s\) molecule is given by:

\[
\frac{A^{AS}}{NkT} = x^{(s)} (\ln X_o^{(s)} + \frac{\bar{n}}{2}) + (1 - x^{(s)}) \sum_{A \in \Gamma^{(p)}} (\ln X_A^{(p)} - \frac{X_A^{(p)}}{2} + \frac{1}{2})
\] (7.4)

where the superscript \((s)\) and \((p)\) are used for \(s\) and \(p\) molecules, respectively. \(x\) is the mole fraction, \(X_o^{(s)}\) is the monomer fraction of \(s\) molecules, \(\Gamma^{(p)} = (A, B)\) is the set of short range attractive patches on \(p\) molecules, \(X_A^{(p)}\) and \(X_B^{(p)}\) are the fraction of \(p\) molecules not bonded at patch \(A\) and \(B\), respectively. The important term here is \(\bar{n}\) which is average number of bonds per \(s\) type molecule

\[
\bar{n} = \sum_{n=0}^{n_{max}} n X_n^{(s)}
\] (7.5)

where \(n_{max}\) is the maximum number of \(p\) colloids which can fit into the bonding shell of the \(s\) colloid and the fraction of spherically symmetric colloids bonded \(n\) times is
defined as:

\[ X_n^{(s)} = \frac{\rho_n^{(s)}}{\rho^{(s)}} \]  

(7.6)

where \( \rho^{(s)} \) represents the density of spherically symmetric colloids which are bonded to \( n \) patchy colloids. The monomer fractions are given by

\[ X_0^{(p)} = X_A^{(p)} X_B^{(p)} \]  

(7.7)

\[ X_0^{(s)} = \frac{1}{1 + \sum_{n=1}^{n_{\text{max}}} \frac{1}{n!} \Delta^n \Xi^{(n)} \delta^{(n)}} \]  

(7.8)

where for a two patch colloid

\[ \Delta = y_{HS}(d) X_A^{(p)} \rho_A^{(p)} f_A^{(s,p)} \sqrt{\kappa_{AA}} \]  

(7.9)

and \( \sqrt{\kappa_{AA}} \) is the probability that colloid \( p \) are oriented such that patch \( A \) on \( p \) colloid can bond to colloid \( s \), \( f_A^{(s,p)} \) is the magnitude of the association Mayer function for association between \( p \) and \( s \) colloids given by

\[ f_A^{(s,p)} = \exp\left(\frac{\varepsilon_A^{(s,p)}}{kT}\right) - 1 \]  

(7.10)

In Eq. 7.8, \( \delta^{(n)} \) is the second order correction to the first order superposition of the many body correlation function for the associated cluster. This term is obtained from Marshall-Chapman work [67]. \( \Xi^{(n)} \) is the cluster partition function for a cluster of one spherical colloid and \( n \) patchy colloids given by

\[ \Xi^{(n)} = \nu_b^n P^{(n)} \]  

(7.11)

where \( \nu_b \) is the bonding volume and \( P^{(n)} \) is the probability that there is no hard sphere overlap for randomly generated \( p \) colloids in the bonding shell of \( s \) colloids. Details of obtaining these isolated cluster probabilities have been shown in chapters 3 and 4.
7.1.2 Semiresricted non-primitive MSA

In the semirestricted non primitive MSA [121], the system is modeled as a mixture of hard sphere with ions of same size and a different size for solvent molecules. The free energy contribution due to electrostatic interactions calculated using a semirestricted non primitive MSA model \( A^{npMSA} \) can be expressed as sum of three types of interactions i.e. charge-charge (CC), charge-dipole (CD) and dipole-dipole (DD), as follows:

\[
A^{npMSA} = A^{CC} + A^{DD} + A^{CD} \tag{7.12}
\]

In the non primitive MSA model, the following set of three non-linear equations are solved to yield three dimensionless energy parameters i.e. \( b_0 \) for ion-ion interactions, \( b_1 \) for ion-dipole and \( b_2 \) for dipole-dipole interactions

\[
0 = a_1^2 + a_2^2 - d_0^2 \tag{7.13}
\]

\[
0 = a_1 k_{10} - a_2 (1 - k_{11}) - d_0 d_2 \tag{7.14}
\]

\[
0 = k_{10}^2 + (1 - k_{11})^2 - y_1^2 - d_2^2 \tag{7.15}
\]

where \( d_0^2 \) represents the charge density and \( d_2^2 \) represents the dipole density of the solvent, and are given as

\[
d_0^2 = \frac{4\pi}{kT} e^2 \sigma_{ion}^2 \sum_j \rho_j z_j^2 \tag{7.16}
\]

\[
d_2^2 = \frac{4\pi}{3kT} \mu_{D,solv} \rho_{solv} \tag{7.17}
\]

where \( \sigma_{ion} \) is the salt specific ion diameter (hydrated diameter) used for the semirestricted non primitive MSA term and \( \mu_{D,solv} \) is the dipole moment of the solvent molecule. Other auxiliary parameters in Eqs. 7.13, 7.14, and 7.15 are defined by the
following set of equations:

\[
\begin{align*}
\beta_3 &= 1 + \frac{b_2}{3} \\
\beta_6 &= 1 - \frac{b_2}{6} \\
\beta_{12} &= 1 + \frac{b_2}{12} \\
\lambda &= \frac{\beta_3}{\beta_6} \\
\Delta &= \frac{b_2}{4} + \beta_6^2 \\
y_1 &= \frac{\beta_6}{\beta_{12}} \\
D_F &= 0.5 \left( \beta_6 (1 + b_0) - \frac{b_2 \sigma_{solv}}{12\sigma_{ion}} \right) \\
a_1 &= \frac{1}{2D_F^2} (\Delta - 2\beta_6 D_F) \\
a_2 &= \frac{b_1}{2\beta_6 D_F} \left( \frac{\Delta}{2} + D_F \beta_3 \frac{\sigma_{solv}}{\sigma_{ion}} \right) \\
\Lambda &= 0.5 \left( 1 + b_0 \right) + \frac{\beta_6 \sigma_{solv}}{6\sigma_{ion}} \\
k_{10} &= \frac{\sigma_{solv}}{\sigma_{ion}} \cdot \frac{b_1}{2\Delta} (1 + a_1 \Lambda) \\
k_{11} &= 1 - \frac{1}{\Delta} \left( \beta_3 - a_2 b_1 \Lambda \frac{\sigma_{solv}}{2\sigma_{ion}} \right)
\end{align*}
\]

where \( \sigma_{solv} \) is the diameter of the solvent molecules. The initial values used for solving Eqs. 7.13, 7.14, and 7.15 should be chosen correctly to get physically meaningful solution. Following are the values suggested by Harvey et. al. [123]

\[
\begin{align*}
b_0 &= \frac{-2d_0(1+d_0)}{(4+8d_0+3d_0^2)} F_H^{0.5} \\
b_2 &= \frac{3d_2}{2+d_2} F_H \\
b_1 &= -b_0 (2b_2)^{0.5} \\
F_H &= 1 - 1.5 x_{ion} x_{solv} \sigma_3^{0.5}
\end{align*}
\]
where $x_{ion}$ is the total mole fraction of ions and $\zeta_3$ is the packing fraction. The free energy contributions can be calculated as

\[
\begin{align*}
A_{CC}^{\text{NC}} & = \frac{1}{12\pi \rho \sigma_{ion}^3} \left( 2d_0^2 b_0 - [Q'_{ii}]^2 \right) \\
A_{CD}^{\text{NC}} & = \frac{1}{12\pi \rho \sigma_{ion}^3} \left( -2d_0 d_2 b_1 \frac{\sigma_{ion}}{\sigma_{solv}} - \left[ 1 + \left( \frac{\sigma_{ion}}{\sigma_{solv}} \right) \right] \left( \frac{\sigma_{ion}}{\sigma_{solv}} \right) [Q'_{id}]^2 \right) \\
A_{DD}^{\text{NC}} & = -\frac{1}{12\pi \rho \sigma_{solv}^3} \left( [Q'_{dd}]^2 + 2 [q']^2 \right)
\end{align*}
\]

where

\[
\begin{align*}
Q'_{ii} & = -a_1 - 2 + \frac{\beta_6}{D_F} \\
D & = 1 + \frac{b_1}{2\beta_6} \\
Q'_{id} & = \frac{b_1}{2\beta_6} [\beta_3 + a_1 (3\Lambda - 2D_F)] \\
Q'_{dd} & = \frac{2}{\Lambda} \left( \beta_3^2 - \left( \frac{\sigma_{solv}}{\sigma_{ion}} \right) b_1 a_2 (3\Lambda - 2D_F) \right) - 2 \\
q' & = b_2 \left( 1 - b_2 / 2\beta_6 \right)
\end{align*}
\]

The expressions for chemical potential for ions ($\mu_{i}^{\text{npMSA}}$) and solvent ($\mu_{solv}^{\text{npMSA}}$) and the internal energy ($U^{\text{npMSA}}$) of the system can be obtained from the expression of free energy and are given by:

\[
\begin{align*}
\frac{\mu_{i}^{\text{npMSA}}}{kT} & = \frac{\gamma_i^2 d_0 \left( d_0 b_0 - d_2 b_1 \frac{\sigma_{ion}}{\sigma_{solv}} \right)}{4\pi \rho \sigma_{solv}^3 \left( \sum_j \rho_j \gamma_j^2 \right)} \\
\frac{\mu_{solv}^{\text{npMSA}}}{kT} & = \frac{-d_2^2}{4\pi \rho \sigma_{solv}^3} \left( 2b_2 - d_0 b_1 \frac{\sigma_{solv}^2}{\sigma_{ion}^2} \right) \\
\frac{U^{\text{npMSA}}}{NkT} & = \frac{1}{4\pi \rho \sigma_{solv}^3} \left( \frac{\sigma_{solv}}{\sigma_{ion}} \right)^3 d_0^2 b_0 - 2 \left( \frac{\sigma_{solv}}{\sigma_{ion}} \right)^2 d_0 d_2 b_1 - 2d_2^2 b_2
\end{align*}
\]

In the MSA, the excess Gibbs free energy equals the excess internal energy. Thus, the compressibility factor can be given as

\[
Z^{\text{npMSA}} = \frac{U^{\text{npMSA}} - A^{\text{npMSA}}}{NkT}
\]
7.2 Methods

In SAFT model, five parameters need to be determined for each pure associating component: the temperature independent diameter of a segment $\sigma$, the depth of the potential model $\epsilon$, the number of segments per chain $m$ and two association parameters namely, the association energy $\epsilon_{AB}$ and the effective association volume $\kappa_{AB}$. Based on the work by Herzog et. al. [122] we use a two site model for water and these parameters are fitted to pure component experimental data of vapor pressure and densities (See Table 7.1).

<table>
<thead>
<tr>
<th>Segment number</th>
<th>Segment diameter $\sigma$ (A)</th>
<th>Dispersion energy $\epsilon/k_B$ (K)</th>
<th>Association parameters $\epsilon_{AB}/k_B$ (K)</th>
<th>$\kappa_{AB}$</th>
<th>Dipole moment $\mu_D$ (D)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.98</td>
<td>199.74</td>
<td>1937.52</td>
<td>0.0654</td>
<td>2.28</td>
</tr>
</tbody>
</table>

We study aqueous solutions of alkali halides based on an improved ion-solvation model presented in the theory section 7.1.1. In this study it is assumed that in vapor phase there is no salt present. For a physically motivated parameter set for these alkali halides, we seek insights from molecular dynamic simulations.

7.2.1 Insights from molecular simulation

Molecular Dynamic simulations can be used effectively to obtain a realistic picture of interactions at the atomistic length scale. In our EoS based model for electrolyte solutions, guidance from molecular dynamic simulations have been taken at various points to gain physical insight while modeling. For electrolyte solutions, simulations were done for systems varying from a single ion (in 2150 water molecules) to a 4 molal solution (with 1950 water molecules). Isothermal Isobaric (NpT) simulations were
done using NAMD, which is a parallel molecular dynamics code designed for high-
performance simulation of large biomolecular systems. Systems were equilibrated for 2 ns and data was then collected over 10 ns. For water, we use SPC/E parameters. For ions, we tested different parameters based on their performance for solution densities. For aqueous NaCl solution at 298.15 K, the study with different parameter sets for MD simulation is shown in the Fig. 7.2.

![Figure 7.2: Density of aqueous NaCl at 298.15 K. Symbols represent experimental data [4] and lines are corresponding to the molecular simulation studies MD1 [124], MD2 [125], and MD3 [126].](image)

Based on the above comparison for the results obtained from MD1 [124], MD2 [125], MD3 [126], with experimental data [4], results shown in this work are obtained using Horinek-Netz [126] parameters.

To aid in understanding the relative stiffness of the coordination shell, MD simulations were performed on Na⁺ and Cl⁻ and the energy to push water molecules away from the first hydration shell computed (Fig. 7.3). It was observed that, for anion,
the energies for these short range interactions were much lower than that for cation. Also, with increasing temperature, it is easier to push waters away from the chloride anion but much less so for sodium cation. This analysis suggests that sodium ion holds on to its shell of waters more tightly than chloride ion. Thus, while developing EoS model for electrolyte systems, cation-hydration information is important and can guide in obtaining parameters which are more fundamental.

![Comparison of short range interactions in ions](image)

Figure 7.3 : Comparison of short range interactions in ions. Symbols represents the molecular simulation results based on parameters given by Horinek et. al. [126] and the lines serve only to guide the eyes.

### 7.3 Results

Based on the theory introduced for ion-solvation, the modified association scheme was incorporated in SAFT based model with semi-restricted non primitive MSA, developed by Herzog et. al. [122]. For aqueous aklai halides, Herzog et. al.[122] obtained the parameters to be used with SAFT+npMSA EoS based on the activity coefficient and osmotic coefficient data at 298.15 K. Based on the same approach we
estimated salt specific parameters (3 parameters for each salt) for alkali halides and the activity coefficients at 298.15 K are shown in the Fig. 7.4. It was observed that, as

the cation size increases, disagreements between the model values and experimental data [127] also increases. The reason for this disagreement comes from over counting certain interactions since the free energy is represented as a sum of contributions from various interactions.

7.3.1 Ion-specific parameters for alkali halides

For electrolyte systems, it is important to study their behavior in mixtures of different salts and solvents. For this reason, it becomes important to develop ion-specific parameter instead of salt specific parameters. Also, realizing the importance of ion-hydration, we have utilized the ion-hydration information at infinite dilution obtained from MD simulations to guide ion-specific parameter estimation. Fig. 7.5 shows the distribution of water around a sodium ion obtained from MD simulations.

Figure 7.4: Activity coefficients of alkali halides at 298.15 K. Symbols represent the experimental data [127] and lines are SAFT model results with 3 parameters for each salt.
Figure 7.5: Distribution of solvent around a sodium ion at infinite dilution and 4 molal obtained with MD simulations. The distribution for infinite dilution is used as a guide for parameter fitting in SAFT EoS.

Apart from the activity coefficient data at 298.15 K for the concentration range, we also use ion-solvation information to get physically meaningful parameters. We calculate the distribution of solvent around the ion at infinite dilution using the new theory and compare it with MD simulation results (Fig. 7.5). For concentrated solutions, we compared the densities of the solution with experimental data [5, 127]. It was observed that the density predictions, at high temperatures, with model were in excellent agreement with the experimentally [5, 127] observed values. Fig. 7.6 and 7.7 show the density prediction for aqueous NaCl and NaBr at different temperatures. Table 7.2 gives the ion specific parameters obtained based on SAFT model with an improved ion-solvent association.

Agreement is better than what has been reported in the literature for a model with as few parameters. Since ion-specific parameters were developed for SAFT EoS, the parameters for Na+, developed using NaCl as reference, were used for modeling NaBr as well. While, excellent agreement for densities is obtained, predicting activity coefficient at high temperature is still a challenge.
Figure 7.6: Density prediction of NaCl aqueous solution at different temperatures. Symbols represent the experimental data [4] and lines are predictions based on our SAFT model with improved ion-solvent association.

Figure 7.7: Density prediction for NaBr aqueous solution at different temperatures. Symbols represent the experimental data [5] and lines are predictions based on our SAFT model with improved ion-solvent association. Notice that for sodium ion, same parameters, developed with NaCl as reference, were used.
Table 7.2: Ion-specific parameters for aqueous NaCl and NaBr obtained with an improved ion-solvent association. $\epsilon_{iw}$ is the association strength for ion-water association and $\kappa_{iw}$ is the corresponding volume factor.

<table>
<thead>
<tr>
<th></th>
<th>Cation</th>
<th>Anion</th>
<th>Hydrated diameter</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\epsilon_{iw}/k_B(K)$</td>
<td>$\kappa_{iw}$</td>
<td>$\epsilon_{iw}/k_B(K)$</td>
</tr>
<tr>
<td>NaCl</td>
<td>3082.9</td>
<td>8.59E-03</td>
<td>1932.4</td>
</tr>
<tr>
<td>NaBr</td>
<td>3082.9</td>
<td>8.59E-03</td>
<td>1737.6</td>
</tr>
</tbody>
</table>

### 7.3.2 Application of new theory for calculating dielectric constant

We also studied the effect of using new ion-solvation theory with primitive models in getting insights for dielectric constant. The dielectric constant which is a fundamental property of solvents, is involved in all modern theories of aqueous solutions and determines the strength of electrostatic interactions of ionic solutes in solvents. Water has a high value of dielectric constant, which makes it a very good solvent for ionic and polar substances. When a salt is dissolved in water, the molar concentration of free water decreases due to hydration of ions. For mixed solvents as well, the dielectric constant will be a function of concentration. The addition of salt alters the electric configuration and decreases the influence of dipoles of the neighboring molecules on the moment of central molecule. A negative ion leaves water partially free to rotate and so saturates it less than a cation. Near an ion, the electric field experienced by a dipole is highly divergent and it experiences both attractive and orienting forces. Hence, for the first layer of molecules around an ion, the bulk dielectric constant of the medium is not relevant. This can be observed from the interaction energy between a point dipole and the electric field from an ion which is expressed as follows:
\[ w(r, \theta) = -\frac{\mu q}{4\pi \varepsilon_r \varepsilon_0} \frac{\cos \theta}{r^2} \] (7.28)

where \( \mu \) is the dipole moment, and \( \theta \) is the angle between the axis of dipole and the radius vector.

It can be observed from Eq. 7.28 that, as the distance from the ion increases the interaction energies decreases rapidly. Therefore, the effect of ion dipole interactions is maximum in the vicinity of ion. Correlations are, thus, needed for the dielectric constant vs. concentration relationships. Recently Maribo-Mogensen et al.[128] developed a methodology to calculate dielectric constant for mixture of solvents with an equation of state. It is based on the extension given by Fröhlich on the theory developed by Onsager [129] and Kirkwood [130] as follows:

\[
\frac{(2\varepsilon_r + \varepsilon_{\infty})(\varepsilon_r - \varepsilon_{\infty})}{\varepsilon_r(\varepsilon_{\infty} + 2)^2} = \frac{\rho}{9\varepsilon_0 kT} \sum_i x_i g_i \mu_{i,0}^2
\] (7.29)

where \( \varepsilon_{\infty} \) is the permittivity at infinite frequency, \( \varepsilon_r \) is the dielectric constant, \( \varepsilon_0 \) is the vacuum permittivity, \( x_i \) is the mole fraction of component \( i \), \( \rho \) is the number density, \( \mu_{i,0} \) is the vacuum dipole moment of component \( i \) and \( g \) is the Kirkwood factor accounting for the local structures. Maribo-Mogensen et al. [128] proposed a geometric model for calculation of the Kirkwood factor for a mixture of associating compounds and the final expression obtained is as follows:

\[
g_i = 1 + \sum_j z_{ij} P_{ij} \cos \gamma_{ij} \mu_{0,j} \frac{\mu_{i,0}}{P_i \cos \theta_{ij} + 1} \] (7.30)

where \( z_{ij} \) is the coordination number of molecule \( j \) around a central molecule \( i \), \( P_{ij} \) is the probability of molecules \( i \) and \( j \) being associated, \( P_i \) is the probability of the molecule \( i \) to be bonded to any other molecule, \( \gamma_{ij} \) is the angle between two dipole moments and \( \theta_{ij} \) is the rotation angle around hydrogen bond. Maribo-Mogensen
et al. [118] extended the above model to aqueous salt solutions by accounting for cancellation of dipole moments in the first hydration shells of ions and obtained the expression for static permittivity as follows:

\[
\frac{(2\varepsilon_r + \varepsilon_\infty)(\varepsilon_r - \varepsilon_\infty)}{\varepsilon_r} = \left(\frac{\varepsilon_\infty + 2}{3}\right)^2 \frac{\rho}{\varepsilon_0 k_B T} \sum_i x_i \Theta_i g_i \mu_{i,0}^2
\]

where \(\Theta_i\) is the fraction of component \(i\) that is not bound to an ion and is obtained from the probability

\[
\Theta_i = 1 - \sum_j P_{ij}
\]

Maribo-Mogensen et al. [118, 128] calculated these fractions from the SAFT association model where the number of sites on ion are fixed and are input to the model. As mentioned before, this method of assuming fixed number of sites for ion is not efficient for ions, the extension of this approach at high temperature is not sufficient. Incorporating an improved ion-hydration model to calculate dielectric with the above

Figure 7.8: Concentration dependence of dielectric constant of aqueous NaCl solution at 298.15 K.
theory, we were able to get very good agreement with less number of parameters (See Fig. 7.8). Also, as the model generates the hydration distribution and calculates the most probable coordination state, it has the ability of changing the coordination state based on temperature and concentration effects. Due to the inherent ability of this model to include the dielectric saturation effects and the reduction of dielectric constant with salt concentration, better estimation of temperature, pressure and concentration effects can be obtained compared to empirical models.

7.4 Conclusions

Short range structuring is important in determining the mean density of electrolyte systems. Ion water association or ion-hydration describes arrangement of water or solvent molecules around an ion. A new statistical mechanics based model has been implemented to describe molecular aspects of ion solvation. Hydration shell structure with the new approach agrees well with Monte Carlo and Molecular dynamic simulation results. A study is done to show that this novel approach can represent the hydration behavior in electrolyte systems better. Beyond ion solvation, for brines, the statistical associating fluid theory (SAFT) is used to model solvent association and long-range effects are obtained using an integral equation method. It is observed that prediction of solution density with the new ion-hydration model agrees well with experimental data at high temperatures. While, excellent agreement for densities is obtained, predicting activity coefficient at high temperature is still a challenge.
Chapter 8

Concluding discussions & future directions

Patchy colloids, model systems for associating fluids, can self-assemble into different structures based on the number, arrangement, and shape/size of the attractive patches. For example, by changing the number and arrangement of patches, different linear, triangular, or tetrahedral structures can be obtained. More complex geometries such as star polymers, kagome lattice structures, etc., can be observed when the attractive patch can bond multiple times. Such systems are being actively studied in designing materials from the nanoscale level. Also, the multi-bonding colloidal solutes have applications in various fields like advanced surfactant molecules, gelation, specific drug delivery, supramolecular polymers, and viscosity modifiers [12, 74–79]. In particular, studies have shown advantages of Janus particles as surfactant molecules and in stabilizing emulsions and foams [75, 80, 81] as compared to homogeneous molecules of the same size. These systems can be helpful models to understand short range ion-solvation and ion-pairing effects in electrolyte systems. Due to the limited knowledge of multi-body correlations, a general theory to describe the self-assembly and thermodynamics of these systems is not available. In this thesis, we have developed a simple and effective way to model multi-body effects in colloidal mixtures.

We have developed a new approach where we capture the multi-body correlations in the reference fluid using information about distribution of clusters around a distinguished solute molecule in the reference. These multi-body clusters were represented in terms of occupancy distributions to accurately describe the packing in the hard
sphere system. These occupancy distributions were obtained by particle simulations. Importantly, based on a quasichemical analysis of clustering around a distinguished solute and its interactions with the medium, we developed parametric models to describe occupancy distributions in the hard sphere systems of different densities and size asymmetries that can be readily incorporated in perturbation theories (for eg. statistical associating fluid theory).

Using the multi-body correlation information in the reference fluid we presented a perturbation theory for short-range association between a solute with isotropic association in a bath of patchy solvent molecules. The isotropic interactions of the solute can allow multiple solvent molecules to associate and hence multi-body effects become important for these systems. We discussed the limitation of earlier Marshall-Chapman approach that uses multi-body correlations for the reference in the gas phase together with an approximation for bulk solvent effects. We extended this Marshall-Chapman approach to incorporate information in all orders, not just pairs, of physical clusters in the reference. With an accurate model of packing effects, our approach gives excellent agreement with MC simulation for the symmetric and asymmetric associating mixtures. Analysis of a wide range of association and concentration regimes showed that our approach of incorporating complete hard sphere information accurately captures the behavior for bonding states, the prediction of the chemical potential contribution due to association is within \(1 \kappa_b T\) of the Monte Carlo simulation results.

A critical test was in analyzing the energy and entropy contributions to the chemical potential of the solute. For a system where solvent-solvent association is not present, such a decomposition of chemical potential in energy and entropy contributions with complete reference theory showed excellent agreement with MC sim-
ulations. The apparently reasonable agreement of the second order perturbation approach is shown to arise from the balancing of errors in the energy and entropy contributions. This important finding suggests the need to study different properties while validating perturbation theories for fluids.

The quasichemical (QC) approach offers a physically transparent and intuitive way to model the physics of association given the properties of a reference fluid. In particular, the approach provides a simple path to incorporate the physics of multi-body correlations. We studied solutes with varying patch sizes, ranging from a solute that bonds only once, to solutes with larger patch sizes including a Janus particle, and a particle whose entire surface is available for bonding, using quasichemical organization of the potential distribution theorem. We studied bonding of solute and solvent for a mixture of infinitely dilute multi-bonding solute with patchy solvent, in the absence of solvent-solvent bonding. In the context of such multi-body correlations, the QC approach led to the identification of a term, \( Q(i|n) \), that plays a central role in the theory. \( Q(i|n) \) is a reference fluid property that gives the average factors in isolated clusters with \( i \) particles being in the association patch volume given that \( n \) particles are in the spherical observation volume of the solute. For a generic bonding patch, we developed a Monte Carlo procedure for estimating \( Q(i|n) \); for limiting cases where the orientation of the solvent can be decoupled from occupancy in the solute’s inner-shell, we develop analytical expressions for \( Q(i|n) \). For such a mixture and for solutes with varying patch sizes, the theory led to predictions of bonding and occupancy that agree very well with results based on particle simulations. For the systems studied, the quasichemical approach also directly provides the excess chemical potential of the solute, as the logarithm of the monomer fraction of the solute molecule. With our QC approach we discovered that for limiting cases, the expression for the
nonbonded fraction of the solute is the same as the expression based on Wertheim’s theory/SAFT.

The QC approach for association is more straightforward for infinitely dilute solutes in the absence of solvent-solvent association. We implemented the multi-body effects based on the QC approach within Wertheim’s theory and presented a general molecular theory to study structure and phase behavior of mixtures of multi-bonding single site solutes in patchy colloid solvents. Marshall-Chapman theory, which was originally developed for spherically symmetric solute molecules with a second order perturbation, was extended to study different multiple bonding geometries of the solute beyond second order perturbation. We studied the effect of concentration and association strength on the thermodynamics of these mixtures. A detailed study for Janus particles was presented due to their application in physical systems. Our theory is able to capture accurately the behavior for different site geometries over a range of concentrations and association strengths. We also discover very low density gels for these mixtures based on the equilibrium phase studies. Experiments and theoretical investigations of these systems can prove rewarding in understanding different gel forming regions for these self-assembling mixtures.

We also study electrolyte systems based on the spherically symmetric interactions for ions with a TPT2 based approach for multi-body effects. The central challenge in describing electrolytes is the need to model both the long-range electrostatic interactions and the short range ion-water interactions. Variation of the short range interactions are expected to be important especially in challenging conditions of high temperature, high pressure and concentrated brines as encountered in deep off-shore oil and gas exploration. We focused on the short range aspect by specifically seeking to model coordination shell distribution (using data from molecular simulation
as reference). This model based on an improved ion-hydration provides an excellent
description of solution density for alkali halides studied in this work.

8.1 Future directions

In this thesis, we have extended Wertheim’s theory/SAFT beyond second order
perturbation by incorporating the physical understanding of the multi-body effects
based on the quasichemical organization of the potential distribution theorem. The
present approach can elucidate the structure and thermodynamics of mixtures of
patchy-solvent and multi-bonding single site solutes with size and interaction asym-
metry, cases where multi-body effects are potentially important. This work opens the
way to model, for example, ion-hydration, where multi-body effects are crucial and
can allow prediction of bulk and interfacial properties of fluids. We have also done
some preliminary analysis of the phase equilibrium behavior of these mixtures, and a
detailed analysis can provide insights into different regions of gel formation. Solvent-
solvent association interactions can also be analyzed within a quasichemical theory
approach for physical understanding of the various contributions to the chemical po-
tential. Following are some other future directions based on the theory developed in
this thesis.

8.1.1 Revisiting electrolyte model

The electrolyte model presented in chapter 7, where ion-solvation is modeled with
spherically symmetric interactions for ions, is based on a TPT2 approximation for
multi-body effects. With the accurate information of multi-body effects obtained
with the cluster distribution theory, this electrolyte model can be revisited to obtain
a more accurate model for ion-solvation. Also, the analysis of the effect of average
8.1.2 Complex patch geometries

The quasichemical theory based approach of obtaining multi-body information is unique and a central contribution of this work. This idea can be extended to study much complex ternary geometries of solute, such as “saturn rings” [27], that were hitherto out of bounds for statistical mechanical theories. The approach can also be implemented to multiple number of multi-bonding sites on the solutes. In our QC approach, the information about solvent orientation is separated from the radial occupancy around the solute molecules. Our approach can be extended to solutes that have multiple sites at small angles by incorporating the information about the solvent orientation within the isolated cluster simulations. Fig. 8.1 shows various examples of geometries on solute molecules that can be analyzed in future studies.
8.1.3 Water model

The role of different occupancy states in the hard sphere reference has also been identified in the study of hydrogen bonding in water [131]. These early models of water can be revisited based on the accurate information for occupancy distributions presented in this work.

8.1.4 Inhomogeneous systems

Janus particles, where the two hemispheres of the molecules have different interactions, are emerging as advanced surfactant molecules. This thesis presents first molecular model which can describe the thermodynamics of Janus solute particles in patchy solvents. Future work may extend these models to inhomogeneous systems.
Bibliography


