INFORMATION TO USERS

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

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

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

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

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

MOLECULAR SIMULATION AND THEORY OF
POLYATOMIC ASSOCIATING FLUIDS

by
Alejandro Javier García-Cuéllar

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

APPROVED, THESIS COMMITTEE

Walter G. Chapman, Chair
Associate Professor of Chemical Engineering

Constantine D. Armeniades
Professor of Chemical Engineering

John S. Hutchinson
Associate Professor of Chemistry

Houston, Texas
May, 1999
ABSTRACT

Molecular Simulation and Theory of Polyatomic Associating Fluids

by

Alejandro Javier García-Cuéllar

In this thesis the thermodynamic properties of model polyatomic molecules with association interactions was studied using molecular simulation and theory. The Metropolis Monte Carlo technique was used to perform simulations and the results were compared with extensions of Wertheim’s theory of association (first order thermodynamic perturbation theory, TPT1). Excellent agreement was found for wide ranges of state conditions.

The case of a telechelic polymer in an associating solvent was studied. This represented one of the first molecular simulation tests of TPT1 for mixtures. The effect of intramolecular association and ring formation was accounted for by a new statistical mechanical theory. The quantities of both intermolecular and intramolecular bonds that form in the chain can be predicted with theory and obtained from molecular simulation. Thermodynamic properties were also calculated and good agreement was obtained.

The limit of complete bonding of the theory for intramolecular association gives an equation of state for cyclic molecules. The case when these cyclic molecules associate is studied for trimer cyclics with one and three bonding sites. The effect of shape and association is captured by the resulting theory. Similar models could be used to study
dendritic structures. The agreement with simulation is remarkable for a wide range of densities and bonding energies.

The case of a chain molecule with a varying density of bonding sites was simulated along with an associating solvent. The solvent molecules can associate with the chains and with themselves. This is another simulation study of mixtures of molecules with dissimilar sizes. The effect of bonding site density on the distribution of bonds in the solvent and on thermodynamic properties was examined with simulation and theory. TPT1 agrees well with the simulation results.
ACKNOWLEDGMENTS

I wish to express my gratitude to the following individuals and institutions.

Professor Walter G. Chapman, for his expert guidance, kind disposition, and patience throughout the project.

Professors Constantine D. Armeniades and John S. Hutchinson, for serving in my thesis committee.

The faculty and staff of the Department of Chemical Engineering, as well as my fellow graduate students. They all made this place extraordinary.

Research group members, former and current, who contributed so much at all stages of my work.

All my friends in Houston, who provided invaluable support and great times. The memories will surely last a lifetime.

Rice University, The Robert A. Welch Foundation, and The Petroleum Research Fund, for financial assistance.

My whole family, for their love, support, and prayers. This thesis is dedicated with love to my parents, Idalia and Roberto Sergio.
TABLE OF CONTENTS

ACKNOWLEDGEMENTS iv

LIST OF FIGURES viii

LIST OF TABLES xi

1 INTRODUCTION 1
   1.1 Molecular Interactions 1
      1.1.1 The Hydrogen Bond and Charge-Transfer Complexes 3
   1.2 Associating Fluids and Their Salient Features 5
   1.3 Thesis Outline 9
   1.4 Conclusions 11

2 THEORIES FOR ASSOCIATING FLUIDS 12
   2.1 Theories of Solutions 12
   2.2 Chemical Theory of Solutions 16
   2.3 Statistical Mechanics Based Theories of Association 17
      2.3.1 Lattice Theories 18
      2.3.2 Perturbation Theories 18
   2.4 Conclusions 22

3 WERTHEIM'S THEORY OF ASSOCIATION 23
   3.1 Elements of the First-Order Thermodynamic Perturbation Theory 23
   3.2 The Statistical Associating Fluid Theory Equation of State 29
      3.2.1 Development of the Equation of State 29
      3.2.2 Applications 35
3.3 Conclusions

4 MOLECULAR SIMULATION

4.1 Molecular Simulation Methods

4.2 The Classical Approximation and Thermodynamic Ensembles

4.3 The Metropolis Monte Carlo Method

4.4 Implementation

4.5 Correlation Functions

4.6 Conclusions

5 SOLVENT EFFECTS ON MODEL TELECHELIC POLYMERS

5.1 Introduction

5.2 Simulation

5.3 Theory

5.3.1 Distribution of Bonds

5.3.2 Thermodynamics

5.4 Results and Discussion

5.5 Conclusions

6 THEORY AND SIMULATION FOR ASSOCIATING CYCLIC MOLECULES

6.1 Introduction

6.2 Molecular Model and Simulation

6.3 Theory

6.4 Results and Discussion

6.4.1 One Association Site (M=1)
6.4.2 Three Association Sites (M=3)  

6.4.3 Change in Compressibility Factor Due to Association  

6.5 Conclusions  

7 MULTIPLE BONDING SITES ON CHAIN MOLECULES IN AN ASSOCIATING SOLVENT  

7.1 Introduction  

7.2 Molecular Models and Simulation  

7.3 Theory  

7.3.1 Two Association Site  

7.3.2 Three Association Sites  

7.3.3 Thermodynamics  

7.4 Results and Discussion  

7.4.1 Results for Chains with Two Association Sites  

7.4.2 Results for Chains with Three Association Sites  

7.5 Conclusions  

8 CONCLUSIONS AND FUTURE WORK  

REFERENCES
**LIST OF FIGURES**

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>Pair potential energy, $\phi$, as function of particle-particle distance, $r$</td>
<td>4</td>
</tr>
<tr>
<td>3.1</td>
<td>Schematic representation of the effects accounted for in SAFT</td>
<td>30</td>
</tr>
<tr>
<td>4.1</td>
<td>Independent testing of theory approximations from inaccuracies in the potential of interaction as related to molecular simulation and experiment</td>
<td>38</td>
</tr>
<tr>
<td>4.2</td>
<td>Application of periodic boundary conditions in molecular simulation</td>
<td>43</td>
</tr>
<tr>
<td>5.1</td>
<td>Intermolecular and intramolecular bonding of model telechelic molecules</td>
<td>50</td>
</tr>
<tr>
<td>5.2</td>
<td>Model hydrogen bonding solvent and interaction between two solvent molecules</td>
<td>52</td>
</tr>
<tr>
<td>5.3</td>
<td>Cross interaction between a solvent molecule and a tetramer</td>
<td>54</td>
</tr>
<tr>
<td>5.4</td>
<td>Average fraction of unbonded chain and solvent molecules as a function of solvent mole fraction</td>
<td>67</td>
</tr>
<tr>
<td>5.5</td>
<td>Average number of interchain and intramolecular bonds per chain molecule as a function of solvent mole fraction</td>
<td>68</td>
</tr>
<tr>
<td>5.6</td>
<td>Average number of cross and solvent-solvent bonds per sphere as a function of solvent mole fraction</td>
<td>73</td>
</tr>
<tr>
<td>5.7</td>
<td>Average configurational internal energy as a function of solvent mole fraction</td>
<td>74</td>
</tr>
<tr>
<td>5.8</td>
<td>Compressibility factor as a function of solvent mole fraction</td>
<td>75</td>
</tr>
<tr>
<td>6.1</td>
<td>Tangent hard sphere cyclic molecules with association sites</td>
<td>80</td>
</tr>
<tr>
<td>6.2</td>
<td>Relative position vectors between two cyclic molecules</td>
<td>81</td>
</tr>
<tr>
<td>6.3</td>
<td>Interaction between two tangent hard sphere cyclic molecules</td>
<td>82</td>
</tr>
</tbody>
</table>
Figure 6.4 Reduced configurational energy as a function of reduced energy for the model system with one association site ($M=1$) 88

Figure 6.5 Compressibility factor as a function of reduced energy for the model system with one association site ($M=1$) 90

Figure 6.6 Fraction of molecules not bonded as a function of reduced energy for the model system with three association sites ($M=3$) 94

Figure 6.7 Reduced configurational energy as a function of reduced energy for the model system with three association sites ($M=3$) 95

Figure 6.8 Compressibility factor as a function of reduced energy for the model system with three association sites ($M=3$) 97

Figure 6.9 Change in compressibility factor due to association as a function of average number of bonds per molecule for the model system with one association site ($M=1$) 98

Figure 6.10 Change in compressibility factor due to association as a function of average number of bonds per molecule for the model system with three association sites ($M=3$) 99

Figure 7.1 Model chain molecules with two and three association sites 104

Figure 7.2 Model hydrogen bonding solvent and interaction between two solvent molecules 105

Figure 7.3 Cross interaction between a solvent molecule and a flexible chain 107

Figure 7.4 Two association site model $NVT$ results for average configurational internal energy and fraction of unbonded chain and solvent molecules 119
Figure 7.5  Two association site model $NVT$ results for average configurational internal energy and fraction of unbonded chain and solvent molecules

Figure 7.6  Two association site model $NVT$ results for average ratio of cross bonds of solvent molecules to total bonds

Figure 7.7  Two association site model $NpT$ results for average configurational internal energy, compressibility factor, and fraction of unbonded chain and solvent molecules

Figure 7.8  Two association site model $NpT$ results for average configurational internal energy, compressibility factor, and fraction of unbonded chain and solvent molecules

Figure 7.9  Three association site model $NVT$ results for average configurational internal energy and fraction of unbonded chain and solvent molecules

Figure 7.10 Three association site model $NVT$ results for average configurational internal energy and fraction of unbonded chain and solvent molecules

Figure 7.11 Three association site model $NVT$ results for average ratio of cross bonds of solvent molecules to total bonds

Figure 7.12 Three association site model $NpT$ results for average configurational internal energy, compressibility factor, and fraction of unbonded chain and solvent molecules

Figure 7.13 Three association site model $NpT$ results for average configurational internal energy, compressibility factor, and fraction of unbonded chain and solvent molecules
LIST OF TABLES

Table 1.1 Relative strengths of different types of interactions 7

Table 1.2 Some properties of the isomers ethanol and dimethyl ether. 8

Table 5.1 Values for parameter $D$ for tetramers 65

Table 5.2 $NVT$ simulation results for average fraction of unbonded chain and solvent molecules, and for average reduced configurational energy 66

Table 5.3 $NVT$ simulation results for average fraction of chain molecules bonded intermolecularly and intramolecularly 69

Table 5.4 $NVT$ simulation results for average fraction of solvent molecules Bonded to a chain molecule and to a like molecule 70

Table 5.5 $NpT$ simulation results for average compressibility factor, average fraction of unbonded chain and solvent molecules, and for average reduced configurational energy 71

Table 6.1 $NVT$ simulations of associating cyclic trimers with one site ($M=1$). Results for average reduced configurational energy 87

Table 6.2 $NpT$ simulations of associating cyclic trimers with one site ($M=1$). Results for average reduced configurational energy and average compressibility factor 89

Table 6.3 $NVT$ simulations of associating cyclic trimers with three sites ($M=3$). Results for average fraction of unbonded molecules and average reduced configurational energy 91
Table 6.4 \( NpT \) simulations of associating cyclic trimers with three sites (\( M=3 \)).
Results for average fraction of unbonded molecules, average reduced configurational energy, and average compressibility factor 92

Table 6.5 \( NpT \) simulations of non-associating cyclic trimers of hard sphere segments.
Results for average compressibility factor 96

Table 7.1 Two site model \( NVT \) simulations for average fraction of unbonded chain and solvent molecules, and for average reduced configurational energy 114

Table 7.2 Three site model \( NVT \) simulations for average fraction of unbonded chain and solvent molecules, and for average reduced configurational energy 115

Table 7.3 Two site model \( NpT \) simulations for average fraction of unbonded chain and solvent molecules, and for average reduced configurational energy 116

Table 7.4 Three site model \( NpT \) simulation results for average fraction of unbonded chain and solvent molecules, for average reduced configurational energy, and average compressibility factor 117

Table 7.5 Two site model \( NVT \) simulations for the average ratio of cross bonds to total bonds formed by the solvent molecules 118

Table 7.6 Three site model \( NVT \) simulations for the average ratio of cross bonds to total bonds formed by the solvent molecules 120
INTRODUCTION

Association has been of interest to scientists and engineers due to the highly nonideal thermodynamic behavior that it causes in fluids. Numerous attempts to describe theoretically the phase behavior and thermophysical properties of these systems have been made. This represents a true challenge due to the complexity of the molecular interactions, but nevertheless it is of great practical importance to possess a reliable theory for this process that occurs throughout industry and nature.

The cause of departure from ideality in fluids is the interactions between molecules. These are discussed in the next section, paying special attention to hydrogen bonding. Subsequently, a brief description of what makes associating fluids so peculiar is given.

1.1 Molecular interactions

In the ideal gas, the molecules do not interact with each other in any way. Thus, the exact results for the properties of this fluid may be obtained from statistical mechanics. However, real particles exert forces on one another. Let us first identify the origin of the predominant forces that determine these properties. Maitland et al. [1] make one such analysis and classify forces between particles in electromagnetic, gravitational, strong nuclear forces and weak nuclear forces (this latter type is of electromagnetic nature). Both nuclear forces are very short-range and circumscribed to the nucleus of the atom. Gravitational force is long-range, but of many orders of magnitude less than that of a
typical molecular interaction for a given separation. Therefore, it can be inferred that the important forces are those caused by the electromagnetic interactions between protons and electrons. It is convenient to break down further the different types of interactions to understand them better.

There exist repulsive and attractive forces. The former result from electron cloud overlaps between molecules at short range. The Pauli exclusion principle dictates that the involved electrons restrain from occupying the overlap volume at the same time, causing the two nuclei to be more exposed to each other with the consequent repulsion of their like charges.

Attraction manifests itself at longer range and is caused by three distinctive kinds of energy. Standard electrostatic energy is present between molecules with electric moments due to their electric charge distribution. Induction energy arises when a molecule sees its charge distribution changed by the influence of that of a second molecule as in a non-polar molecule that develops an induced dipole when in the presence of a dipolar molecule. Finally, dispersion energy results from the quantum mechanical fact that electrons are in rapid motion around the nucleus, generating at any given time an instantaneous dipole that can in turn induce a dipole in another molecule and in this way produce an attractive interaction.

Repulsive forces almost completely define the structure of simple liquids at high density, while attractive forces provide the necessary cohesion for the molecules, without having a great impact on structure (at low densities, e.g., near the critical point, attraction
becomes more important) [2]. Perturbation theories rely on this important result, as it will be discussed in §2.3.2.

It is obvious at this point that the degree of complexity of molecular interactions is enormous. If one were to consider rigorously all of these contributions, the endeavor becomes in most cases intractable. Therefore, reasonable simplifications must be made. It is in this way that model intermolecular potential energy functions are introduced [3]. Statistical mechanics makes frequent use of pair potential models for simple spherical, non-polar molecules, such as the hard sphere, the square well, and the Lennard-Jones potentials (to name only a few), each of increasing realism but also of increasing complexity (see Fig. 1.1).

It is interesting to point out that we can obtain the same value for any single thermodynamic property using potentials that are very different from each other (e.g., square-well and Lennard-Jones). Thus, agreement between the model and experiment does not guarantee that the true potential of interaction is that of the proposed potential-energy function [4, 5]. That model potentials are not necessarily the real potentials should not stop us from using them to advantage. There exist simple potentials that retain the essential physics of real systems and that have been widely studied. In this way, the results obtained for simple model particles, for example hard spheres, can be used in powerful methods like perturbation theory (see §2.3.2) [2].

1.1.1 The Hydrogen Bond and Charge-Transfer Complexes

A special case of dipolar interaction, known as hydrogen bonding, plays a preeminent
\[
\phi(r) = \begin{cases} 
\infty & r < \sigma \\
0 & \sigma \leq r
\end{cases} \quad \phi(r) = \begin{cases} 
\infty & r < \sigma \\
-\epsilon & \sigma \leq r < D\sigma \\
0 & D\sigma \leq r
\end{cases} \quad \phi(r) = 4\epsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^{6} \right]
\]

(a) \hspace{2cm} (b) \hspace{2cm} (c)

**Figure 1.1** Pair potential energy, $\phi$, as function of particle-particle distance, $r$, and parameterized by one or two molecular diameters, $\sigma$ and $D\sigma$, and a characteristic energy, $\epsilon$. (a) Hard sphere potential. (b) Square-well potential. (c) Lennard-Jones potential.

role in association and thus will be discussed here in detail [6]. When a hydrogen atom forms a covalent bond with an electronegative atom such as oxygen, nitrogen or fluorine, its small nucleus is found almost bare of its electron, now shared in the covalent bond. Moreover, the electronegative atom contains lone pairs of electrons, that along with the positively charged nucleus, form a dipole. The small size of the hydrogen atom nucleus allows it to come close to a second electronegative atom, giving rise to a stronger than typical dipole-dipole interaction.
Examples of molecules that present hydrogen bonding include water, amines, alcohols, ammonia and carboxylic acids [3]. The force is fairly strong and directional, causing the formation of short-lived clusters that can be detected by spectroscopic methods such as absorption of infrared, ultraviolet and visible light. According to Prausnitz et al. [4] the typical hydrogen bond energy is between 8 and 40 kJ/mol, only one order of magnitude less than that of a covalent bond (200 to 400 kJ/mol). In addition, the two bond distances (X-H---Y) are smaller than the sum of the corresponding van der Waals radii. As we have seen, the nature of the two types of bonds is different and this is why the effect of hydrogen bonding is seen on the physical properties rather than on the chemical properties (see §1.2).

Charge-transfer complexes present a second kind of interaction that gives rise to association. The most common methods to detect the formation of this type of complex are ultraviolet spectroscopy and thermodynamic measurements, for example volumes and enthalpies of mixing which take negative values [4]. A typical example is the complex formed between benzene and halogen molecules (e.g., iodine). This is an interaction of quantum mechanical nature where a loose bond is formed which is thought, in the case of the previously mentioned example, to keep the axis of symmetry of the halogen molecule perpendicular and pointing to the center of the benzene ring plane [3].

1.2 Associating Fluids and Their Salient Features

It is the complex behavior of associating fluids that makes them so interesting. Their physical properties are drastically different from those of similar molecules that lack the
hydrogen bonding interaction. Table 1.1 taken from the book by Israelachvili [6] shows this very well. The normal boiling point of fluids of similar molecular weight increases for molecules that can associate. This denotes the higher cohesion that exists between these molecules.

Prausnitz et al. [4] use Table 1.2 to illustrate the effect of hydrogen bonding in yet another physical property. This table compares some properties of ethanol and dimethyl ether, both molecules having the same formula: C₂H₆O. In this case, the latent heat of vaporization is higher for ethanol, the molecule that can hydrogen bond. This is also a result of the stronger attraction that exists between associated molecules. The same occurs with the normal boiling points that are different by more than 100 °C. Trouton’s “constant” or rule is greater than the normal range (75-90 J/K mol [6]) for ethanol, again because of association. Finally, ethanol is infinitely soluble in water and dimethyl ether only partially soluble as expected due to hydrogen bond formation between ethanol and water.

Water shows a few other peculiarities that arise from its ability to associate [6]. In addition to having high boiling and melting points and high heat of vaporization (considering its low molecular weight) it shows a maximum in density at 4°C. The arrangement between water molecules is tetrahedral (i.e. four nearest neighbors) and ice is less dense than liquid water, suggesting an almost perfect ordering of the molecules through hydrogen bonds in the solid and a somewhat more disordered structure in the liquid, with molecules packed more closely.
Table 1.1 Relative strengths of different types of interactions as reflected in the boiling points of compounds. † Taken from Ref. 6.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Molecular weight</th>
<th>Dipole moment (D)</th>
<th>Boiling point (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethane</td>
<td>CH₃CH₃</td>
<td>30</td>
<td>0</td>
</tr>
<tr>
<td>Formaldehyde</td>
<td>HCHO</td>
<td>30</td>
<td>2.3</td>
</tr>
<tr>
<td>Methanol</td>
<td>CH₃OH</td>
<td>32</td>
<td>1.7</td>
</tr>
<tr>
<td>n-Butane</td>
<td>CH₃CH₂CH₂CH₃</td>
<td>58</td>
<td>0</td>
</tr>
<tr>
<td>Acetone</td>
<td>CH₃COCH₃</td>
<td>58</td>
<td>3.0</td>
</tr>
<tr>
<td>Acetic acid</td>
<td>CH₃COOH</td>
<td>60</td>
<td>1.5</td>
</tr>
<tr>
<td>n-Hexane</td>
<td>CH₃(CH₂)₄CH₃</td>
<td>86</td>
<td>0</td>
</tr>
<tr>
<td>Ethyl propyl ether</td>
<td>C₃H₁₂O</td>
<td>88</td>
<td>1.2</td>
</tr>
<tr>
<td>1-Pentanol</td>
<td>C₅H₁₁OH</td>
<td>88</td>
<td>1.7</td>
</tr>
</tbody>
</table>

† In order to make comparisons meaningful, molecules have been put into three groups of similar molecular weights and size. Within each group the first molecule is non-polar and interacts purely via dispersion forces, the second is polar and the third also interacts via H-bonds.
Table 1.2 Some properties of the isomers ethanol and dimethyl ether. Taken from Ref. 4.

<table>
<thead>
<tr>
<th></th>
<th>Ethanol</th>
<th>Dimethyl ether</th>
</tr>
</thead>
<tbody>
<tr>
<td>Normal boiling point (°C)</td>
<td>78</td>
<td>-25</td>
</tr>
<tr>
<td>Enthalpy of vaporization at normal boiling point (kJ / mol)</td>
<td>42.6</td>
<td>18.6</td>
</tr>
<tr>
<td>Trouton’s constant † (J mol / K)</td>
<td>121</td>
<td>74.9</td>
</tr>
<tr>
<td>Solubility in water at 18 °C and 1 bar (g / 100 g)</td>
<td>∞</td>
<td>7.12</td>
</tr>
</tbody>
</table>

† Trouton’s constant is the entropy of vaporization at the normal boiling point

Besides affecting these physical properties and the arrangement of the molecules, association also affects phase behavior. One example is telechelic polymers, where the ability of the chain molecule to hydrogen bond with other chains and with itself can affect the phase behavior in a nontrivial way (see Chapter 5). It is also known that clathrate formation in gas hydrates is due to the tetrahedral coordination of water molecules into small “cages” around a solute with the subsequent impact on phase behavior and thermophysical properties. Another example closely related is asphaltene precipitation. This is a major safety hazard in oil pipelines where clogging can cause explosions and the interruption of operations. Association has been found to be responsible in part for this phenomenon when (at certain operating state conditions) precipitation occurs. Being able to predict this phase behavior would be most valuable.
The importance of association and specifically the hydrogen bond to living organisms is seen clearly in the DNA double helix where the two strands are kept together by hydrogen bonds, as well as in the example of protein folding and unfolding, where the "hydrophilic" and hydrophobic effects are noticeable [6]. A hydrogen bonding group may find itself avoiding contact with the solvent molecules or on the contrary, trying to interact as much as possible with the solvent, depending of how favorable thermodynamically an interaction is. The formation of bonds decreases internal energy but the ordering that results decreases entropy which is an unfavorable situation. There is a delicate balance that determines the extent of hydrogen bonding. A better understanding of this phenomenon is important for improvement and innovation in these and many other fields in industry and science.

1.3 Thesis Outline

The purpose of the first four chapters of the thesis is to present the reader with relevant background to deal successfully with the subject of associating fluids. This includes reviewing the various existing theories used to describe their behavior, the types of systems where they are found, and the computational techniques commonly used for their study.

In this first chapter the origins of nonideal behavior in associating fluids were reviewed. By presenting some basic principles of intermolecular interactions and the nature of the hydrogen bond the stage is set to better describe and explain association.
In Chapter 2, theories that have been proposed to explain association in fluids are discussed, along with their relative strengths and drawbacks.

A particular theory is selected in Chapter 3 to be investigated further. This is the first-order thermodynamic perturbation theory (TPT1) due to Michael S. Wertheim [7-11] and its extensions, that have become known as the statistical associating fluid theory equation of state (SAFT EOS) and is discussed in greater detail. This choice is justified by reviewing recent reports that indicate that SAFT is useful in describing and predicting the thermodynamic properties of a wide variety of complex systems.

Chapter 4 presents the computer simulation method used to obtain the results in the remainder of the thesis. The molecular simulation technique known as Metropolis Monte Carlo is used to test rigorously and to validate the approximations made in arriving to the proposed theories. Also, the elements of statistical mechanics necessary for these studies are briefly discussed.

The results of computer simulations of model molecules in Chapters 5 through 7 test the SAFT equation of state and some proposed extensions for various systems. The sound fundamental basis of this approach should prove valuable for both industrial and academic applications.

Chapter 5 presents simulation results for a model telechelic polymer along with an associating solvent. A theory for intramolecular association improves SAFT and by using these two approaches jointly, the thermodynamic properties and bonding distributions of this system are explained.
Chapter 6 contains results for associating cyclic molecules. The effect of both shape and association in cyclic trimers is studied using the cyclic equation of state of Ghonasgi et al. [12, 13] and Wertheim’s theory of association.

Further studies of TPT1 and its applicability to mixtures of associating compounds appear in Chapter 7. The effect of number and spacing of association sites of a tangent hard-sphere chain molecule in solution with hard spheres with association sites is examined.

In Chapter 8 conclusions for this work are presented and recommendations for future research are made.

1.4 Conclusions

Departures from ideal behavior in fluids arise from the interactions between their molecules. These interactions are of electromagnetic nature and are both attractive and repulsive. In the vast majority of associated fluids, the molecules interact through the formation of hydrogen bonds or charge-transfer complexes. The direct consequence of association is a considerable effect in the physical properties of systems that present this phenomenon, which are as varied and apparently apart as protein folding and gas hydrate formation. The possibility of describing and explaining association in a fairly fundamental way is the motivation for the work presented herein.
THEORIES FOR ASSOCIATING FLUIDS

The nature of the interactions that give rise to association, the effects that hydrogen bonding has on physical properties, and various examples where this phenomenon is important, have been discussed in the previous chapter. Let us now turn to reviewing the different approaches that have been used to explain the behavior of associating fluids both qualitatively and quantitatively.

First, a review of theories of solutions is made since in most cases they constitute the basis for proposed theories of associating fluids. These generally fall in one of two broad classes: chemical theory and statistical mechanical theories. The theories are reviewed and their usefulness briefly discussed.

2.1 Theories of Solutions

A brief discussion of the most commonly used theories of solutions is presented in this section. This treatment follows closely that of Prausnitz et al. [14], Chapter 7. All theories try to make sensible approximations as to what the excess Gibbs energy of mixing is, by making considerations about the excess enthalpy and entropy of mixing. This will limit the applicability of the theories as is discussed next.

The first theory to be considered is that of van Laar [15]. Using the van der Waals equation of state (vdW EOS), he considered mixing two components assuming a process with zero volume change and zero excess entropy of mixing. Van Laar obtained an
expression for excess Gibbs energy (and hence, the activity coefficients) as a function of pure component vDW EOS parameters, temperature and composition. The mixing rules used by van Laar result invariably in positive deviations from Raoult’s law. Therefore, the two parameters that appear in the expressions for the activity coefficients of a binary mixture are often regressed to fit experimental data, although in this way the model loses predictive capability.

The theory of Scatchard-Hildebrand [16, 17] improves that of van Laar by defining the cohesive energy density and the solubility parameter for like and unlike molecular interactions of the components of the mixture. The vdw (or any other) equation of state is no longer needed. The assumptions of zero excess entropy of mixing and zero change in volume are still in effect. The choice of a geometric mean of the pure component parameters to obtain the cohesive energy density of the unlike interactions causes this theory to also predict positive deviations from Raoult’s law. The cases where this model works best are for non-polar molecules that form highly non-ideal mixtures. This theory is readily extended to mixtures.

Because of the assumption of zero excess entropy of mixing, the theories of van Laar and Scatchard-Hildebrand perform poorly for hydrogen bonded, polar, and polymeric molecules.

Lattice theory is an alternative method for the development of theories of solutions. In this approach, the liquid is seen more as a solid with a very ordered structure than as a gas. Again, the Gibbs excess energy is taken to be approximately equal to the excess
internal energy. This time, however, the molecules are restricted to occupy specific sites on the lattice, and consequently, the total number of combinations of the arrangement of the molecules can be calculated assuming complete randomness, that all lattice sites are occupied, and that all molecules are the same size [18]. The interactions between the like and unlike molecules are taken into account to calculate the potential energy of the system, considering pairwise additivity and assuming that only nearest neighbor interactions contribute. The result is an expression for excess Gibbs energy as a function of an interchange energy (dependent on the strength of the different pair interactions), temperature, and composition.

The quasi-chemical approximation of Guggenheim [19] introduces the notion of non-randomness in the previous formalism. This is done by defining an equilibrium constant that relates the number of like neighbor pairs to unlike neighbor pairs and that depends on the interchange energy and the temperature. In this theory the excess entropy of mixing is no longer zero.

A very important advance in this approach accounts for the different size of molecules and is known as the Flory-Huggins model [20-23]. This model takes into consideration the chain connectivity of the segments (or repeat units) that make up a larger molecule, such as a polymer chain. Each segment sits on a single lattice site and is the same size as the solvent molecules. The total number of combinations in which the molecules can be arranged on the lattice is affected by the aforementioned connectivity. Flory and Huggins independently calculated the appropriate statistics to obtain the excess
entropy of mixing the chain and solvent molecules, which is a function of volume and mole fractions. Their result is valid for athermal solutions, i.e., those cases where the excess enthalpy of mixing is zero. To obtain a more accurate expression for excess Gibbs energy, an expression similar to the Scatchard-Hildebrand theory is adopted to approximate the excess enthalpy of mixing as a function of temperature, volume fractions, and solution volume. Flory-Huggins theory is the basis for most of the preferred treatments for polymer solution thermodynamics (see also §2.3.2).

An extension of the Flory-Huggins theory of athermal solutions made by Wilson exploits the concept of local compositions, which in his empirical approach are proportional to the mole fractions and Boltzmann factors of the like and unlike strengths of interaction. No correction is made to the athermal assumption and the excess Gibbs energy is a function of volume and mole fractions, and the different molecular interactions. A similar approach is that of the non-random two-liquid (NRTL) theory of Renon and Prausnitz [24].

Group contribution methods are in essence correlations that consider that an arbitrary collection of atoms (a functional group) has the same type of interaction in a molecule despite what the rest of the molecule is. UNIFAC (universal functional activity coefficient) [25, 26] and ASOG (analytical solution of groups) [27, 28] are two examples of methods that follow this approach. Experimental results are used to fit the values for the parameters needed for excess property estimation and lengthy tables of group interaction parameters have been compiled.
Integral equation theories that have been successful in describing the liquid state include the Born-Green [29], Percus-Yevik [30], and hypernetted chain theories [31-35]. The approach is to suggest a mathematical representation for the correlation function of the fluid along with some appropriate simplifications to attain, in most cases, a numerical solution. These are theories mainly of the fluid structure and the thermodynamic quantities obtained are often times inconsistent, due to the approximations made [36].

Perturbation theories (which include conformal solution theory, as Hansen and McDonald suggest [2]) are discussed in §2.3.2.

It is worth mentioning that the preceding presentation is by no means an exhaustive review of theories of solutions. Also, a special note needs to be made about models for electrolyte solutions that are necessarily more elaborate and fall beyond the scope of this research.

2.2 Chemical Theory of Solutions

In 1908, Dolezalek [37] proposed the chemical theory of solutions, which has been used to explain the properties of associated fluids. This method essentially takes into consideration all the possible clusters that can form when a species is capable of associating into dimers, trimers, etc. In this way, chemical reactions are written down for all the pseudo components. In the case of dimers we have, for instance

\[ A + A \rightleftharpoons A_2 \]  \hspace{1cm} (2-1)

and in general
\[ nA \leftrightarrow A_n. \] (2-2)

This approach needs the equilibrium constants for all "reactions" involved and is complete only after it is determined which are all the pseudo components that are formed. Moreover, for accurate phase behavior calculations it is necessary to obtain the activity coefficients for all pseudo components, which further complicates matters. The approach is correct, but impractical for most cases. The large number of parameters that are needed, and the lack of a general formulation (the reactions and phase equilibrium relations need to be written for each particular case) make this treatment cumbersome, except for the simplest systems.

Some work has been done [38-43 as discussed in 44] in coupling the chemical theory of solutions to an equation of state to obtain a closed form valid for a wide range of densities and include association. These equations are generally not easy to extend to mixtures, depend on special mixing rules, and as in the chemical theory, need the relevant "reactions" for all the pseudo components that form [44].

2.3 Statistical Mechanics Based Theories of Association

Statistical mechanical methods have resulted in several theories for the study of association. Lattice theories rely on a solid-like picture of fluids, while perturbation theories use the well-known properties of a reference fluid, in most cases the hard sphere fluid, and correct upon it. In the first case, the effect of association is factored out from the partition function and in the second it is included as a perturbation term.
2.3.1 Lattice Theories

The following equation for the partition function of the lattice fluid, in general, is assumed to include the effect of association in lattice theories:

\[ Q = Q_{LF} Q_{H}. \tag{2-3} \]

This particular separation is suggested by Sanchez and Panayiotou [45]. Here, \( Q_{LF} \) is the "physical" contribution to the partition function and \( Q_{H} \) the "chemical" (association) contribution. \( Q_{LF} \) is the lattice partition function for the Sanchez-Lacombe equation of state for polymers [46, 47] and \( Q_{H} \) is the correction à la Guggenheim [18, 19] for association, i.e., a quasi-chemical expression with an equilibrium constant for a general "reaction" of the associated species that can form.

Similar approaches have been presented for other lattice theories and the closely related theories based on local compositions [46-55 as discussed in 14], but in general the parameters needed to obtain phase equilibria are different to those used for excess properties.

2.3.2 Perturbation Theories

In perturbation theory, the properties of a real fluid are related to a not too dissimilar reference fluid for which the properties are well known [2, 36, and 56]. The van der Waals equation of state (vdW EOS) represents one of the earliest successful perturbation theories [57].
Van der Waals pictured a fluid consisting of attractive spheres with hard cores and assumed that the effects of molecular interactions could be separated into repulsion and attraction. He proposed the following analytical expression to express this idea:

$$P = \frac{RT}{v-b} - \frac{a}{v^2}.$$  (2-4)

Here, $P$ is pressure, $R$ the universal gas constant, $T$ the absolute temperature, $v$ the molar volume and $a$ and $b$ are positive constant parameters for each particular substance.

The first term in the right hand side of Eq. 2-4 is the repulsive contribution to the pressure. The basic idea is the concept of excluded volume, i.e., that for molecules of nonzero volume not all the system volume is accessible due to molecular collisions. Assuming $b$ equal to four times the volume of a spherical molecule, van der Waals intended to capture this effect. Nevertheless, this is a good approximation only at low densities, but not very much so when closer packing of the molecules reduces this value (although paradoxically, it is exact for a hard sphere fluid in one dimension [57]). The second term in the equation is known as the internal pressure, and arises from the assumption of a weak, long-range attraction between the molecules.

It is remarkable that such a simple theory can account for such a wide range of fluid states, from liquid to gas, to supercritical. Thus, much effort has been made to improve the vdW EOS. The advent of computer simulations made it possible to obtain the equation of state for hard spheres in three dimensions by Carnahan and Starling [58], providing the thermodynamic properties for the vdW EOS reference fluid. Work by
several researchers [59, 60] used the concept of molecules with hard cores and small attractive forces (usually of the Lennard-Jones type) as a perturbation. Two refined theories [61, 62] treat the repulsive interaction as being of a “soft” nature and therefore the hard core diameter is a decreasing function of collision energy [57]. This approach to atomic, spherical, neutral molecules is similar in principle to the more complex case of molecular fluids. For the case of mixtures, the previous approach is readily extended without further complication [2].

An approach especially devised for mixtures is conformal solution theory. The fundamental idea is that of corresponding states theory, i.e., to consider a mixture to be a hypothetical fluid with critical constants obtained from the critical constants of the pure components with the mixing rules of the vdW EOS for mixtures. This is equivalent to a perturbation expansion about a reference system with parameters $\varepsilon_z$ and $\sigma_z$ (assuming a force model of the form: $\phi(r) = \varepsilon f(r/\sigma)$ for the pure fluids and the mixture) in powers of the individual pure fluid parameters $\varepsilon\sigma^3$ and $\sigma^3$ [2]. If we assume a mixture of two hypothetical components using the previous mixing rules, we obtain a so-called two-fluid theory [63]. For good results the molecules should be conformal, i.e., similar in shape and size [36].

As for the effect of association, several theories have been proposed within the last thirty years. They involve integral equations obtained from thermodynamic expansions that are used in a perturbation theory framework. The first theory to be considered is that of Andersen [64, 65] that introduces the concept of association site. That is, the bonding
interaction is localized in a small bonding volume on the molecule. This anisotropic interaction is consistent with the idea that hydrogen bonds are fairly strong but directional and of short range. The implication of all the latter is that no more than one molecule can bond per association site; this was used by Andersen to renormalize the strength of the interaction using a graph cancellation theorem.

His expansion in terms of overall densities is difficult to apply [66] as is the approach of "physical cluster" formation due to Chandler and Pratt [67], which inconveniently uses a spherically symmetric potential.

A theory similar to that of Andersen by Høye and Olaussen [68] considered a fugacity expansion in terms of monomer densities for a solvating binary mixture. They suggested that this modification could lead to more rapid convergence.

Cummings and Stell [69] also considered a solvating binary mixture but with a spherically symmetric potential. To correct for this inappropriate assumption, Cummings and Blum [70] coupled the Percus-Yevick approximation with the effect of an anisotropic surface adhesion interaction. A similar approach that consists of charged sites forming a tetrahedral quadrupole (to mimic water molecules) was used by Carnie et al. [71].

The approach of Wertheim [7-11] builds upon the theories of Andersen and Høye and Olaussen. By considering that only one molecule can bond to each association site, he eliminates numerous graphs in his expansion with respect to fugacity as a function of the
monomer and overall densities. It is this theory that has been investigated further in this thesis.

2.4 Conclusions

The interactions between molecules are the key to describing the properties of liquids. However, these interactions are so dependent on the nature of the molecules that it seems very difficult today to aspire to a general theory of liquids. Nevertheless, statistical mechanical techniques have advanced our understanding of the liquid state and liquid mixtures to a level where systematic improvement can and has been achieved. For example, the effect of chain size and association can be treated reasonably well in a perturbation theory approach (Wertheim’s TPT1) that has been expressed as an equation of state (SAFT) and is discussed in the next chapter.
WERTHEIM'S THEORY OF ASSOCIATION

The first-order thermodynamic perturbation theory (TPT1) developed by Michael S. Wertheim for associating molecules is presented in this chapter, as well as the statistical associating fluid theory equation of state (SAFT EOS) that is derived from it.

3.1 Elements of the First-Order Thermodynamic Perturbation Theory

The first-order thermodynamic perturbation theory (TPT1) [7-11] was developed for associating fluids, i.e., molecules that present highly directional and short-ranged interactions. The nature of this type of interaction leads to the assumption of an association site with a small volume available for bonding. Moreover, it can be assumed that this site allows only one other molecule to approach sufficiently close and in the correct orientation to form a bond. The reduced bonding volume in addition to the opposition caused by the repulsive cores of the molecules already forming the bond, prevent a third molecule from participating in the bonding interaction.

These arguments translate in a theory where the system partition function can be expressed as graphs representing a cluster expansion. These graphs can then be examined and, based on the previous discussion, the nonphysical representations be eliminated. The remaining graphs are then used to renormalize the strength of the association interaction. The resummation of these graphs converges rapidly due to the choice of monomer and overall densities to express the fugacity expansion.
These ideas can be better explained with an example. Although no attempt is made to use cluster expansions, graphs and similar concepts, the intuitive character of the theory should become clear from the following derivation for a low-density associating fluid.

Consider a fluid of associating molecules with one bonding site (so that dimers can form) [44, 66, 72] at low density. The pair potential of interaction, $\phi$, is divided into that of a reference fluid, $\phi_{\text{ref}}$, and the contribution due to association, $\phi_{\text{assoc}}$,

$$\phi = \phi_{\text{ref}} + \phi_{\text{assoc}}.$$  

(3-1)

The potential depends on intermolecular separation and orientation, to include the directionality of the bonding interaction.

The fraction of monomer molecules, $X_A$, is equal to the fraction not bonded at site $A$ (a label for the site), $X_A$. When two molecules form a bond, the number of 'free' molecules is reduced by one. From these values the total number of 'free' molecules can be obtained,

$$N_O + N_{\text{dimers}} = N\left[1 - \frac{(1-X_A)}{2}\right]$$  

(3-2)

where $N$ is the total number of molecules, the number of monomers is $N_O = NX_A$, and $N_{\text{dimers}}$ is the number of dimer molecules.

In the low-density limit, the chemical potential of monomers is:
\[ \mu_{\text{unbonded}} = kT \ln(\rho_o \Lambda^3). \] (3-3)

\( k \) is Boltzmann's constant, \( T \) is absolute temperature, \( \rho_o = N_o/V \), \( V \) is total volume, and \( \Lambda \) is the de Broglie wavelength.

The chemical potential of the monomers in solution must be equal to the chemical potential of each segment in the dimers formed by association [4]:

\[ \mu_{\text{dimer}} = \mu_{\text{unbonded}}. \] (3-4)

Thus, the Helmholtz free energy of the system can be calculated from

\[ A = N_o \mu_{\text{unbonded}} + 2N_{\text{dimers}} \mu_{\text{dimer}} - PV, \] (3-5)

where \( P \) is the system pressure. Assuming \( P \) to be proportional to the number of 'free' molecules, \( N_o + N_{\text{dimers}} \), it follows that

\[ A = NkT \ln(\rho_o \Lambda^3) - NkT \left[ 1 - \frac{1}{2} \right]. \] (3-6)

Taking the reference fluid to be nonassociating, \( \rho_o = \rho = N/V \) and \( X_A = 1 \), and the Helmholtz free energy of the reference fluid becomes

\[ A^{\text{ref}} = NkT \ln(\rho \Lambda^3) - NkT. \] (3-7)

The result for the change in Helmholtz free energy due to association is

\[ a_{\text{assoc}} = \frac{A - A^{\text{ref}}}{NkT} = \ln X_A - \frac{X_A}{2} + \frac{1}{2} \] (3-8)

since \( X_A = X_o = \rho_o / \rho \).
To determine the change in free energy due to association, $X_A$ must be defined. This can be accomplished by considering a hard core reference fluid. In this case, the change in configurational energy due to association equals half the number of molecules in the bonding orientation times the bonding energy. To be consistent with our definition of the reference fluid, $X_A$ must equal 1 when the bonding strength is equal to zero, $\varepsilon = 0$. In the limit of zero bonding strength, there might well be molecules in the correct orientation to form a bond if the association interaction would suddenly be “switched on”. Assuming that the pair correlation function (see Chapter 4) is the same for monomers and for the reference fluid, an expression is obtained for total number of molecules in the bonding orientation,

$$N^*_b = N \left( \frac{1 - X_A}{2} \right) + N \rho D \frac{X_A^2}{2}.$$  \hfill (3-9)

$\rho D$ is the fraction of molecules in the bonding orientation about any given molecule and $X_A^2$ is the fraction of these molecules not bonded at site $A$. Hence, the second term is the number of bonds that would form in the reference fluid should association interactions be turned on in the one site example being considered.

The change in configurational energy can be calculated from the number of molecules in the bonding orientation or from thermodynamic differentiation of the configurational free energy. For consistency, \( \frac{\varepsilon N^*_b}{N} = \frac{\partial a_{assoc}}{\partial \beta} \) with $\beta = 1/kT$, should hold and this gives the expression for the fraction of molecules not bonded at site $A$: 
\[ X_A = \frac{1}{1 + \rho DFX_A}, \quad (3-10) \]

where

\[ F = \exp(-\beta \varepsilon) - 1 \quad (3-11) \]

is the Mayer \( f \)-function for a square-well type association interaction and

\[ D = \int_{\text{bonding volume}} g^{\text{ref}}(12)d(12) \quad (3-12) \]

where \( \rho D \) is the fraction of molecules in the reference fluid oriented correctly for bonding to occur. \( g^{\text{ref}} \) is the pair correlation function of the reference fluid and \( d(12) \) is a notation for an unweighted average over all bonding interactions and integration over all distances of the bonding volume. For a hard core fluid, \( D \) is a function only of density. The product \( DF \) is commonly known as \( \Delta \), the association strength.

The generalization for a molecule with \( M \) bonding sites is

\[ a^{\text{assoc}} = \sum_{A \in \Gamma} \ln X_A - \frac{X_A}{2} + \frac{M}{2} \quad (3-13) \]

where the index \( A \) runs through the \( M \) elements of the set \( \Gamma \) of bonding sites and \( X_A \), the fraction of molecules not bonded at site \( A \), is given by

\[ X_A = \frac{1}{1 + \rho \sum_{B \in \Gamma} X_B \Delta_{AB}}. \quad (3-14) \]
Again, the index \( B \) runs through all the \( M \) elements of \( \Gamma \) and \( \Delta_{AA} \) represents the association strength between a site \( A \) and a site \( B \).

For mixtures, the equations in the theory are very similar to Eqs. 3-13 and 3-14:

\[
a^{\text{assoc}} = \sum_{i=1}^{c} x^{(i)} \left\{ \sum_{i \in \Gamma^{(i)}} \left[ \ln X^{(i)}_{A} - \frac{X^{(i)}_{A}}{2} \right] + \frac{M^{(i)}}{2} \right\}.
\]  

(3-15)

Index \( i \) runs from 1 to \( c \), the number of components. \( x^{(i)} \) is the mole fraction of molecules of component \( i \), \( \Gamma^{(i)} \) is the set of association sites on molecules of component \( i \), \( X^{(i)}_{A} \) is the fraction of molecules of component \( i \) not bonded at site \( A \), and \( M^{(i)} \) is the total number of sites on a molecule of component \( i \).

The expression for \( X^{(i)}_{A} \) is:

\[
X^{(i)}_{A} = \frac{1}{1 + \sum_{j=1}^{c} x^{(j)} \left[ \rho \sum_{i \in \Gamma^{(i)}} X^{(j)}_{B} \Delta^{(j)}_{AB} \right]}
\]  

(3-16)

where \( \Delta^{(j)}_{AB} \) is the association strength between site \( A \) on molecules of component \( i \) and site \( B \) on molecules of component \( j \).

Finally, the fraction of monomers of component \( i \) is:

\[
X^{(i)}_{o} = \prod_{i \in \Gamma^{(i)}} X^{(i)}_{A}.
\]  

(3-17)
3.2 The Statistical Associating Fluid Theory Equation of State

The statistical association fluid theory equation of state (SAFT EOS) [73, 74] was developed from Wertheim's theory of association (TPT1) [7-11] to capture in a closed form EOS the effect of chain formation and association. It has been applied to a wide range of different systems that include small, large, polydisperse, nonassociating and associating molecules [14]. A discussion of the development and applications of the EOS is presented.

3.2.1 Development of the Equation of State

The SAFT equation of state was developed in a statistical mechanical framework, from the simpler to the more complex molecular structures and interactions. The theory can be expressed in terms of the different contributions to the residual Helmholtz free energy of a system of spheres or segments as they undergo the processes of chain formation and association as shown in Fig. 3.1.

The different contributions to the residual molar Helmholtz free energy can be expressed as follows [14, 44, 75]:

\[ a^{\text{res}} = \frac{A^{\text{res}}}{N_{ch} kT} = a^{\text{seg}} + a^{\text{chain}} + a^{\text{assoc}}, \quad (3-18) \]

where \( N_{ch} \) is the number of moles of chains formed in the system. Each contribution will now be discussed separately.
Firstly, the segment term, $a^{seg}$, consists of a hard sphere, $a_o^{HS}$, and a dispersion, $a_o^{disp}$. contribution,

$$a^{seg} = m(a_o^{HS} + a_o^{disp}) ,$$  \hfill (3-19)

---

Figure 3.1 Schematic representation of the effects accounted for in the SAFT equation of state. Segments interact in the limit of complete bonding to form chains. Association interactions lead to the formation of clusters.
where \( m \) is the number of segments that make up a chain molecule. Thus, \( a_o^{HS} \) and \( a_o^{dasp} \) are quantities based per mole of segments and \( a^{seg} \) is expressed per mole of chains. \( a_o^{HS} \) is given by the expression of Carnahan and Starling [58]:

\[
a_o^{HS} = \frac{4\eta - 3\eta^2}{(1-\eta)^2}, \tag{3-20}
\]

and the packing fraction is

\[
\eta = \frac{\pi N_{AV}}{6} \rho_{ch} md_{ii}^3. \tag{3-21}
\]

\( N_{AV} \) is Avogadro's number. \( \rho_{ch} \) is the molar density of chains, and \( d_{ii} \) is the temperature dependent segment diameter proposed by Chen and Kreglewski [76]:

\[
d_{ii} = \sigma_{ii} \left[ 1 - 0.12 \exp \left( -\frac{3u_{ii}^0}{kT} \right) \right], \tag{3-22}
\]

where \( \sigma_{ii} \) is the segment diameter at \( T=0 \) K and \( u_{ii}^0 \) is an energy parameter for their proposed potential model for pure component \( i \).

For mixtures, Eqs. 3-20 and 3-21 are substituted by the expression of Mansoori et al. [77]:

\[
a_o^{HS} = \frac{6RT}{\pi \rho} \left[ \frac{\zeta_3^2 + 3\zeta_1 \zeta_2 \zeta_3 - 3\zeta_1 \zeta_2 \zeta_3^2}{\zeta_3^2 (1-\zeta_3)} - \left( \frac{\zeta_3}{\zeta_3^2} \right) \ln(1-\zeta_3) \right] \tag{3-23}
\]

with
\[ \zeta_k = \frac{\pi N_{AV}}{6} \rho \sum_{i=1}^{c} x_i m_i d_i^k \]  

(3-24)

for \( k=0, 1, 2, 3 \). \( R \) is the universal gas constant, \( \rho \) is the mixture molar density, \( c \) is the number of components, \( m_i \) is the number of segments in each chain of component \( i \), and \( x_i \) is the mole fraction of component \( i \).

Generally, an expression in terms of a characteristic volume is preferred over a segment diameter. Such a parameter is derived from the previous concepts as

\[ \nu_i = \nu_i^{00} \left[ 1 - 0.12 \exp \left( -\frac{3u_{i0}}{kT} \right)^3 \right] \]  

(3-25)

with

\[ \nu_i^{00} = \frac{\pi N_{AV}}{6\tau} \sigma_i^3 \]  

(3-26)

and \( \tau = \frac{\pi \sqrt{2}}{6} \) is the packing fraction at the closest packing that can be achieved for spherical segments.

As for the dispersion term, the expression used is that of Alder et al. [78] from molecular simulation results with some modifications by Kreglewski [79]:

\[ a^{\text{disp}}_o = RT \sum_i \sum_j D_{ij} \left[ \frac{U}{kT} \right] \left[ \frac{\zeta_j}{\tau} \right]^j. \]  

(3-27)

These researchers have tabulated the 24 constant values of \( D_{ij} \). Moreover, \( m \) in Eq. 3-19 is expressed for the case of mixtures as:
\[ m = \sum_{i=1}^{c} x_i m_i, \quad (3-28) \]

and another mixing rule is

\[ \frac{u}{kT} = \frac{\sum_{i=1}^{c} \sum_{j=1}^{c} x_i x_j m_i m_j \left[ u_{ij} \right]_{v_{ij}^0}}{\sum_{i=1}^{c} \sum_{j=1}^{c} x_i x_j m_i m_j v_{ij}^0}, \quad (3-29) \]

where the temperature dependence of the energy parameter is given by

\[ u_{ii} = u_i^0 \left[ 1 + \frac{e_{ii}}{kT} \right], \quad (3-30) \]

and for mixtures

\[ u_{ij} = (1 - k_{ij}) u_i u_j \left(1 + \frac{e_{ii}}{kT}\right)^{\frac{1}{2}}. \quad (3-31) \]

In these expressions, \( k_{ij} \) is a binary interaction parameter, and \( e_{ii}/kT \) is taken to be a constant related to Pitzer's acentric factor and to critical temperature [79]. It is adjusted only for a few small molecules to zero making \( u_{ii} \) independent of temperature for these cases.

The final equation is a mixing rule for the characteristic volume,

\[ v_{ij}^0 = \left( \frac{1}{2} \left( v_i^0 \left( \frac{1}{3} + v_i^0 \left( \frac{1}{3} + v_j^0 \left( \frac{1}{3} + v_j^0 \left( \frac{1}{3} \right) \right) \right) \right) \right)^\frac{1}{3} \quad (3-32) \]

The next term to be considered is the contribution to the residual molar Helmholtz free energy due to chain formation, \( a^{chain} \), which is based on the association theory.
presented in the first part of this chapter. To obtain the expression it is necessary to take
the limit of complete bonding for associating segments. Some restrictions in the
stoichiometry of the different types of segments and in the order and selectivity of their
connectivity lead to the following expression for a mixture:

\[ a^{assoc} = RT \sum_{i=1}^{c} x_i (1 - m_i) \ln y^{ref}_i (d_{ii}). \]  \hspace{1cm} (3-33)

The cavity correlation function (see Chapter 4) of the reference fluid at contact, \( y^{ref}_i (d_{ii}) \),
equals the radial distribution function evaluated at contact, \( g^{ref}_i (d_{ii}) \), and is given by the
hard sphere expression of Mansoori et al.\[77]\ :

\[ g^{ref}_i (d_{ij}) = \frac{1}{1 - \zeta_3} + 3 \left[ \frac{d_{ii}d_{jj}}{d_{ij} + d_{ij}} \right] \frac{\zeta_2}{(1 - \zeta_3)^2} + 2 \left[ \frac{d_{ii}d_{jj}}{d_{ij} + d_{ij}} \right]^2 \frac{\zeta_2^2}{(1 - \zeta_3)^3} \]  \hspace{1cm} (3-34)

with

\[ d_{ij} = \frac{d_{ii} + d_{jj}}{2}. \]  \hspace{1cm} (3-35)

The association contribution, \( a^{assoc} \), was derived in the first part of this chapter and is
rewritten here for the general case of mixtures and multiple associating sites.

\[ a^{assoc} = RT \sum_{i=1}^{c} x_i \left( \sum_{\Delta(i)} \left[ \ln \frac{X^{(i)}_A}{2} - \frac{X^{(i)}_A}{2} \right] + \frac{M^{(i)}}{2} \right). \]  \hspace{1cm} (3-36)

The reader is referred to \$3.1\ for the expressions to obtain \( X^{(i)}_A \) and further explanation.
3.2.2 Applications

Various systems have been studied using SAFT. One example is the work of Huang and Radosz [80-82] who have fitted vapor pressure and saturated liquid density data using SAFT for over 100 components including simple inorganics, alkanes, alkenes, alkanols, acids, ethers, ketones, esters, polymers, and chlorinated hydrocarbons, among others.

An important observation from these results is that the fitting parameters (segment number, volume, and energy) correlate well with molecular weight, providing for a useful predictive tool.

However SAFT, in its original formulation, does not account for intramolecular association or ring formation. Other factors that SAFT does not capture totally are the effects on physical properties of the relative orientation and position of the association sites on the molecules.

3.3 Conclusions

The approach to modeling association in fluids based on the first-order thermodynamic perturbation theory that has been presented in this chapter represents a satisfactory way to account for this important effect in a statistical mechanical framework. The SAFT equation of state derived from this theory and based on rigorous fundamentals gives good results for highly nonideal systems. Moreover, the SAFT parameters correlate well with molecular weight, a useful characteristic for property prediction purposes. However,
improvement of the equation of state is necessary to include factors not considered, e.g., intramolecular association, ring formation, and site position and orientation.
MOLECULAR SIMULATION

The molecular simulation techniques used for the study of fluids provide a way to obtain results for the thermodynamic properties of a model system with a completely known potential of interaction. In this way, the results from a theory can be tested against the "computer experiments" with no uncertainty related to the force model. This uncertainty of force model is introduced when comparing with properties for a real fluid.

The Metropolis Monte Carlo (MMC) method is discussed in this chapter, as it is the method used in the remainder of the thesis. A second method known as molecular dynamics (MD) is covered in the general references for computer simulation of fluids [2, 5, 83, 84].

4.1 Molecular Simulation Methods

The two general methods to perform molecular simulations given a certain potential of interaction are molecular dynamics (MD) and Metropolis Monte Carlo (MMC). MD relies on solving Newton's equations at each small time increment of which the simulation consists. In MMC, random displacements and molecular reorientations originate successive molecular configurations to sample the most probable states.

The purpose of these techniques is to provide validation for theories that otherwise would be ambiguously tested, if compared solely against real fluid experiments. This is
because the potential of interaction of real molecules is difficult to determine. Fig. 4.1 shows the tests that a certain type of experiment poses to a particular theory.

\[\text{Theory} \quad \xrightarrow{\text{Approximations}} \quad \text{Molecular Simulation} \quad \xrightarrow{\text{Potential of}} \quad \text{Real Fluid Experiment} \quad \xrightarrow{\text{Potential of Interaction}} \]

**Figure 4.1** The process for independent testing of theory approximations from inaccuracies in the potential of interaction as related to molecular simulation and experiment.

The vertices of the triangle represent the three sources of information for thermophysical properties, namely, fluid theories, simulation, and experiments. When comparing theory to experimental results the discrepancies result from two sources that already have been mentioned: poor approximations and the use of inexact potential functions. Agreement between theory and molecular simulation results is a reflection of the appropriateness of the simplifying approximations, made for the particular system that is studied. Moreover, the diagram also suggests that simulation could serve the same
purpose of real fluid experiments if the real potential of interaction function were known exactly or accurately enough. This approach, of course, also encounters the obstacle of computer speed and computer code optimization and reliability.

The previous discussion reveals the great value and importance of a good theory. A reliable theory provides a means to correlate and predict thermodynamic properties and do it for a wide range of conditions whereas molecular simulations and real fluid experiments give results at discrete state points. Moreover, theories that express the functionality of the thermodynamic properties in terms of the state variables provide an invaluable tool for engineering analysis. Nevertheless, the molecular simulation validation step is necessary before using the theories with entire confidence.

4.2 The Classical Approximation and Thermodynamic Ensembles

In general, a classical (as opposed to quantum) treatment can be given to most fluids with the exception of hydrogen and neon [2]. Classical mechanics apply and the Hamiltonian of the system can be written as:

$$H(\vec{r}^N, \vec{p}^N) = \sum_{i=1}^{N} \frac{\vec{p}_i^2}{2m_i} + \phi(\vec{r}^N)$$  (4-1)

where $\vec{r}^N$ are the positions and $\vec{p}^N$ the momenta of the $N$ particles. $\vec{r}^N$ and $\vec{p}^N$ define the system completely and are known as the $6N$ coordinates of phase space. $m_i$ is the molecular mass of particle $i$ and $\phi$ is the potential energy given by the intermolecular
interactions. The Hamiltonian expresses the system energy as the sum of the kinetic and potential energy contributions.

The concept of ensemble is useful to obtain the probability with which molecules forming a system with positions \( \vec{r}^N \) and momenta \( \vec{p}^N \), i.e., with the Hamiltonian being completely defined, occupy the different points of phase space. Consider the \( N \) particle system with \( H \) given by Eq. 4-1. There are a large number of available states that are consistent with the overall macroscopic measurements of, for example, volume and temperature. This is the canonical, or constant \( NVT \) ensemble. The probability density function of finding the system around a particular point \((\vec{r}^N, \vec{p}^N)\) in phase space is:

\[
P_N(\vec{r}^N, \vec{p}^N) d\vec{r}^N d\vec{p}^N.
\]  

(4-2)

In the canonical ensemble this probability is given by

\[
P_N = \frac{\exp(-\beta E_i)}{\sum_i \exp(-\beta E_i)}
\]  

(4-3)

where \( \beta = 1/kT \), \( k \) is Boltzmann's constant, \( T \) is absolute temperature, and \( E_i \) is an energy level. Applying the classical approximation the canonical partition function is obtained:

\[
Q_N = \frac{1}{\hbar^{3N} N!} \int \cdots \int \exp[-\beta H(\vec{r}^N, \vec{p}^N)] d\vec{r}^N d\vec{p}^N
\]  

(4-4)

where \( \hbar \) is Planck's constant and the probability density function is
\[
P_N = \frac{\exp[-\beta H(\bar{r}_N, \bar{p}_N)]}{Q_N}.
\]

(4-5)

The *ergodic hypothesis* assumes that the probability of Eq. 4-5 based on a multitude of states at constant \(N, V,\) and \(T,\) is equivalent to the probability density function followed by any particular state drifting through time, as it occupies other points in phase space. In effect, this is the same as assuming the ensemble average to be equal to the time average, when an observable dynamical property is calculated from:

\[
\langle B \rangle = \frac{\int \cdots \int B(\bar{r}_N)P_N(\bar{r}_N, \bar{p}_N) d\bar{r}_N}{\int \cdots \int P_N(\bar{r}_N, \bar{p}_N) d\bar{r}_N d\bar{p}_N}.
\]

(4-6)

\(\langle B \rangle\) is called the ensemble average of property \(B\) and is the quantity of interest. However, it is necessary to solve the integrals that appear in Eq. 4-6. The integration over momenta can be done, leaving this expression:

\[
\langle B \rangle = \frac{\int \cdots \int B(\bar{r}_N)\exp[-\beta \phi(\bar{r}_N)] d\bar{r}_N}{\int \cdots \int \exp[-\beta \phi(\bar{r}_N)] d\bar{r}_N}.
\]

(4-7)

Metropolis *et al.* [85] proposed a method to sample phase space efficiently to obtain the value of the ratio of the two integrals without evaluating the two individually. The method is explained in the next section.

### 4.3 The Metropolis Monte Carlo Method

To obtain ensemble averages of properties of interest from equations such as Eq. 4-7 is a formidable task for most systems. A computational technique devised in the late 1940’s
in Los Alamos attacks this problem. It is termed the Metropolis Monte Carlo Method (MMC) [85]. It recognizes that the probability density function of the system being around $\mathcal{F}^N$ is

$$M(\mathcal{F}^N) = \frac{\exp[-\beta \phi(\mathcal{F}^N)]}{\cdots \exp[-\beta \phi(\mathcal{F}^N)]/\mathcal{H}^N}. \quad (4-8)$$

If it were possible to randomly choose points in phase space with this probability, then the ensemble average could be approximated for large $L$ by:

$$\langle B \rangle = \frac{1}{L} \sum_{i=1}^{L} n_i B(\mathcal{F}^N_i). \quad (4-9)$$

where $L$ is the total number of $n_i$ trial configurations.

The Metropolis method consists of randomly and uniformly displacing and reorienting the molecule around its original position and accepts this new configuration with probability $p_{acc}$, and

$$p_{acc} = \begin{cases} 1 & \text{if } \exp[-\beta [\phi(\text{new}) - \phi(\text{old})]] > 1 \\ \exp[-\beta [\phi(\text{new}) - \phi(\text{old})]] & \text{otherwise.} \end{cases} \quad (4-10)$$

### 4.4 Implementation

The general algorithm for performing MMC simulation is as follows [84]:

1. Select a particle and calculate its potential energy, $\phi$.

2. Displace the particle randomly and calculate the new value for $\phi$. 
3) Adopt the new configuration with probability $p_{acc}$.

The number of particles used in simulations is usually between 100 and 1000, which is much smaller than the quantities of a typical macroscopic system. The trick that is used to "fool" the computer simulation system into thinking that it is part of a larger system is the use of periodic boundary conditions. The system is in essence infinitely replicated by placing identical cells surrounding the primary cell completely, on all sides. When these conditions are applied, a particle entering the system through one boundary leaves the system through another. This process can be seen in Fig. 4.2.

![Figure 4.2 Application of periodic boundary conditions in molecular simulation](image)

It is worthwhile mentioning that in the same way that the position of a particle is modified as dictated by the Monte Carlo algorithm, the orientation must be changed as well for nonspherical molecules. This is done very commonly and conveniently by defining three Euler angles that relate coordinates in a space-fixed axis to those of a body-fixed coordinate system. The three angles and the position of each molecule are
displaced randomly. The maximum changes must be such that an attempted
displacement and reorientation is accepted between 25 and 40% of the time to explore
phase space efficiently [5, 66].

The simulations are started from an initial configuration with no overlaps in the case
of hard sphere type interactions. An "equilibration run" follows, where the system
relaxes close to the conditions that correspond to the input parameters (e.g., the
configurational internal energy changes according to volume and temperature). Once
equilibration is attained, a "production run" is started and the ensemble averages that are
calculated become the simulation results.

4.5 Correlation Functions

In this section the radial distribution function is introduced to exemplify the type of
structural quantities that can be obtained using molecular simulation. Also, this is an
important function for the theories developed in this thesis. The radial distribution
function is defined as:

$$\rho \left( \tilde{r}_1, \tilde{r}_2 \right) = \frac{N(N-1) \int \cdots \int \exp \left[ - \beta \phi \left( \tilde{r}^N \right) \right] d\tilde{r}_5 d\tilde{r}_4 \cdots d\tilde{r}_N}{\rho^2 \int \cdots \int \exp \left[ - \beta \phi \left( \tilde{r}^N \right) \right] d\tilde{r}^N} \quad (4-11)$$

and gives the probability of finding two atoms at a given distance \( r \) apart from each other,
relative to the corresponding (i.e., same density) probability for a random distribution.

In a simulation, the number of molecules contained in a spherical shell of thickness
\( \Delta r \), at a distance \( r_i - \Delta r/2 \) to \( r_i + \Delta r/2 \) from any particular test molecule is stored in a
histogram bin, \( b(r_i) \). The histogram is averaged over all pairs of \( N \) molecules in the system. Here, \( r_i = i \frac{\Delta r}{2} \), for \( i=1,2,...,n \), with \( n \) being the total number of histogram bins and \( \Delta r = \frac{\ell}{2n} \), with \( \ell \) being the length of the simulation box (\( \ell = V^{-3} \)).

\[ g(r) \] is computed from:

\[
g(r_i) = \frac{b(r_i)V}{N^2 \frac{4}{3} \pi \left[ \left( r_i + \frac{\Delta r}{2} \right)^3 - \left( r_i - \frac{\Delta r}{2} \right)^3 \right]}
\]

where \( V \) is the system volume.

A related function is the indirect or background correlation function, defined as:

\[
y(r) = \exp[\beta \phi(r)] g(r).
\]

This function is used when the derivative of the pair distribution function is needed and cannot be obtained, as is the case with hard spheres at contact and other discontinuous potentials. \( y(r) \) is continuous even for these cases.

4.6 Conclusions

Molecular simulation is in a sense a “brute force” method to obtain the thermodynamic properties of model molecules for which the exact potential function is known.

The importance of this approach besides testing theories, is the possibility of obtaining results for a dangerous or otherwise inaccessible state point. Also important is
the possibility of engineering molecules, or to calculate quantities that are difficult or impossible to measure in standard experiments. These methods are becoming more important as computers become faster and less expensive.
SOLVENT EFFECTS ON MODEL TELECHELIC POLYMERS

In this chapter we extend Wertheim's theory to predict the competition between intermolecular and intramolecular hydrogen bonding to mixtures, and apply it to a model telechelic mixture. The theory is tested by comparing with simulation results for a mixture of fully flexible linear chains that can associate in a hydrogen bonding solvent. The simulation model for the telechelic is a flexible linear tetramer hard sphere chain with two hydrogen bonding sites, one on each terminal segment. The solvent is modeled as a hard sphere with four tetrahedrally arranged hydrogen bonding sites. The solvent is seen to affect the ability of the solute to bond intermolecularly and intramolecularly. The extent of hydrogen bonding and thermodynamic properties of the system were studied using Monte Carlo simulation and compared with predictions from the proposed theory for mixtures. Agreement of simulation and theory is good over the range of densities, temperatures and compositions studied.

5.1 Introduction

Telechelic polymers are low molecular weight, monodisperse, amorphous molecules that contain functional groups at the ends of the chain [86, 87]. They are used as the starting material for block and graft copolymer synthesis. It is this functionality that allows the molecule to form both inter- and intramolecular hydrogen bonds. Gregg et al. [86, 87] studied the cloud point pressure (the pressure below which a solution splits into two
phases) of telechelics in various supercritical solvents. They found experimentally that adding a single hydroxyl group to a terminal segment of polyisobutylene caused the cloud point pressure of the solution to be shifted upwards compared to the nonfunctional (blank) polymer. This shift in cloud point pressure is due to intermolecular association that results in an increase in the effective molecular weight of the telechelic. Surprisingly, for polyisobutylene with a hydroxyl group attached to each end of the chain in a polar solvent, the cloud point pressure was similar to that of the blank polyisobutylene. It is suspected that this peculiar phase behavior arises from the ability of the dihydroxy polymer chain to associate intramolecularly with itself. Moreover, many other polymer systems important to industry (e.g. Nylon-6 solutions [88] and carboxylic acid based copolymers [89]) and processes in living organisms (e.g. protein folding) have in common internal bonding of the macromolecule involved. This is the motivation to study the competition between inter- and intramolecular bonding of associating chain fluids [13].

Numerous statistical mechanics based theories have advanced our ability to predict the thermodynamic properties of non-spherical molecules. These include the reference interaction site model (RISM) [90, 91], polymer RISM [92-96], perturbed hard chain theories [97], generalized Flory dimer theory [98], lattice fluid theories [46], a Percus-Yevick theory based chain equation of state [99], Wertheim’s first order thermodynamic perturbation theory (TPT1) [7-10], and its extensions [11, 73].
Wertheim's theory is particularly applicable to molecules that can associate with strong, highly directional forces (hydrogen bond). Numerous computer simulation studies have been carried out to validate this theory [100-104] and an equation of state, the statistical associating fluid theory (SAFT EOS), has been developed from extensions and simplifications of TPT1 [73, 74, 80]. SAFT reproduces the complex phase behavior and fluid phase properties of hydrogen-bonding fluids [105-107]. Nevertheless, SAFT can only deal with intermolecular bonding and not with intramolecular bonding [87]. Efforts toward extending the theory have been made by Ghanasgi and Chapman [12, 13] and Sear and Jackson [108], using equivalent approaches.

Here we extend this approach to mixtures of telechelic chains in a hydrogen-bonding solvent. Computer simulation results for our model system are presented and compared with theory.

5.2 Simulation

Consider a flexible, tangent hard sphere chain with four segments and two associating (or hydrogen-bonding) sites. One association site is on each terminal segment; one site is designated type A and the other is type B. The sites are placed on a line forming a right angle with the vector joining the last to the next-to-last segment centers of the tetramer, as shown in Figure 5.1.

The potential of interaction between two different chain molecules is

\[ \phi_{\text{inter}} = \phi_{\text{HS}} + \phi_{\text{assoc}} \]  

(5-1)
where $\phi_{HS}^c$ is a hard sphere interaction given by

![Diagram](image)

(a)  

(b)

Figure 5.1 Intermolecular (a) and intramolecular (b) bonding of model telechelic molecules.

$$
\phi_{HS}^c(\mathbf{r}, \Omega_1, \Omega_2) = \begin{cases} 
\infty & \text{if } r_{ij} < \sigma_c \\
0 & \text{if } r_{ij} \geq \sigma_c 
\end{cases} \quad (5-2)
$$

Here, $\mathbf{r}$ is the vector pointing from the center of molecule 1 to the center of molecule 2, $\Omega_k$ is the orientation of molecule $k$, $r_{ij}$ is the center to center distance from segment $i$ of molecule 1 to segment $j$ of molecule 2, and $\sigma_c$ is the segment diameter. For the attractive part of the potential we have
\[ \phi_{\text{assoc}} (r, \Omega_1, \Omega_2) = \begin{cases} -\varepsilon_{\text{intra}} & \text{if } r < R_c, \Theta_1 < \Theta_c, \text{ and } \Theta_2 < \Theta_c \\ 0 & \text{otherwise} \end{cases} \quad (5-3) \]

where \( r \) is the distance between the center of the terminal segment with bonding site of type \( A \) of one molecule to the center of the terminal segment with bonding site of type \( B \) of the second molecule (no \( AA \) or \( BB \) bonds are permitted). \( \Omega_k \) is the orientation of molecule \( k \), \( \varepsilon_{\text{intra}} \) is the intramolecular association energy between chains, \( R_c \) and \( \Theta_c \) are the distance and orientation cutoff parameters (respectively) for the potential. Additionally, \( \Theta_k \) is the angle subtended from the vector joining the centers of the terminal segments of interest to the line connecting these centers to their corresponding bonding site (see Fig. 5.1a).

Intramolecular association of the chain molecules is depicted in Figure 5.1b. The potential for this kind of interaction is of the following form:

\[ \phi_{\text{intra}} = \phi_{\text{HS}} + \phi_{\text{assoc}} \quad (5-4) \]

where

\[ \phi_{\text{assoc}} (r, \Omega_A, \Omega_B) = \begin{cases} -\varepsilon_{\text{intra}} & \text{if } r < R_c, \Theta_A < \Theta_c, \text{ and } \Theta_B < \Theta_c \\ 0 & \text{otherwise} \end{cases} \quad (5-5) \]

\( r \) is the center to center distance between the end segments of the tetramer, \( \Omega_A \) and \( \Omega_B \) are the orientations of the two terminal segments. \( \varepsilon_{\text{intra}} \) is the intramolecular association energy, \( \Theta_A \) and \( \Theta_B \) are the angles subtended from the vector joining the centers of the terminal segments to the lines connecting the centers of each of these two segments to their bonding sites, \( A \) and \( B \) respectively (see Fig. 5.1a).
For the solvent, four association sites labeled \( A, B, C \) and \( D \) are placed on the vertices of a tetrahedron embedded in a sphere (see Figure 5.2a). This is intended to be a simple molecular model for water [103, 109].

![Diagram of tetrahedron with association sites](image)

**Figure 5.2** Model hydrogen bonding solvent with four association sites in a tetrahedral arrangement (a) and interaction between two solvent molecules (b).

The interaction between solvent molecules (see Figure 5.2b) is given by

\[
\phi_{\text{solv}} = \phi_{\text{HS}} + \phi_{\text{assoc}}
\]  

(5-6)

where

\[
\phi_{\text{HS}}(r) = \begin{cases} 
\infty & \text{if } r < \sigma_s \\
0 & \text{if } r \geq \sigma_s
\end{cases}
\]  

(5-7)

and

\[
\phi_{\text{assoc}}(r, \omega_1, \omega_2) = \begin{cases} 
-\varepsilon_{\text{solv}} & \text{if } r < r_c, \theta_1 < \theta_c, \text{ and } \theta_2 < \theta_c \\
0 & \text{otherwise}
\end{cases}
\]  

(5-8)
$r$ is the distance between the centers of the two solvent molecules and $\sigma_s$ is the sphere diameter. Also, $\omega_k$ is the orientation of molecule $k$, $\varepsilon_{\text{solv}}$ is the association energy between solvent molecules, and $r_c$ and $\theta_c$ are the usual radial and orientation (respectively) cutoff parameters for the potential. The angles $\theta_1$ and $\theta_2$ are formed from the vector joining the centers of spheres 1 and 2 to the vectors connecting these centers to any of the four associating sites. Only bonds of types $AB$, $AD$, $BC$ and $CD$ are allowed (see Fig. 5.2b).

Lastly, for interactions of solvent and chain molecules, or cross associations, the potential of interaction is the following:

$$\phi_{\text{cross}} = \phi_{H2}^{c-s} + \phi_{\text{cross}}^{assoc}$$  \hspace{1cm} (5-9)

where

$$\phi_{H2}^{c-s}(r) = \begin{cases} \infty & \text{if } r < \sigma_{c-s} \\ 0 & \text{if } r \geq \sigma_{c-s} \end{cases}$$  \hspace{1cm} (5-10)

and

$$\phi_{\text{cross}}^{assoc}(r, \Omega, \omega) = \begin{cases} -\varepsilon_{\text{cross}} & \text{if } r < r_c^{c-s}, \Theta_1 < \theta_c^{c-s}, \text{and } \theta_2 < \theta_c^{c-s} \\ 0 & \text{otherwise} \end{cases}.$$  \hspace{1cm} (5-11)

Here, $r$ is the distance between the center of the solvent molecule and a segment of the chain molecule and $\sigma_{c-s} = (\sigma_c + \sigma_s) / 2$. $\Omega$ is the orientation of the chain molecule, $\omega$ is the orientation of the solvent molecule, $\varepsilon_{\text{cross}}$ is the cross association energy between molecules, $r_c^{c-s}$ and $\theta_c^{c-s}$ are the cutoff parameters. The angle $\Theta_1$ is formed from the
vector joining the centers of the solvent molecule and of the proper terminal segment of the chain molecule, to the vector connecting the center of the terminal segment and its bonding site (see Fig. 5.3). Similarly, \( \theta_2 \) is the angle formed from the center-to-center vector described previously to the vector that connects the center of the solvent molecule to its proper bonding site. Again, bonds of types \( AB, AD, BC \) and \( CD \) are the only allowed.

Figure 5.3. Cross interaction between a solvent molecule and a tetramer.

As has been discussed, the potentials of interaction consist of the attractive part, which is an association interaction, and the repulsive part, a hard-sphere type interaction. The model we have presented lacks dispersion interactions that would require defining mixing rules that can be readily incorporated into the theory.
The model system was simulated with the Metropolis Monte Carlo (MMC) method [85] in the canonical ($NVT$) and isothermal-isobaric ($NpT$) ensembles. A total of 640 spheres that could act either as solvent molecules or segments of the tetramers (depending on the compositions of interest) were first sufficiently equilibrated. Subsequently, 62,500 MMC cycles (in each cycle an attempt is made to sequentially displace and reorient each molecule once and for the $NpT$ simulations a change of volume is attempted also once) were run for each state point and averages accumulated.

The solvent molecules were displaced in the conventional way during simulation of the $NVT$ ensemble [5], i.e. random translation in the three Cartesian coordinates. Additionally, three Euler angles were associated to each sphere and by randomly modifying them, particle reorientation was attained. For the chain molecules, a similar procedure was followed. Random translation of the whole chain preceded reorientation of the end segments in the same fashion as for the solvent molecules (leaving the "head" segment position fixed at the trial position and building from there on). Since the vectors from the center of each terminal segment to their respective bonding site and to their next-to-last segment are perpendicular to each other, their relative positions are completely determined. It is only left to define the relative position between segments with no association sites. This is done [110] by adding a random vector to the vector joining the segments and then renormalizing the resultant vector to a magnitude of $\sigma_r$. The maximum change in position and orientation is controlled by parameters that were adjusted to yield an acceptance ratio of approximately 40%. For the $NpT$ simulations, the molecules were moved as described above and additionally the volume of the simulation
cell was randomly modified as prescribed by Wood [111]. Again, 40% acceptance was the target when adjusting the maximum volume change parameter. The cutoff parameters for the associating potentials were taken to be 1.1 times the sphere diameter (which was chosen to be equal for chains and for solvent molecules) for the distance parameters and 27° for all orientation cutoff parameters. These values guarantee that an association site will bond only once.

We do not anticipate the formation of ordered crystalline phases, even at high densities, since we are modeling flexible hard chains that do not necessarily orient in a rod-like fashion. Therefore, our computer code calculates ensemble averages for the different types of possible bonding and thermodynamic properties but does not calculate structural quantities.

5.3 Theory

5.3.1 Distribution of Bonds

Consider the model system described in the simulation section. We are interested in the equilibrium bonding distribution for this system and obtain it by combining Wertheim's theory for intermolecular association with the theory of Ghonasgi and Chapman and of Sear and Jackson for intramolecular association. For the two-site chains, assume that all intramolecular bonding has occurred. Then only molecules that are not intramolecularly bonded can form intermolecular bonds. The fraction of chain molecules not bonded intramolecularly is given by
\[ x_0^{\text{intra}} = \frac{\rho_2 - \rho_{AB}^{\text{intra}}}{\rho_2} = \frac{\rho_o^{\text{intra}}}{\rho_2}. \tag{5-12} \]

where \( \rho_2 \) is the number density of chains (component 2), \( \rho_{AB}^{\text{intra}} \) is the number density of chain molecules bonded intramolecularly and \( \rho_o^{\text{intra}} \) is the number density of chain molecules not bonded intramolecularly.

Assuming that the intramolecular bonding of some molecules has little effect on the intermolecular distribution functions of the other molecules in the fluid, we can apply Wertheim's theory for intermolecular association. From Wertheim's theory (using the notation of Chapman et al. [73]), the fraction of chain molecules not intramolecularly bonded that are also not intermolecularly or cross bonded at site A is given by

\[ x_A^{(2)} = 1 - \rho_o^{\text{intra}} x_A^{(3)} x_B^{(2)} \Delta_{AB}^{(2,3)} - 2 \rho_1 x_B^{(1)} x_A^{(2)} \Delta_{AB}^{(1,2)}. \tag{5-13} \]

Similarly for site B,

\[ x_B^{(2)} = 1 - \rho_o^{\text{intra}} x_A^{(3)} x_B^{(2)} \Delta_{AB}^{(2,3)} - 2 \rho_1 x_A^{(1)} x_B^{(2)} \Delta_{AB}^{(1,2)} \tag{5-14} \]

where \( \rho_1 \) is the number density of solvent molecules (component 1) and \( x_A^{(1)} \) is the fraction of solvent molecules not bonded at site A. Note that due to the symmetry of the model \( x_A^{(2)} = x_B^{(2)} \) and \( x_A^{(1)} = x_B^{(1)} = x_C^{(1)} = x_D^{(1)} \). Also, we approximate \( \Delta_{AB}^{(i,j)} \) as [112]

\[ \Delta_{AB}^{(1,2)} = 4 \pi g_{HS} (\sigma_{e-1}) k_{AB}^{(1,2)} F_{AB}^{(1,2)} \tag{5-15} \]

and

\[ \Delta_{AB}^{(2,2)} = 4 \pi g_{HS} (\sigma_e) k_{AB}^{(2,2)} F_{AB}^{(2,2)}. \tag{5-16} \]
Here, $g_{ns}$ is the radial distribution function of the hard sphere fluid created by dissolving all bonds, evaluated at contact and at the same packing fraction as the chain and sphere system of interest. $K_{AB}^{(i,j)}$ is the available volume for bonding between sites $A$ and $B$ of two molecules of components $i$ and $j$,

$$K_{AB}^{(i,j)} = \frac{(1 - \cos \theta_e)^2}{4} \sigma_{i,j}^3 (r_e - 1). \tag{5-17}$$

Finally, $F_{AB}^{(1,2)}$ is the Mayer $f$ function for the attractive part of the potential:

$$F_{AB}^{(1,2)} = \exp(\beta \varepsilon_{intr}) - 1 \tag{5-18}$$

and

$$F_{AB}^{(2,2)} = \exp(\beta \varepsilon_{sw}) - 1. \tag{5-19}$$

In these expressions, $\beta = 1/kT$ where $k$ is Boltzmann's constant and $T$ is the absolute temperature of the system. The terms in Eq. 5-13 can be interpreted as the components of a mass balance in the following way. Of the chain molecules not intramolecularly bonded, the fraction not bonded at site $A$ equals one minus the fraction bonded at site $A$ to another chain molecule minus the fraction bonded at site $A$ to a solvent molecule. We use this interpretation of the terms in Eq. 5-13 in comparisons with simulation results.

For the solvent we have that the fraction of molecules of component 1 not bonded at site $A$ is given by

$$x_A^{(1)} = \frac{1}{1 + \rho_o^{intr} \Delta_{AB}^{(1,2)} + 2 \rho_1 x_B^{(1)} \Delta_{AB}^{(1,1)}} \tag{5-20}$$
with the approximation [112]

\[ \Delta_{AB}^{(1,3)} = 4\pi g_{HS} (\sigma_s) K_{AB}^{(1,1)} F_{AB}^{(1,1)} \]

where

\[ F_{AB}^{(1,1)} = \exp(\beta \varepsilon_{solv}) - 1. \]

Keeping in mind that all four association sites are equivalent, we obtain

\[ x_A^{(1)} = x_B^{(1)} = x_C^{(1)} = x_D^{(1)}. \]

With this result it is possible to rewrite Eq. 5.20 as

\[ x_A^{(1)} + \rho_0^{\text{intra}} x_A^{(2)} + x_A^{(1)} \Delta_{AB}^{(1,1)} + 2 \rho_0 x_A^{(1)} \Delta_{AB}^{(1,1)} = 1. \]

We identify the second term in the left hand side as the fraction of solvent molecules bonded at site \( A \) to a chain molecule and the third term as the fraction of solvent molecules bonded at site \( A \) to another solvent molecule. These two quantities plus \( x_A^{(1)} \) must add up to one.

Now, for the intramolecular association of chains let us imagine that all intermolecular bonds have formed. Assuming that the intramolecular distribution function of free chain molecules does not depend on the extent of intermolecular bonding of the system then, as given by Ghonasgi and Chapman [12], the ratio of the density of molecules bonded intramolecularly to the density of monomer (unbonded) chains is

\[ \frac{\rho_{AB}^{\text{intra}}}{\rho_0^{(2)}} = \Delta_{AB}^{\text{intra}} \]

where
\[ \Delta_{AB}^{\text{intra}} = \frac{F_{AB}^{\text{intra}}}{(4/3)^{2/3}(m-1)^{1/3}} \sigma_{\text{bonding}}^3 \int_R g_{R,\text{intra}}(12)d(12) \]  

(5-25)

and \( F_{AB}^{\text{intra}} = \exp(\beta \varepsilon_{\text{int},AB}) - 1 \) is the Mayer \( f \) function for the attraction between the two terminal segments of a single chain molecule. The interpretation of the ratio \( \Delta_{AB}^{\text{intra}} / F_{AB}^{\text{intra}} \) in Eq. 5-25 is the following. The factor outside the integral represents the reciprocal of the volume accessible to a terminal segment given that the position of the other terminal segment on the chain is fixed. \( m \) is the number of segments that make up a chain, \( \sigma_z \) is the bond length and segment diameter, and \( g_{R,\text{intra}} \) is the intramolecular pair correlation function between the chain's two end segments for the reference fluid of tangent hard sphere chain molecules with no association. The notation \( d(12) \) represents an unweighted average over all orientations and a subsequent integration over all separations in the bonding volume. This ratio appears in Ref. 13 as parameter \( D \) \((\Delta_{AB}^{\text{intra}} = D F_{AB}^{\text{intra}})\). This parameter was correlated as a function of density from simulation for tetramers.

Scar and Jackson [108] proposed a more general expression for chains of any length that agrees very closely with the aforementioned simulations. However, preliminary molecular simulation results for chains of three, and five to eight segments do not agree with the values predicted by their theory. Values for parameter \( D \) for four segment chains from these two sources are shown in Table 5.1.

From Ghonasgi and Chapman [13] and from Wertheim's theory, assuming each site is independent, we can obtain expressions for the fraction of monomers of both components:
\[ x_o^{(2)} = x_o^{\text{intra}} \left( x_A^{(2)} \right)^4 \]  
\[ \text{(5-26)} \]

and

\[ x_o^{(1)} = \left( x_A^{(1)} \right)^4. \]  
\[ \text{(5-27)} \]

Additionally, the overall fraction of chains not bonded at site \( A \) is

\[ x_A^{(2)^*} = x_A^{(2)^*} x_o^{\text{intra}}. \]  
\[ \text{(5-28)} \]

This is related to \( x_A^{(2)^*} \), the fraction of chain molecules not intermolecularly bonded at site \( A \) to another chain or solvent molecule, by

\[ x_A^{(2)} - x_A^{(2)^*} = 1 - x_o^{\text{intra}}. \]  
\[ \text{(5-29)} \]

With values for the two component densities and the temperature, and the three potentials of interaction, we first use Eqs. 5-12, 5-13, 5-20, 5-24 and 5-26 in an iterative method and next Eqs. 5-27 to 5-29 to obtain a complete definition of the bonding in the model system.

### 5.3.2 Thermodynamics

The derivation presented here extends Ghonasgi and Chapman's approach to mixtures. Since the theory is exact in the low-density limit, the form of the Helmholtz free energy can be obtained in this limit. First consider the chemical potential of monomers of component \( i \) at low density which is approximately

\[ \mu_o^{(i)} = kT \ln \left( \rho_o^{(i)} \lambda_i^{(3)} \right) \]  
\[ \text{(5-30)} \]
where \( \Lambda_i \) is the de Broglie wavelength of component \( i \) and \( \rho_o^{(i)} \) is the density of monomers of component \( i \). But a condition of equilibrium is that the chemical potential of \( i \) as a monomer be equal to that of \( i \) associated to itself or to one or more other molecules. So we can write the following:

\[
\mu_o^{(i)} = \mu_{\text{banded}}^{(i)} .
\]  

(5-31)

\( \mu_{\text{banded}}^{(i)} \) is, of course, the chemical potential of component \( i \) when bonded. The pressure of our low-density fluid can be written \( PV \approx \overline{N}kT \), where \( \overline{N} \) is the number of "free" molecules. Each intermolecular bond reduces the number of "free" molecules by one assuming that no rings are formed. \( \overline{N} \) is then given by

\[
\overline{N} = \sum_{i=1}^{\text{No. of components}} \left\{ N_i \left[ 1 - \frac{1}{2} \sum_{j=1}^{\text{No. of sites on component } i} (1 - x_j^{(i)}) \right] \right\} = N_i (2x_A^{(i)} - 1) + N_x^{x_A^{(i)}} .
\]  

(5-32)

We can now write an expression for the Helmholtz free energy of the mixture,

\[
A = \sum_{i=1}^{\text{No. of components}} \left[ N_i^{(i)} \mu_o^{(i)} + \sum_j^{\text{No. of bonding states}} N_j^{(i)} \mu_{\text{banded}}^{(i)} \right] - PV .
\]  

(5-33)

\( N_i^{(i)} \) is the number of monomers of component \( i \) and \( N_j^{(i)} \) is the number of molecules of component \( i \) bonded in state \( j \) (once, twice, etc.). Eq. 5-33 may be rewritten considering that \( PV \approx \overline{N}kT \) as

\[
\frac{A}{NkT} = x_1 \ln(\rho_o^{(1)} \Lambda_1^3) + x_2 \ln(\rho_o^{(2)} \Lambda_2^1) - \frac{\overline{N}}{N} .
\]  

(5-34)
where \( x_i \) is the mole fraction of component \( i \) and \( N \) is the total number of molecules.

Subtracting an appropriate reference value of \( A \), e.g. a low density nonassociating fluid at the same state conditions, results in the change in Helmholtz free energy of association:

\[
\frac{A^{\text{assoc}}}{NkT} = \frac{A - A^{\text{ref}}}{NkT} = x_1 \ln x_o^{(1)} + x_2 \ln x_o^{(2)} - \frac{N}{N} + 1 \quad (5-35)
\]

and by virtue of Eq. 5-32,

\[
\frac{A^{\text{assoc}}}{NkT} = x_1 \left( \ln x_o^{(1)} - 2x_o^{(1)} + 1 \right) + x_2 \left( \ln x_o^{(2)} - x_o^{(2)} \right) + 1. \quad (5-36)
\]

Although derived for an associating gas, Ghonasgi and Chapman [13] have demonstrated the validity of the resulting expression for a pure associating liquid.

The change in configurational internal energy and in compressibility factor due to association are determined by thermodynamic differentiation.

Following Chapman et. al. [73], the compressibility factor of the nonassociating, hard chain reference fluid can be written as

\[
Z^{\text{ref}} = \frac{1 + \eta + \eta^2 - \eta^3}{(1 - \eta)^3} \left( x_1 + x_2 m \right) - (m - 1) \left( 1 + \eta \frac{5 - 2\eta}{(1 - \eta)(2 - \eta)} \right) x_2. \quad (5-37)
\]

The first term on the right hand side of Eq. 5-37 is the Carnahan-Starling equation of state [2, 113] and the packing fraction, \( \eta \), is given by
\[ \eta = \frac{\pi}{6} \left( \rho, \sigma_1^3 + m \rho, \sigma_c^3 \right) \] (5-38)

where \( m \) is the number of segments in a chain molecule; in this work \( m=4 \).

The compressibility factor of the fluid mixture is then,

\[ Z = Z^{\text{assoc}} + Z^{\text{ref}} \] (5-39)

where \( Z^{\text{assoc}} \), the change in compressibility factor due to association is

\[ \rho \frac{\partial (A^{\text{assoc}} / NkT)}{\partial \rho} \]

5.4 Results and Discussion

The simulations described above were performed at various state conditions. Reduced densities (packing fractions) studied were \( \eta = .1093, .2494 \) and .3379. These represent low to intermediate density liquid states. Reduced hydrogen bonding energies studied were \( \beta \varepsilon = \varepsilon = 5 \) and 7. (In all simulations \( \varepsilon_{\text{inter}} = \varepsilon_{\text{intra}} = \varepsilon_{\text{cross}} = \varepsilon_{\text{solv}} = \varepsilon \).) Solvent (spheres) mole fractions were \( x_1 = .293, .706 \) and .898. The results of the \( NVT \) simulations appear in Tables 5.2, 5.3 and 5.4 and those of the \( NpT \) simulations in Table 5.5. These simulation results appear in Figures 5.4 to 5.8 depicted by symbols. Furthermore, curves in these figures represent results from theory using the values of Gharasgi and Chapman for parameter \( D \) in Table 5.1, obtained from their correlation [13]:

\[ D = \frac{2(10)^{-4}}{(1- \eta)^3} \] (5-40)
Table 5.1 Values for parameter $D$ for tetramers from Ghonasgi and Chapman [13] and Sear and Jackson [114].

<table>
<thead>
<tr>
<th>$\eta$</th>
<th>Ref. 13</th>
<th>Ref. 114</th>
</tr>
</thead>
<tbody>
<tr>
<td>.1093</td>
<td>.000261</td>
<td>.000238</td>
</tr>
<tr>
<td>.1573</td>
<td>.000281</td>
<td>.000274</td>
</tr>
<tr>
<td>.2013</td>
<td>.000308</td>
<td>.000315</td>
</tr>
<tr>
<td>.2494</td>
<td>.000355</td>
<td>.000369</td>
</tr>
<tr>
<td>.3379</td>
<td>.000483</td>
<td>.000510</td>
</tr>
</tbody>
</table>

Figure 5.4 shows the average fraction of unbonded chain (broken line, plus sign) and solvent (full line, multiplication sign) molecules. For all packing fractions, compositions and energies of interaction studied here, the fraction of monomers is higher for chains than for spheres. This occurs due to the larger number of sites available for bonding on a solvent molecule than on a chain (4 and 2 respectively). Also, as the solvent mole fraction increases at any particular packing fraction or energy, the fraction of unbonded molecules of both species decreases, as expected since the density of association sites increases. At a fixed composition, either lowering the temperature at fixed density or increasing the density at fixed temperature results in more bonding and a decrease in the fraction of monomers. The predictions of the theory reproduce very closely the simulation results.

In Figure 5.5 theory and simulation results for average number of interchain (full line, multiplication sign) and intramolecular (broken line, plus sign) bonds per chain
Table 5.2. NVT simulation results for average fraction of unbonded chain, $\langle x^{(l)}_o \rangle$, and solvent molecules, $\langle x^{(z)}_o \rangle$, and for average reduced configurational energy, $\langle U/N\varepsilon \rangle$, with their respective standard deviations (S. D.) at different packing fractions, $\eta$, bonding energies, $\varepsilon^*$, and solvent mole fractions, $x_i$.

<table>
<thead>
<tr>
<th>$\eta$</th>
<th>$\varepsilon^*$</th>
<th>$x_i$</th>
<th>$\langle x^{(l)}_o \rangle$</th>
<th>S.D.</th>
<th>$\langle x^{(z)}_o \rangle$</th>
<th>S.D.</th>
<th>$\langle U/N\varepsilon \rangle$</th>
<th>S.D.</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>.7058</td>
<td>6.050e-01</td>
<td>6.801e-03</td>
<td>7.694e-01</td>
<td>5.134e-03</td>
<td>2.047e-01</td>
<td>4.805e-03</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>.8979</td>
<td>4.718e-01</td>
<td>4.968e-03</td>
<td>6.857e-01</td>
<td>2.819e-02</td>
<td>3.272e-01</td>
<td>4.100e-03</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>.2926</td>
<td>3.078e-01</td>
<td>2.959e-02</td>
<td>4.682e-01</td>
<td>2.943e-02</td>
<td>4.070e-01</td>
<td>1.622e-02</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>.7058</td>
<td>1.288e-01</td>
<td>1.475e-02</td>
<td>3.415e-01</td>
<td>2.165e-02</td>
<td>7.048e-01</td>
<td>2.264e-02</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>.8979</td>
<td>6.777e-02</td>
<td>5.014e-03</td>
<td>2.896e-01</td>
<td>6.048e-02</td>
<td>9.700e-01</td>
<td>1.298e-02</td>
<td></td>
</tr>
<tr>
<td>.2494</td>
<td>.2926</td>
<td>4.878e-01</td>
<td>1.652e-02</td>
<td>6.691e-01</td>
<td>2.902e-02</td>
<td>2.369e-01</td>
<td>1.215e-02</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>.7058</td>
<td>2.630e-01</td>
<td>6.866e-03</td>
<td>5.037e-01</td>
<td>2.843e-02</td>
<td>4.911e-01</td>
<td>1.296e-02</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>.8979</td>
<td>1.632e-01</td>
<td>5.143e-03</td>
<td>4.146e-01</td>
<td>2.717e-02</td>
<td>6.980e-01</td>
<td>9.492e-03</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>.2926</td>
<td>7.683e-02</td>
<td>4.179e-02</td>
<td>2.442e-01</td>
<td>4.018e-02</td>
<td>6.727e-01</td>
<td>3.075e-02</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>.7058</td>
<td>1.932e-02</td>
<td>5.789e-03</td>
<td>1.345e-01</td>
<td>2.144e-02</td>
<td>1.072e+00</td>
<td>1.935e-02</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>.8979</td>
<td>7.133e-03</td>
<td>1.355e-03</td>
<td>5.417e-02</td>
<td>3.159e-02</td>
<td>1.365e+00</td>
<td>1.035e-02</td>
<td></td>
</tr>
<tr>
<td>.3379</td>
<td>.2926</td>
<td>3.055e-01</td>
<td>2.314e-02</td>
<td>5.476e-01</td>
<td>4.029e-02</td>
<td>3.436e-01</td>
<td>2.157e-02</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>.7058</td>
<td>1.415e-01</td>
<td>1.046e-02</td>
<td>3.611e-01</td>
<td>2.351e-02</td>
<td>6.773e-01</td>
<td>2.169e-02</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>.8979</td>
<td>7.936e-02</td>
<td>4.206e-03</td>
<td>3.061e-01</td>
<td>3.320e-02</td>
<td>9.076e-01</td>
<td>1.603e-02</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>.2926</td>
<td>3.120e-02</td>
<td>1.302e-02</td>
<td>1.468e-01</td>
<td>2.401e-02</td>
<td>7.868e-01</td>
<td>3.689e-02</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>.7058</td>
<td>1.127e-02</td>
<td>4.004e-03</td>
<td>7.123e-02</td>
<td>1.374e-02</td>
<td>1.212e+00</td>
<td>1.813e-02</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>.8979</td>
<td>2.108e-03</td>
<td>1.372e-03</td>
<td>4.784e-02</td>
<td>1.673e-02</td>
<td>1.509e+00</td>
<td>1.328e-02</td>
<td></td>
</tr>
</tbody>
</table>
Figure 5.4 Average fraction of unbonded chain (broken line, plus sign) and solvent (full line, multiplication sign) molecules as a function of solvent mole fraction for a range of reduced energies and packing fraction. Results are from theory (curves) and molecular simulation (symbols).
Figure 5.5 Average number of interchain (full line, multiplication sign) and intramolecular (broken line, plus sign) bonds per chain molecule as a function of solvent mole fraction for a range of reduced energies and packing fraction. Results are from theory (curves) and molecular simulation (symbols).
Table 5.3 $NVT$ simulation results for average fraction of chain molecules bonded intermolecularly, $<\text{inter-}>$, and intramolecularly, $<\text{intra-}>$, with their respective standard deviations (S. D.) at different packing fractions, $\eta$, bonding energies, $\varepsilon^*$, and solvent mole fractions, $x_i$.

<table>
<thead>
<tr>
<th>$\eta$</th>
<th>$\varepsilon^*$</th>
<th>$x_i$</th>
<th>$&lt;\text{inter-}&gt;$</th>
<th>S.D.</th>
<th>$&lt;\text{intra-}&gt;$</th>
<th>S.D.</th>
</tr>
</thead>
<tbody>
<tr>
<td>.1093</td>
<td>5</td>
<td>.2926</td>
<td>2.626e-02</td>
<td>4.261e-03</td>
<td>3.280e-02</td>
<td>3.513e-03</td>
</tr>
<tr>
<td>5</td>
<td>.7058</td>
<td>1.626e-02</td>
<td>3.576e-03</td>
<td>2.503e-02</td>
<td>5.077e-03</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>.8979</td>
<td>6.099e-03</td>
<td>3.429e-03</td>
<td>2.688e-02</td>
<td>1.444e-02</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>.2926</td>
<td>1.071e-01</td>
<td>1.876e-02</td>
<td>1.471e-01</td>
<td>2.378e-02</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>.7058</td>
<td>5.491e-02</td>
<td>1.353e-02</td>
<td>9.652e-02</td>
<td>1.635e-02</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>.8979</td>
<td>2.407e-02</td>
<td>1.738e-02</td>
<td>6.384e-02</td>
<td>1.970e-02</td>
<td></td>
</tr>
</tbody>
</table>

| .2494  | 5               | .2926| 8.090e-02         | 1.352e-02 | 4.115e-02         | 6.805e-03 |
| 5      | .7058           | 4.012e-02 | 1.175e-02 | 2.500e-02 | 9.899e-03 |
| 5      | .8979           | 1.742e-02 | 1.095e-02 | 2.051e-02 | 1.561e-02 |
| 7      | .2926           | 2.148e-01 | 2.117e-02 | 1.157e-01 | 7.841e-03 |
| 7      | .7058           | 8.477e-02 | 1.877e-02 | 5.318e-02 | 1.022e-02 |
| 7      | .8979           | 3.455e-02 | 9.634e-03 | 4.768e-02 | 1.067e-02 |

| .3379  | 5               | .2926| 1.247e-01         | 2.247e-02 | 3.033e-02         | 6.112e-03 |
| 5      | .7058           | 6.073e-02 | 1.558e-02 | 2.526e-02 | 9.434e-03 |
| 5      | .8979           | 2.200e-02 | 9.706e-03 | 1.569e-02 | 7.656e-03 |
| 7      | .2926           | 2.668e-01 | 1.213e-02 | 8.861e-02 | 6.243e-03 |
| 7      | .7058           | 1.219e-01 | 8.364e-03 | 4.581e-02 | 6.210e-03 |
| 7      | .8979           | 4.670e-02 | 1.342e-02 | 3.987e-02 | 1.560e-04 |

molecule appear. The agreement between theory and simulation is again remarkable. We find that the average number of intramolecular bonds per chain molecule decreases with increasing solvent composition, reaching a limiting value when the chains are infinitely dilute at $x_i = 1$. As was the case with the curve for intramolecular bonding, the average number of interchain bonds also decreases with $x_i$, only more sharply, reaching
Table 5.4 \textit{NVT} simulation results for average fraction of solvent molecules bonded to a chain molecule, \(<\text{cross}>\), and to a like molecule, \(<\text{solv-solv}>\), with their respective standard deviations (S.D.) at different packing fractions, \(\eta\), bonding energies, \(\epsilon^*\), and solvent mole fractions, \(x_i\).

<table>
<thead>
<tr>
<th>(\eta)</th>
<th>(\epsilon^*)</th>
<th>(x_i)</th>
<th>(&lt;\text{cross}&gt;)</th>
<th>S.D.</th>
<th>(&lt;\text{solv-solv}&gt;)</th>
<th>S.D.</th>
</tr>
</thead>
<tbody>
<tr>
<td>.1093</td>
<td>.2926</td>
<td>3.184e-02</td>
<td>2.600e-03</td>
<td>2.706e-02</td>
<td>3.398e-03</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>.7058</td>
<td>1.943e-02</td>
<td>8.290e-04</td>
<td>9.757e-02</td>
<td>2.625e-03</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>.8979</td>
<td>8.691e-03</td>
<td>1.013e-03</td>
<td>1.629e-01</td>
<td>2.696e-03</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>.2926</td>
<td>1.397e-01</td>
<td>1.991e-02</td>
<td>1.084e-01</td>
<td>1.481e-02</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>.7058</td>
<td>6.569e-02</td>
<td>4.609e-03</td>
<td>3.363e-01</td>
<td>1.583e-02</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>.8979</td>
<td>2.242e-02</td>
<td>2.824e-03</td>
<td>4.902e-01</td>
<td>8.253e-03</td>
<td></td>
</tr>
<tr>
<td>.2494</td>
<td>.2926</td>
<td>9.243e-02</td>
<td>8.904e-03</td>
<td>7.246e-02</td>
<td>8.016e-03</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>.7058</td>
<td>4.917e-02</td>
<td>3.579e-03</td>
<td>2.359e-01</td>
<td>3.518e-03</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>.8979</td>
<td>1.871e-02</td>
<td>1.664e-03</td>
<td>3.490e-01</td>
<td>6.043e-03</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>.2926</td>
<td>2.628e-01</td>
<td>2.847e-02</td>
<td>2.241e-01</td>
<td>1.349e-02</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>.7058</td>
<td>1.030e-01</td>
<td>5.547e-03</td>
<td>5.248e-01</td>
<td>6.290e-03</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>.8979</td>
<td>3.763e-02</td>
<td>2.215e-03</td>
<td>6.804e-01</td>
<td>6.801e-03</td>
<td></td>
</tr>
<tr>
<td>.3379</td>
<td>.2926</td>
<td>1.445e-01</td>
<td>1.462e-02</td>
<td>1.105e-01</td>
<td>1.405e-02</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>.7058</td>
<td>6.872e-02</td>
<td>5.819e-03</td>
<td>3.244e-01</td>
<td>8.589e-03</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>.8979</td>
<td>2.405e-02</td>
<td>1.452e-03</td>
<td>4.551e-01</td>
<td>8.011e-03</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>.2926</td>
<td>3.378e-01</td>
<td>2.053e-02</td>
<td>2.389e-01</td>
<td>1.226e-02</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>.7058</td>
<td>1.196e-01</td>
<td>2.382e-03</td>
<td>5.845e-01</td>
<td>1.041e-02</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>.8979</td>
<td>4.024e-02</td>
<td>6.013e-04</td>
<td>7.551e-01</td>
<td>7.783e-03</td>
<td></td>
</tr>
</tbody>
</table>

zero for infinitely dilute chains. It is interesting to note that for the intermediate and high packing fractions intramolecular bonds are more numerous than interchain bonds only for high values of \(x_i\) (approximately .85 for \(\eta = .2494\) and .9 for \(\eta = .3379\)). For \(\eta = .1093\) intramolecular bonding is more prevalent than interchain bonding for the entire composition range at \(\epsilon^* = 5\) and 7. At low concentration of chains intramolecular
Table 5.5  *NpT* simulation results for average compressibility factor, \(<Z>\), average fraction of unbonded chain, \(\langle x^{(0)}_o \rangle\), and solvent molecules, \(\langle x^{(2)}_o \rangle\), and for average reduced configurational energy, \(\langle U/N\varepsilon \rangle\), with their respective standard deviations (S. D.) at different packing fractions, \(\eta\), bonding energies, \(\varepsilon^*\), and solvent mole fractions, \(x_i\).

<table>
<thead>
<tr>
<th>(\eta)</th>
<th>(\varepsilon^*)</th>
<th>(x_i)</th>
<th>(&lt;Z&gt;)</th>
<th>S.D.</th>
<th>(\langle x^{(0)}_o \rangle)</th>
<th>S.D.</th>
<th>(\langle x^{(2)}_o \rangle)</th>
<th>S.D.</th>
<th>(\langle U/N\varepsilon \rangle)</th>
<th>S.D.</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>.7058</td>
<td>1.525</td>
<td>3.057e-02</td>
<td>5.945e-01</td>
<td>9.742e-03</td>
<td>7.630e-01</td>
<td>1.382e-02</td>
<td>2.126e-01</td>
<td>6.587e-03</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>.8979</td>
<td>1.260</td>
<td>2.751e-02</td>
<td>4.677e-01</td>
<td>8.481e-03</td>
<td>6.811e-01</td>
<td>2.519e-02</td>
<td>3.304e-01</td>
<td>6.559e-03</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>.2926</td>
<td>1.652</td>
<td>4.799e-02</td>
<td>2.720e-01</td>
<td>3.727e-02</td>
<td>5.137e-01</td>
<td>2.303e-02</td>
<td>3.999e-01</td>
<td>1.962e-02</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>.8979</td>
<td>.4810</td>
<td>1.021e-02</td>
<td>6.282e-02</td>
<td>9.454e-03</td>
<td>3.041e-01</td>
<td>5.059e-02</td>
<td>1.003e+00</td>
<td>2.014e-02</td>
<td></td>
</tr>
<tr>
<td>.2494</td>
<td>5</td>
<td>.2926</td>
<td>4.539</td>
<td>5.758e-02</td>
<td>4.745e-01</td>
<td>2.923e-02</td>
<td>6.704e-01</td>
<td>2.814e-02</td>
<td>2.422e-01</td>
<td>1.957e-02</td>
</tr>
<tr>
<td>5</td>
<td>.7058</td>
<td>3.214</td>
<td>3.235e-02</td>
<td>2.588e-01</td>
<td>1.015e-02</td>
<td>4.975e-01</td>
<td>2.989e-02</td>
<td>4.968e-01</td>
<td>8.024e-03</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>.8979</td>
<td>2.201</td>
<td>3.101e-02</td>
<td>1.605e-01</td>
<td>1.121e-02</td>
<td>3.787e-01</td>
<td>2.605e-02</td>
<td>7.062e-01</td>
<td>2.364e-02</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>.2926</td>
<td>4.384</td>
<td>7.766e-02</td>
<td>7.789e-02</td>
<td>1.759e-02</td>
<td>2.550e-01</td>
<td>2.410e-02</td>
<td>6.472e-01</td>
<td>1.875e-02</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>.7058</td>
<td>2.179</td>
<td>6.190e-02</td>
<td>1.840e-02</td>
<td>5.070e-03</td>
<td>1.352e-01</td>
<td>2.157e-02</td>
<td>1.125e+00</td>
<td>1.874e-02</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>.8979</td>
<td>1.065</td>
<td>1.621e-02</td>
<td>5.518e-03</td>
<td>1.608e-03</td>
<td>1.285e-01</td>
<td>2.580e-02</td>
<td>1.377e+00</td>
<td>1.965e-02</td>
<td></td>
</tr>
<tr>
<td>.3379</td>
<td>5</td>
<td>.2926</td>
<td>9.249</td>
<td>1.600e-01</td>
<td>2.615e-01</td>
<td>1.489e-02</td>
<td>5.280e-01</td>
<td>4.786e-02</td>
<td>3.635e-01</td>
<td>2.482e-02</td>
</tr>
<tr>
<td>5</td>
<td>.7058</td>
<td>5.581</td>
<td>5.707e-02</td>
<td>1.358e-01</td>
<td>5.639e-03</td>
<td>3.625e-01</td>
<td>4.594e-02</td>
<td>6.789e-01</td>
<td>1.216e-02</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>.8979</td>
<td>3.676</td>
<td>3.277e-02</td>
<td>8.137e-02</td>
<td>4.034e-03</td>
<td>2.578e-01</td>
<td>4.192e-02</td>
<td>8.974e-01</td>
<td>1.725e-02</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>.2926</td>
<td>8.472</td>
<td>7.563e-02</td>
<td>2.809e-02</td>
<td>1.642e-02</td>
<td>1.234e-01</td>
<td>1.210e-02</td>
<td>8.270e-01</td>
<td>1.890e-02</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>.7058</td>
<td>4.398</td>
<td>2.393e-02</td>
<td>5.387e-03</td>
<td>1.724e-03</td>
<td>9.785e-02</td>
<td>2.469e-02</td>
<td>1.230e+00</td>
<td>1.438e-02</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>.8979</td>
<td>2.438</td>
<td>1.471e-02</td>
<td>2.190e-03</td>
<td>1.638e-03</td>
<td>5.166e-02</td>
<td>1.662e-02</td>
<td>1.502e+00</td>
<td>1.154e-02</td>
<td></td>
</tr>
</tbody>
</table>
interactions are more common than interchain interactions leading to more intramolecular association than interchain association.

In the same way as we have examined inter- and intramolecular bonding in chains we would like to compare theory and simulation results for the bonds formed by the solvent molecules. These can be either cross bonds (sphere bonded to chain) or solvent-solvent bonds. Both average number of cross (full line, multiplication sign) and solvent-solvent (broken line, plus sign) bonds per sphere are favored by increasing packing fraction and energy of interaction as seen in Figure 5.6.

In each figure, as the solvent composition increases at constant packing fraction, the density of solvent association sites increases. Since solvent molecules become more likely to find other solvent molecules, the fraction of solvent molecules involved in solvent-solvent bonds increases while the fraction involved in solvent-chain bonds decreases. Agreement between theory and simulation is very good.

For the thermodynamic properties studied here, simulation results compare also very well with our theory. The average configurational internal energy values from simulation fall below, but very close to theory as shown in Figure 5.7. The configurational energy becomes more negative as the solvent mole fraction, and thus the density of bonding sites, increases. The energy also decreases with increasing packing fraction and increasing energy of interaction (lowering temperature).

The compressibility factor of the mixture decreases with increasing solvent mole fraction as seen in Figure 5.8. The case of the pure fluids ($x_1 = 0$ and 1) has been studied
Figure 5.6 Average number of cross (full line, multiplication sign) and solvent-solvent (broken line, plus sign) bonds per sphere as a function of solvent mole fraction for a range of reduced energies and packing fraction. Results are from theory (curves) and molecular simulation (symbols).
Figure 5.7 Average configurational internal energy as a function of solvent mole fraction for a range of reduced energies and packing fraction. Results are from theory (curves) and molecular simulation (symbols).
Figure 5.8 Compressibility factor as a function of solvent mole fraction for a range of reduced energies and packing fraction. Results are from theory (curves) and molecular simulation (symbols).
before [13, 103] and now this extension of the theory to mixtures shows how these points are connected for the whole concentration range. The simulation results suggest that the approximations in the theory are well founded.

5.5 Conclusions

In this chapter a new theory for mixtures of associating fluids has been presented and tested favorably against molecular simulation. This theory should be of value in the understanding of polymer and protein solution thermodynamics. The theory is the result of extending Wertheim's theory for intermolecular association to mixtures and merging this extension to a theory for intramolecular association of chain molecules. A range of packing fractions and solvent concentrations for the model system was studied as well as two different values of bonding energy (temperature). Both bonding and thermodynamic properties predicted by the theory fall very close to simulation results at the state points studied here.
THEORY AND SIMULATION FOR ASSOCIATING CYCLIC MOLECULES

The theory for intramolecular association studied in Chapter 5 has been used to obtain an equation of state for cyclic molecules. A step further is to extend this equation using Wertheim's first order thermodynamic perturbation theory to predict the degree of bonding and thermodynamic properties of associating cyclic molecules. This new theory is proposed and tested against molecular simulation results for pure fluids of cyclic trimers with either one or three association sites. The trimers' association potential of interaction is modeled by an orientation dependent square-well, and the segment-segment interactions are of the hard-sphere type. A wide range of densities and temperatures is studied. Values for fraction of molecules not bonded, configurational internal energy and compressibility factor were obtained using Metropolis Monte Carlo simulations in the canonical and isothermal-isobaric ensembles. The theory predictions are in excellent agreement with these simulation results.

6.1 Introduction

The study of polyatomic molecules by statistical mechanical methods has recently provided powerful methods to explain the thermodynamic behavior of fluids of great scientific and industrial interest. Theories that have advanced our understanding in this field include the reference interaction site model (RISM) [90-91], polymer RISM [92-
perturbed hard chain theories [97], generalized Flory dimer theory [98], lattice fluid theories [46], a Percus-Yevick theory based chain equation of state [99], and Wertheim's first order thermodynamic perturbation theory (TPT1) [7-10] and its extensions [11, 73]. Recently, Ghonasgi et al. [12] and Sear and Jackson [108] have independently proposed a new theory for intramolecular association and an accurate equation of state for cyclic molecules of tangent hard spheres. In this paper we extend this ring equation of state to intermolecularly associating rings that can form linear chains or branched dendritic structures.

We first study a dimerizing cyclic molecule (one association site) to understand how the degree of association affects the thermodynamics of our model system. Previously, associating hard-spheres have been studied using molecular simulation and good agreement of TPT1 with these results has been observed [13]. Here, the effect of shape is studied by considering these planar, rigid cyclic molecules which are able to associate. We also consider a cyclic molecule with multiple (three) association sites, allowing in this way the possibility of complex structure formation, e. g. clusters, chains and even branched chains of cyclic molecules. The effect of shape and association is also studied for this case.

The motivation to look at this problem comes from recent successes in describing complex molecular systems with relatively simple but powerful statistical mechanical theories. The statistical associating fluid theory equation of state (SAFT EOS) [13, 66, 73, 74], for example, has been applied to accurately describe the phase behavior and
thermodynamic properties of polymer solutions [80, 107] and other complex fluids. SAFT provides a reliable tool for property estimation and prediction that is essential for process design and optimization and is also necessary for solving industrial problems related to safety and the environment. These theories and their extensions are tested rigorously against molecular simulation for validation and improvement. Particularly, our extension of the ring EOS may become important in the case of polymers with cyclic molecules in the backbone or pendant from it (e. g. polystyrene) and in complex structures (e. g. dendrimers) where further study will be necessary to assess the usefulness of our approach.

6.2 Molecular Model and Simulation

To test our new theory a model molecule made up of three tangent hard sphere segments (all of the same size) was considered. An association site was then placed on one or all three segments of the molecule as observed in Figure 6.1. The sites are placed on the line running from the geometric center of the cyclic molecule through the center of the segment.

The simulations were carried out for the pure fluids of cyclic molecules with either one or three association sites on each molecule for different values of packing fraction and association energy. The total potential of interaction between two cyclic molecules is made up of two distinct contributions as follows:

$$\phi = \phi_{HS} + \phi_{assoc}.$$
Figure 6.1 Tangent hard sphere cyclic molecules with (a) one and (b) three association sites. The sites are placed on the line passing through the center of the segment and the center of the cyclic molecule.

Here $\phi_{HS}$ is the hard-sphere potential of interaction

$$\phi_{HS}(\vec{r}, \Omega_1, \Omega_2) = \begin{cases} \infty & \text{if } r_{ij} < \sigma \\ 0 & \text{if } r_{ij} \geq \sigma \end{cases}$$

(6-2)

where $\vec{r}$ is the vector from the geometric center of molecule 1 to the geometric center of molecule 2, $\Omega_k$ is the orientation of molecule $k$, $r_{ij}$ is the center to center distance from segment $i$ of molecule 1 to segment $j$ of molecule 2. Finally, $\sigma$ is the segment diameter (see Fig. 6.2).
Figure 6.2 Relative position vectors between two tangent hard sphere cyclic molecules.

The second contribution to $\phi$ is the association potential:

$$
\phi_{asst}(r_{ij}, \Omega_1, \Omega_2) = \begin{cases} 
-\varepsilon & \text{if } r_{ij} < R_c, \Theta_1 < \Theta_c, \text{ and } \Theta_2 < \Theta_c, \\
0 & \text{otherwise}
\end{cases}
$$  
(6-3)

where $r_{ij}$ is the center to center distance between two segments, each containing an association site, in two different molecules ($k = 1, 2$). $\Omega_k$ is the orientation of these two segments, $\varepsilon$ is the association energy, and $\Theta_k$ is the angle subtended from the vector joining the centers of the aforementioned segments to the line connecting the center of a segment to its bonding site. $R_c$ and $\Theta_c$ are the distance and orientation cutoff parameters (respectively) for the potential (see Fig. 6.3).

Metropolis Monte Carlo (MMC) simulations [85] in the canonical ($NVT$) and isothermal-isobaric ($NpT$) ensembles were performed using 256 trimer cyclic molecules.
with either one or three association sites. For the case of one association site, 20,000 MMC cycles (with one cycle consisting in an attempt to move and reorient each molecule once and, for the NpT simulations, also attempting to change the simulation volume once) were carried out for equilibrated configurations at each state point studied. 40,000 MMC cycles were performed for the three association site model.

![Diagram of two tangent hard sphere cyclic molecules](image)

**Figure 6.3** Interaction between two tangent hard sphere cyclic molecules.

Displacement was achieved by random translation of the molecules in the three Cartesian coordinates. Additionally, three Euler angles were associated to each molecule to randomly reorient them. Displacement, reorientation, and maximum volume change (for NpT simulations) parameters were set to values that yielded an acceptance ratio of ca. 40%. The cut-off parameters chosen for the associating potentials were 1.1σ for the distance parameter and 27° for the orientation parameter. Only one bond can form per association site given these geometric specifications.
6.3 Theory

Thermodynamic perturbation theory expresses the residual Helmholtz free energy as

\[ a^{\text{res}} = a^{\text{res}}_R + a^{\text{chain}} + a^{\text{ring}} + a^{\text{assoc}}. \]  

(6-4)

Here, \( a^{\text{res}}_R \) is the residual Helmholtz free energy of a reference fluid, \( a^{\text{chain}} \) and \( a^{\text{ring}} \) are the changes in Helmholtz free energy due to chain and ring formation, respectively, and \( a^{\text{assoc}} \) is the change in Helmholtz free energy due to association.

Wertheim’s theory [7-10] gives \( a^{\text{assoc}} \) by

\[ a^{\text{assoc}} = \sum_{i=1}^{M} \left( \ln X - \frac{X}{2} \right) + \frac{M}{2} \]  

(6-5)

where \( M \) is the number of association sites on the cyclic molecule and \( X \) is the fraction of molecules not bonded at one of the different sites on the molecule. Since all sites are equivalent, \( X = X_1 = X_2 = \cdots = X_M \). Also from Wertheim’s theory we have an expression for \( X \),

\[ X = \frac{1}{1 + \sum_{i=1}^{M} \rho X_i \Delta} \]  

(6-6)

and an expression for the fraction of monomers

\[ X_0 = X^{\nu}. \]  

(6-7)

In Eq. 6-6 \( \rho \) is the number density of cyclic molecules and

\[ \Delta = \int g_2(12) f(12) d(12). \]  

(6-8)
The parameter $\Delta$ is thus a function of $g_R$, the reference fluid pair correlation function, and $f$, the Mayer $f$-function given (for the potential described in Eq. 6-3) by

$$f = \exp(-\beta \phi_{assoc}) - 1$$  \hspace{1cm} (6-9)

where $\beta = \frac{1}{kT}$, being $k$ Boltzmann's constant and $T$ the absolute temperature, and $\phi_{assoc}$ is the association potential. In Eq. 6-8, $d(12)$ stands for an unweighted average over all possible orientations and an integration in the bonding volume.

For the reference fluid we will consider a fluid of hard spheres at the same packing fraction, $\eta$, as the fluid of cyclic molecules. $\eta$ is given by

$$\eta = \frac{\pi}{6} m \rho \sigma^3,$$  \hspace{1cm} (6-10)

$m$ being the number of segments per cyclic molecule and $\sigma$ the segment diameter as discussed for Fig. 6.2. We consider $g_R$ to be approximately equal to the hard sphere correlation function as obtained from the Carnahan-Starling equation of state [2, 113]. We further consider $r^2 g_R(r)$ to be nearly constant over the bonding volume and equal to the contact value, $\sigma^2 g_R(r = \sigma)$, and obtain

$$\Delta = 4\pi K g_R(\sigma) f,$$  \hspace{1cm} (6-11)

where $4\pi K$ is the bonding volume given for the discussed potential cutoffs by

$$K = \frac{(1 - \cos \Theta)^2}{4} \sigma^3 (R_c - 1),$$  \hspace{1cm} (6-12)
Θ_c and R_c are the potential of interaction cutoff parameters presented in the previous section. The result for the Δ parameter within the bonding volume is

\[ \Delta = \pi (1 - \cos \Theta_c)^2 \sigma^2 (R_c - 1)^3 \left( \frac{1 - \eta}{2} \right) \frac{\exp(\beta \sigma) - 1}{(1 - \eta)^2}. \] (6-13)

The configurational internal energy of our model fluid is then given by the partial derivative with respect to β of \( a_{assoc} \)

\[ \frac{U^c}{N} = \frac{\partial a_{assoc}}{\partial \beta} = -\frac{X^2 M^2}{2} \rho \frac{\partial \Delta}{\partial \beta}. \] (6-14)

From Chapman et al. [73] the compressibility factor of the nonassociating, hard chain fluid is

\[ Z_{RC} + Z_{chain} = \frac{1 + \eta + \eta^2 - \eta^3}{(1 - \eta)^3} m - (m - 1) \left( 1 + \eta \frac{5 - 2\eta}{(1 - \eta)(2 - \eta)} \right). \] (6-15)

And from Ghonasgi et al. [12] the change in compressibility factor due to ring formation is:

\[ Z^{ring} = -m \eta \frac{5 - 2\eta}{(1 - \eta)(2 - \eta)}. \] (6-16)

Thus, the compressibility factor of our model fluid is given by adding Eqs. 6-15, 6-16 and the contribution due to association

\[ Z_{assoc} = \eta \frac{\partial a_{assoc}}{\partial \eta} = -\frac{X^2 M^2}{2} \eta \frac{\partial \rho \Delta}{\partial \eta}. \] (6-17)
The total compressibility factor is

\[
Z = \frac{1 + \eta + \eta^2 - \eta^3}{(1 - \eta)^3} - m - (m - 1) - m\eta \frac{(5 - 2\eta)}{(1 - \eta)(2 - \eta)} + Z_{\text{cor}}. \tag{6-18}
\]

6.4 Results and Discussion

Computer simulations were run for the model system with one and three association sites \((M=1, 3)\). Using the Metropolis Monte Carlo (MMC) \([85]\) technique in the canonical \((NVT)\) and isothermal-isobaric \((NpT)\) ensembles for the different state points, results were obtained and the theory predictions were compared to them. The values of packing fraction, \(\eta\), used were 0.1028, 0.2527 and 0.4021. For the case of one association site \((M=1)\) the reduced energies, \(\varepsilon^* = \beta \varepsilon\), were 5, 6, 7, 8 and 9 (Tables 6.1 and 6.2) and for three association sites \((M=3)\), \(\varepsilon^* = 2, 4, 6\) and 8 (Tables 6.3 and 6.4).

Values for average reduced configurational internal energies, \(\langle U^c / N\varepsilon \rangle\), average fraction of monomers, \(\langle X_o \rangle\), and average compressibility factor, \(\langle Z \rangle\), (in the \(NpT\) ensemble) were obtained and appear in Tables 6.1 through 6.4 and plotted (as symbols) along with theory predictions (curves) in Figures 6.4 through 6.10.

To obtain results at the specific packing fractions, \(\eta = 0.1028, 0.2527\) and 0.4021 from the \(NpT\) ensemble simulations, the appropriate reduced pressure, \(p^* = p\sigma^3 / kT\), was predicted from theory. As can be seen in Tables 6.2 and 6.4, this approach is reasonably accurate. The results of these simulations are presented as pseudo-isochoric data on Figs. 6.5 and 6.8 through 6.10.
Table 6.1 *NVT* simulations of associating cyclic trimers with one site (M=1). Results for average reduced configurational energy, $\langle U^c / N\varepsilon \rangle$, with the respective standard deviations (S. D.) at different packing fractions, $\eta$, and bonding energies, $\varepsilon^*$.  

<table>
<thead>
<tr>
<th>$\eta$</th>
<th>$\varepsilon^*$</th>
<th>$-\langle U^c / N\varepsilon \rangle$</th>
<th>S.D.</th>
</tr>
</thead>
<tbody>
<tr>
<td>.1028</td>
<td>5</td>
<td>2.5053e-02</td>
<td>2.5233e-03</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>5.4541e-02</td>
<td>3.7336e-03</td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>1.1425e-01</td>
<td>8.6696e-03</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>1.8822e-01</td>
<td>1.5327e-02</td>
</tr>
<tr>
<td></td>
<td>9</td>
<td>2.6891e-01</td>
<td>1.0363e-02</td>
</tr>
<tr>
<td>.2527</td>
<td>5</td>
<td>6.8285e-02</td>
<td>6.8545e-03</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>1.4053e-01</td>
<td>8.0751e-03</td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>2.2051e-01</td>
<td>1.3517e-02</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>2.9447e-01</td>
<td>1.3722e-02</td>
</tr>
<tr>
<td></td>
<td>9</td>
<td>3.5495e-01</td>
<td>1.2417e-02</td>
</tr>
<tr>
<td>.4021</td>
<td>5</td>
<td>1.3888e-01</td>
<td>9.9737e-03</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>2.0960e-01</td>
<td>1.7150e-02</td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>3.1827e-01</td>
<td>1.4495e-02</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>3.8863e-01</td>
<td>2.9425e-03</td>
</tr>
<tr>
<td></td>
<td>9</td>
<td>4.1748e-01</td>
<td>5.5783e-03</td>
</tr>
</tbody>
</table>

6.4.1 One Association Site (M=1)

In Figure 6.4 the reduced configurational internal energy, $U^c / N\varepsilon$, is plotted against reduced energy, $\varepsilon^*$, from simulation (symbols) and from theory (curves) for the case of one associating site per molecule. Since the reduced configurational internal energy is proportional to the fraction of bonds, $U^c / N\varepsilon$ is related to the fraction of monomers, $X_o$. Only the results for reduced configurational energy are presented. As the density increases, the probability of intermolecular interaction increases and $-U^c / N\varepsilon$ also
**Figure 6.4** Reduced configurational energy as a function of reduced energy for the model system with one association site ($M=1$). Theory predictions are shown as curves at constant packing fraction, $\eta$, and labeled. Simulation results are shown as symbols and correspond to the three values of packing fraction used in obtaining theory predictions, $\eta = 0.1028$ (exes), 0.2527 (crosses) and 0.4021 (circles).
Table 6.2 $NpT$ simulations of associating cyclic trimers with one site ($M=1$). Results for average reduced configurational energy, $\langle U'/N\epsilon \rangle$, and average compressibility factor, $<Z>$, with their respective standard deviations (S. D.) at different packing fractions, $\eta$, and bonding energies, $\epsilon^*$. 

<table>
<thead>
<tr>
<th>$p\sigma^3/kT$</th>
<th>$\epsilon^*$</th>
<th>&lt;\eta&gt;</th>
<th>$-\langle U'/N\epsilon \rangle$</th>
<th>S.D.</th>
<th>&lt;Z&gt;</th>
<th>S.D.</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1128</td>
<td>0.0984</td>
<td>2.3949e-02</td>
<td>3.5905e-03</td>
<td>1.8004</td>
<td>2.9309e-02</td>
<td></td>
</tr>
<tr>
<td>0.1103</td>
<td>0.1001</td>
<td>5.7021e-02</td>
<td>9.6419e-03</td>
<td>1.7313</td>
<td>3.3663e-02</td>
<td></td>
</tr>
<tr>
<td>0.1056</td>
<td>0.0991</td>
<td>1.0856e-01</td>
<td>1.6243e-02</td>
<td>1.6724</td>
<td>5.7027e-02</td>
<td></td>
</tr>
<tr>
<td>0.0989</td>
<td>0.0994</td>
<td>1.8663e-01</td>
<td>1.6958e-02</td>
<td>1.5624</td>
<td>4.2980e-02</td>
<td></td>
</tr>
<tr>
<td>0.0918</td>
<td>0.0984</td>
<td>2.7021e-01</td>
<td>9.2106e-03</td>
<td>1.4646</td>
<td>4.1153e-02</td>
<td></td>
</tr>
<tr>
<td>0.7418</td>
<td>0.2498</td>
<td>6.7854e-02</td>
<td>9.8336e-03</td>
<td>4.6651</td>
<td>5.4536e-02</td>
<td></td>
</tr>
<tr>
<td>0.7219</td>
<td>0.2507</td>
<td>1.2944e-01</td>
<td>1.3530e-02</td>
<td>4.5234</td>
<td>6.5501e-02</td>
<td></td>
</tr>
<tr>
<td>0.6968</td>
<td>0.2473</td>
<td>2.0602e-01</td>
<td>1.7324e-02</td>
<td>4.4256</td>
<td>5.6949e-02</td>
<td></td>
</tr>
<tr>
<td>0.6723</td>
<td>0.2506</td>
<td>3.1331e-01</td>
<td>9.1129e-03</td>
<td>4.2137</td>
<td>4.5680e-02</td>
<td></td>
</tr>
<tr>
<td>0.6524</td>
<td>0.2491</td>
<td>3.7078e-01</td>
<td>1.3623e-02</td>
<td>4.1135</td>
<td>7.0107e-02</td>
<td></td>
</tr>
<tr>
<td>3.4187</td>
<td>0.4023</td>
<td>1.3087e-01</td>
<td>2.1097e-02</td>
<td>13.3492</td>
<td>7.8582e-02</td>
<td></td>
</tr>
<tr>
<td>3.3592</td>
<td>0.4029</td>
<td>2.3148e-01</td>
<td>1.5017e-02</td>
<td>13.0960</td>
<td>5.1041e-02</td>
<td></td>
</tr>
<tr>
<td>3.3018</td>
<td>0.3976</td>
<td>2.9627e-01</td>
<td>7.2698e-03</td>
<td>13.0430</td>
<td>1.0023e-01</td>
<td></td>
</tr>
<tr>
<td>3.2556</td>
<td>0.4013</td>
<td>3.8744e-01</td>
<td>9.8313e-03</td>
<td>12.7442</td>
<td>9.4475e-02</td>
<td></td>
</tr>
<tr>
<td>3.2224</td>
<td>0.4058</td>
<td>4.1911e-01</td>
<td>4.1069e-03</td>
<td>12.4726</td>
<td>6.2025e-02</td>
<td></td>
</tr>
</tbody>
</table>

Increases ($X_o$ decreases). This behavior is seen in the simulation and theory results. Similarly, as temperature decreases and $\epsilon^*$ increases at fixed density, the molecules form more bonds and $-U'/N\epsilon$ increases ($X_o$ decreases). Agreement of theory and simulation results is excellent.

Figure 6.5 shows the compressibility factor, $Z$, as a function of the reduced association energy, $\epsilon^*$. For a higher packing fraction a higher value of $Z$ is observed. As
Figure 6.5 Compressibility factor as a function of reduced energy for the model system with one association site (M=1). Curves and symbols as interpreted in Fig. 6.4.
Table 6.3 *NVT* simulations of associating cyclic trimers with three sites ($M=3$). Results for average fraction of unbonded molecules, $\langle X_o \rangle$, and average reduced configurational energy, $\langle U^c / N\varepsilon \rangle$, with their respective standard deviations (S. D.) at different packing fractions, $\eta$, and bonding energies, $\varepsilon^*$.

<table>
<thead>
<tr>
<th>$\eta$</th>
<th>$\varepsilon^*$</th>
<th>$\langle X_o \rangle$</th>
<th>S.D.</th>
<th>$\langle U^c / N\varepsilon \rangle$</th>
<th>S.D.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>4</td>
<td>8.5099e-01</td>
<td>4.1810e-03</td>
<td>7.8546e-02</td>
<td>2.1873e-03</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>4.3171e-01</td>
<td>1.6245e-02</td>
<td>3.6444e-01</td>
<td>1.5543e-02</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>7.1960e-02</td>
<td>1.2563e-02</td>
<td>9.1409e-01</td>
<td>1.7148e-02</td>
</tr>
<tr>
<td>.2527</td>
<td>2</td>
<td>9.1919e-01</td>
<td>1.5999e-03</td>
<td>4.1532e-02</td>
<td>8.7301e-04</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>6.0782e-01</td>
<td>8.8796e-03</td>
<td>2.2978e-01</td>
<td>6.1710e-03</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>1.5775e-01</td>
<td>1.2876e-02</td>
<td>6.9430e-01</td>
<td>2.4049e-02</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>1.2552e-02</td>
<td>4.0547e-03</td>
<td>1.1466e+00</td>
<td>2.1894e-02</td>
</tr>
<tr>
<td>.4021</td>
<td>2</td>
<td>8.1213e-01</td>
<td>1.0947e-02</td>
<td>1.0058e-01</td>
<td>6.4101e-03</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>3.4367e-01</td>
<td>2.2459e-02</td>
<td>4.4862e-01</td>
<td>2.4441e-02</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>5.6473e-02</td>
<td>1.9560e-02</td>
<td>9.0102e-01</td>
<td>1.5806e-02</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>1.3665e-02</td>
<td>1.8610e-03</td>
<td>1.0929e+00</td>
<td>6.3864e-03</td>
</tr>
</tbody>
</table>

the strength of the interaction increases (or temperature decreases), the compressibility factor decreases due to increasing association. The transition from no bonding to almost complete bonding is followed very smoothly by the theory predictions. The agreement with the simulation results in the studied range of $\varepsilon^*$ is very good.

6.4.2 Three Association Sites ($M=3$)

The behavior of the properties studied for the case of three association sites ($M=3$) is similar to the case of $M=1$, except that the changes in properties are sharper and occur in
Table 6.4 $NpT$ simulations of associating cyclic trimers with three sites ($M=3$). Results for average fraction of unbonded molecules, $\langle X_o \rangle$, average reduced configurational energy, $\langle U'/Nε \rangle$, and average compressibility factor, $<Z>$, with their respective standard deviations (S. D.) at different packing fractions, $η$, and bonding energies, $ε'$. 

<table>
<thead>
<tr>
<th>$pσ^3/kT$</th>
<th>$ε'$</th>
<th>$&lt;η&gt;$</th>
<th>$\langle X_o \rangle$</th>
<th>S.D.</th>
<th>$\langle U'/Nε \rangle$</th>
<th>S.D.</th>
<th>$&lt;Z&gt;$</th>
<th>S.D.</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1139</td>
<td>2</td>
<td>0.0979</td>
<td>9.7877e-01</td>
<td>1.2080e-03</td>
<td>1.0694e-02</td>
<td>6.2016e-04</td>
<td>1.8268</td>
<td>2.6146e-02</td>
</tr>
<tr>
<td>0.1087</td>
<td>4</td>
<td>0.0994</td>
<td>8.5792e-01</td>
<td>6.2428e-03</td>
<td>7.4821e-02</td>
<td>3.5704e-03</td>
<td>1.7176</td>
<td>4.7646e-02</td>
</tr>
<tr>
<td>0.0856</td>
<td>6</td>
<td>0.0966</td>
<td>4.4450e-01</td>
<td>1.5201e-02</td>
<td>3.5890e-01</td>
<td>1.1780e-02</td>
<td>1.3914</td>
<td>3.5903e-02</td>
</tr>
<tr>
<td>0.0439</td>
<td>8</td>
<td>0.0941</td>
<td>7.8910e-02</td>
<td>1.3809e-02</td>
<td>8.6966e-01</td>
<td>2.5596e-02</td>
<td>0.7333</td>
<td>1.2331e-02</td>
</tr>
<tr>
<td>0.7521</td>
<td>2</td>
<td>0.2499</td>
<td>9.2141e-01</td>
<td>2.2187e-03</td>
<td>4.0438e-02</td>
<td>1.1881e-03</td>
<td>4.7272</td>
<td>4.4879e-02</td>
</tr>
<tr>
<td>0.6962</td>
<td>4</td>
<td>0.2504</td>
<td>6.1195e-01</td>
<td>1.0818e-02</td>
<td>2.2514e-01</td>
<td>7.2668e-03</td>
<td>4.3666</td>
<td>5.1582e-02</td>
</tr>
<tr>
<td>0.5579</td>
<td>6</td>
<td>0.2445</td>
<td>1.6403e-01</td>
<td>1.5131e-02</td>
<td>6.8357e-01</td>
<td>2.2227e-02</td>
<td>3.5846</td>
<td>4.0341e-02</td>
</tr>
<tr>
<td>0.4273</td>
<td>8</td>
<td>0.2540</td>
<td>2.1610e-02</td>
<td>8.9784e-03</td>
<td>1.1204e+00</td>
<td>1.8550e-02</td>
<td>2.6428</td>
<td>1.4099e-02</td>
</tr>
<tr>
<td>3.4522</td>
<td>2</td>
<td>0.3992</td>
<td>8.2249e-01</td>
<td>6.4699e-03</td>
<td>9.4618e-02</td>
<td>3.6285e-03</td>
<td>13.5842</td>
<td>9.0385e-02</td>
</tr>
<tr>
<td>3.2088</td>
<td>4</td>
<td>0.3934</td>
<td>3.8296e-01</td>
<td>1.7389e-02</td>
<td>4.0979e-01</td>
<td>1.1359e-02</td>
<td>12.8125</td>
<td>9.6887e-02</td>
</tr>
<tr>
<td>2.8574</td>
<td>6</td>
<td>0.3943</td>
<td>6.1769e-02</td>
<td>1.0274e-02</td>
<td>9.2840e-01</td>
<td>1.4882e-02</td>
<td>11.3829</td>
<td>7.9206e-02</td>
</tr>
<tr>
<td>2.6265</td>
<td>8</td>
<td>0.3910</td>
<td>1.1318e-02</td>
<td>2.4696e-03</td>
<td>1.1387e+00</td>
<td>3.7592e-03</td>
<td>10.5512</td>
<td>7.4029e-02</td>
</tr>
</tbody>
</table>
a lower range of $\varepsilon^\ast$. This is a result of the higher concentration of association sites at the same molecular concentration.

The fraction of molecules not bonded, $X_o$, as a function of $\varepsilon^\ast$ appears in Figure 6.6. We notice the same trends where increasing $\eta$ and $\varepsilon^\ast$ result in lower values of $X_o$ as expected due to increased bonding. The degree of association reaches a value of almost 20% (much higher than that for $M=1$) for $\eta=0.4021$ at an $\varepsilon^\ast$ as low as 2. This is due to the higher number of association sites ($M=3$) available for bonding. At a value of $\varepsilon^\ast=8$ we have almost complete bonding for the higher values of packing fraction ($\eta=0.2527$ and 0.4021). At this high value of $\varepsilon^\ast$ and $\eta$ the simulations proceed less efficiently and the agreement between theory and simulation results deteriorates. Under these conditions a large number of simulation cycles or biasing methods would be necessary for the system to properly sample bonding states.

Figure 6.7 shows the plot of $U^\ast / N\varepsilon$ versus $\varepsilon^\ast$. The same trends are seen, but the effect of association is manifested more dramatically at smaller values of $\varepsilon^\ast$ as compared to the case of $M=1$. Increasing $\varepsilon^\ast$ and $\eta$ results in a higher interaction of the molecules ($-U^\ast / N\varepsilon$ increases). The theory agrees with the simulation results in the whole range studied except for the high density and energy case ($\eta=0.4021$ and $\varepsilon^\ast=8$). Once more, this corresponds to a state point where a great extent of bonding occurs. In fact, the simulation results in the $NpT$ ensemble (where the simulation cell volume is allowed to vary) are in better agreement with the theory.
Figure 6.6 Fraction of molecules not bended as a function of reduced energy for the model system with three association sites ($M=3$). Curves and symbols as interpreted in Fig. 6.4.
Figure 6.7 Reduced configurational energy as a function of reduced energy for the model system with three association sites ($M=3$). Curves and symbols as interpreted in Fig. 6.4.
In Figure 6.8, the compressibility factor is plotted against $\varepsilon^*$. For the case ($M=3$) the decrease in compressibility factor as $\varepsilon^*$ increases is noticeably steeper than in that shown in Fig. 6.5 ($M=1$). The predictions of the theory follow the simulation results very closely in the whole range of reduced energy and for the three packing fractions selected for study.

### 6.4.3 Change in Compressibility Factor Due to Association

In Figures 6.9 and 6.10, we present plots of the change in compressibility factor due to association from theory (curves; Eq. 6-17) and simulation (symbols) versus the average number of bonds per molecule, $N_b = \frac{X^2M^2}{2\rho\Delta}$. The theory predicts that this plot should be linear at fixed density. The effect of association on the compressibility factor is calculated by subtracting the simulation result for non-associating molecules from that for the associating molecules. Additional $NpT$ simulations were performed to obtain these values and they are presented in Table 6.5.

### Table 6.5 $NpT$ simulations of non-associating cyclic trimers of hard sphere segments.

Results for average compressibility factor, $<Z>$, with the corresponding standard deviations (S. D.) at different packing fractions, $\eta$.

<table>
<thead>
<tr>
<th>$p\sigma^3/kT$</th>
<th>$&lt;\eta&gt;$</th>
<th>$&lt;Z&gt;$</th>
<th>S.D.</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1147</td>
<td>0.09936</td>
<td>1.8127</td>
<td>3.180e-02</td>
</tr>
<tr>
<td>0.7625</td>
<td>0.2494</td>
<td>4.8029</td>
<td>3.592e-02</td>
</tr>
<tr>
<td>3.5164</td>
<td>0.4004</td>
<td>13.7943</td>
<td>3.908e-02</td>
</tr>
</tbody>
</table>
Figure 6.8 Compressibility factor as a function of reduced energy for the model system with three association sites \((M=3)\). Curves and symbols as interpreted in Fig. 6.4.
Figure 6.9 Change in compressibility factor due to association, $Z^{assoc}$, as a function of average number of bonds per molecule, $N_g$, for the model system with one association site ($M=1$). Curves and symbols as interpreted in Fig. 6.4.
Figure 6.10 Change in compressibility factor due to association, $Z^{assoc}$, as a function of average number of bonds per molecule, $N_B$, for the model system with three association sites ($M=3$). Curves and symbols as interpreted in Fig. 6.4.
Fig. 6.9 shows the results obtained in the one site case \((M=1)\). Agreement between the theory and simulation results is very good for the two lower packing fractions and slightly deteriorates for the highest packing fraction. The theory prediction of a linear relationship between the two quantities is observed also in the behavior of the data points.

In Fig. 6.10 the results for three association sites \((M=3)\) are presented and, as in the previous case of \(M=1\), agreement between theory and simulation is excellent for the lower densities and good with some simulation uncertainty for \(\eta=0.4021\). For both cases, as the strength of the association interaction increases, the change in compressibility factor due to association, \(-Z^{assoc}\), and the number of bonds per molecule, \(N_b\), also increase.

6.5 Conclusions

A new theory for cyclic associating molecules and new molecular simulation results have been presented. The equation of state for cyclics [12] and Wertheim's theory of association [7-10] provide the basis of this new theory. The shape effects and the effect of association here studied should contribute to the better understanding of the properties of cyclic molecules, clusters and polymers. The excellent agreement between this new theory and computer simulation for the various state points of the investigated model supports the validity of the assumptions made in the theory.
MULTIPLE BONDING SITES ON CHAIN MOLECULES IN AN ASSOCIATING SOLVENT

In this chapter, a simulation and theory study of the effect of bonding site density on thermodynamic properties and extent of bonding of a linear flexible chain in a hydrogen bonding solvent is performed. Predictions from Werthem's theory are compared against simulation results. Thermodynamic properties and extent of bonding were obtained. The solvent molecules are modeled as hard spheres with four association sites in a tetrahedral arrangement. The chains are flexible and consist of six tangent segments of hard spheres with bonding sites that interact with the solvent molecules. A solvent molecule can also form a bond with a second solvent molecule. The association interaction is modeled with an orientation dependent square-well. The total number of bonding sites on each chain is varied and the effects studied. This is another test of the theory for the case of mixtures of associating molecules of different sizes. The Metropolis Monte Carlo technique was chosen to perform simulations in the canonical and isothermal-isobaric ensembles. Good agreement was found between theory and simulation.

7.1 Introduction

The study of polymer solution thermodynamics is important to industry because of economic and environmental considerations. Phase behavior must be accurately
described and predicted to prevent phase splitting and the resulting fouling of reactors and separation equipment.

Moreover, the study of the solubility of polymers in water is of special interest to manufacturers who wish to reduce costs and combat environmental problems. Shifting from organic solvents to water or other solvents that are more benign to the environment could represent a very important step forward in polymer processing.

The factors influencing the solubility of polymers include molecular weight and functional group type, position, and density.

An example is that of polypropylene oxide (PPO) which is insoluble in water, polyethylene oxide (PEO) which is water soluble, and polymethylene oxide (PMO) which is insoluble in this solvent. PEO is soluble in water since it has a greater density of association sites than PPO. However, the even greater density of oxygen sites per carbon number of PMO apparently does not create enough hydrogen bonds with water to solubilize PMO. Various explanations have been offered; several related to steric hindrance.

Several advances in statistical mechanical theories for complex fluids have appeared recently. These include the reference interaction site model (RISM) [90, 91], polymer RISM [92-96], perturbed hard chain theories [97], generalized Flory dimer theory [98], lattice fluid theories [46], and a Percus-Yevick theory based chain equation of state [99]. Wertheim's approach known as the first order thermodynamic perturbation theory (TPT1)
[7-10], and its extensions [11, 73, 100, 101] resulted in the development of the statistical
associating fluid theory equation of state (SAFT EOS) [74,80].

The widely tested approach of Wertheim’s TFT1 will be used in this study. This
approach suits especially well systems that present strong, highly directional interactions,
e.g., hydrogen bonds.

The interests in this study lie in testing the applicability of the theory, first to mixtures
of associating molecules of different sizes, and second in chain molecules with varying
bonding site density. Comparisons of theory predictions are done with computer
simulation results for our model systems.

7.2 Molecular Models and Simulation

To study the effect of bonding site density on chain molecules we consider a flexible,
tangent hard sphere chain with six segments and two or three bonding sites. The sites are
labeled type A and are placed along the molecule as shown in Fig. 7.1. The sites are
placed on a line forming a right angle with the vector joining the segment containing the
site and a contiguous segment.

The potential of interaction between two different chain molecules is purely
repulsive:

\[
\phi_{HS}(\mathbf{r}, \Omega_1, \Omega_2) = \begin{cases} 
\infty & \text{if } r_{ij} < \sigma_c \\
0 & \text{if } r_{ij} \geq \sigma_c
\end{cases}
\]  

\text{(7-1)}
where $\vec{r}$ is the vector connecting the center of molecule 1 to the center of molecule 2, $\Omega_k$ is the orientation of molecule $k$, $r_{ij}$ is the center to center distance from segment $i$ of molecule 1 to segment $j$ of molecule 2, and $\sigma_r$ is the segment diameter.

(Figure 7.1 Model chain molecules with two (a) and three (b) association sites.

For the solvent, four association sites labeled type $A$ and $B$ are placed on the vertices of a tetrahedron embedded in a sphere (see Fig. 7.2a).

The interaction between solvent molecules (see Fig. 7.2b) is given by

$$\phi_{\text{solv}} = \phi_{\text{HS}} + \phi_{\text{assoc}}$$  \hspace{1cm} (7-2)

where
Figure 7.2 Model hydrogen bonding solvent with four association sites in a tetrahedral arrangement (a) and interaction between two solvent molecules (b).

\[
\phi_{m3}^i(r) = \begin{cases} 
\infty & \text{if } r < \sigma_i \\
0 & \text{if } r \geq \sigma_i 
\end{cases} \quad (7-3)
\]

and

\[
\phi_{solv}^{assoc}(r, \omega_1, \omega_2) = \begin{cases} 
-\varepsilon_{solv} & \text{if } r < r_c, \theta_i < \theta_c, \text{ and } \theta_2 < \theta_c \\
0 & \text{otherwise} 
\end{cases} \quad (7-4)
\]

\(r\) is the distance between the centers of the two solvent molecules and \(\sigma_i\) is the sphere diameter. Also, \(\omega_i\) is the orientation of molecule \(k\), \(\varepsilon_{solv}\) is the association energy between solvent molecules, and \(r_c\) and \(\theta_c\) are the usual radial and orientation (respectively) cutoff parameters for the potential. The angles \(\theta_i\) and \(\theta_2\) are formed from the vector joining the centers of spheres 1 and 2 to the vectors connecting these centers to any of the four associating sites. Only bonds of type \(AB\) are allowed (see Fig. 7.2b).

Lastly, for interactions of solvent and chain molecules, or cross associations, the potential of interaction is the following:
\[ \phi_{\text{cross}} = \phi_{\text{HS}}^{c} + \phi_{\text{cross}}^{\text{assoc}} \]  

(7-5)

where

\[ \phi_{\text{HS}}^{c}(r) = \begin{cases} 0 & \text{if } r < \sigma_{c^{-1}} \\ \infty & \text{if } r \geq \sigma_{c^{-1}} \end{cases} \]  

(7-6)

and

\[ \phi_{\text{cross}}^{\text{assoc}}(r, \Omega, \omega) = \begin{cases} -\varepsilon_{\text{cross}} & \text{if } r < r_{c^{-1}}, \Theta_{1} < \Theta^{c^{-1}}, \text{and } \Theta_{2} < \Theta^{c^{-1}} \\ 0 & \text{otherwise} \end{cases} \]  

(7-7)

Here, \( r \) is the distance between the center of the solvent molecule and a segment of the chain molecule and \( \sigma_{c^{-1}} = (\sigma_{c} + \sigma_{s})/2 \). \( \Omega \) is the orientation of the chain molecule, \( \omega \) is the orientation of the solvent molecule, \( \varepsilon_{\text{cross}} \) is the cross association energy between molecules, \( r_{c^{-1}} \) and \( \Theta^{c^{-1}} \) are the cutoff parameters. The angle \( \Theta_{1} \) is formed from the vector joining the centers of the solvent molecule and of the segment with the interacting bonding-site of the chain molecule, to the vector connecting the center of the chain segment and its bonding site (see Fig. 7.3). Similarly, \( \Theta_{2} \) is the angle formed from the center-to-center vector described previously to the vector that connects the center of the solvent molecule to its proper bonding site. Again, only bonds of type AB are allowed.

The model system was simulated with the Metropolis Monte Carlo (MMC) method [85] in the canonical \((NVT)\) and isothermal-isobaric \((NpT)\) ensembles. A total of 798 spheres that could act either as solvent molecules or segments of the hexamers (depending on the compositions of interest) were first sufficiently equilibrated. Subsequently, 50,000 MMC cycles (in each cycle an attempt is made to sequentially
displace and reorient each molecule once and for the $NpT$ simulations a change of volume is attempted also once) were run for each state point and averages accumulated.

![Diagram of molecular interaction](image)

**Figure 7.3** Cross interaction between a solvent molecule and a flexible chain.

The solvent molecules were displaced in the conventional way during simulation of the $NVT$ ensemble [5], i.e., random translation in the three Cartesian coordinates. Additionally, three Euler angles were associated to each sphere and by randomly modifying them, particle reorientation was attained. For the chain molecules, a similar procedure was followed. Random translation of the whole chain preceded reorientation of the end segment with a bonding site (the "head" of the chain) in the same fashion as for the solvent molecules. For the segment next to the "head", the vector joining both centers is perpendicular to the vector to the bonding site. Therefore, their relative positions are completely determined. The next segment has no similar restriction, and the relative position is modified [110] by adding a random vector to the vector joining the two segments and then renormalizing the resultant vector to a magnitude of $\sigma_r$. This is
done for the subsequent segments until another segment with an association site is encountered. The process is then repeated considering the segment with the bonding site in the same way as the “head” segment. The maximum change in position and orientation is controlled by parameters that were adjusted to yield an acceptance ratio of approximately 40%. For the $NpT$ simulations, the molecules were moved as described above and additionally the volume of the simulation cell was randomly modified as prescribed by Wood [111]. Again, 40% acceptance was the target when adjusting the maximum volume change parameter. The cutoff parameters for the associating potentials were taken to be 1.1 times the sphere diameter (which was chosen to be equal for chains and for solvent molecules) for the distance parameters and 27° for all orientation cutoff parameters. These values guarantee that an association site will bond only once.

7.3 Theory

The model presented in the previous section is now used to obtain expressions for extent of bonding and of thermodynamic properties by applying Wertheim’s theory.

7.3.1 Two Association Sites

For the case of two bonding sites on the chain molecule we can write the fraction of chains not bonded at a site $A$ as

$$x_{ch(A)} = \frac{1}{1 + 2\rho_{sp}x_{sp(\theta)}\Delta^{cross}}.$$  (7-8)
where \( \rho_{sp} \) is the number density of solvent molecules (spheres), \( x_{sp(\theta)} \) is the fraction of spheres not bonded at a site \( B \), and \( \Delta^{cross} \) is the association strength for cross interactions given by:

\[
\Delta^{cross} = 4\pi g_{HS}(\sigma_{c-1})K_{AB}^{cross}F_{AB}^{cross}.
\]  

(7-9)

Here, \( g_{HS} \) is the radial distribution function of the hard sphere fluid created by dissolving all bonds, evaluated at contact and at the same packing fraction as the chain and sphere system of interest. \( K_{AB}^{cross} \) is the available volume for bonding between sites \( A \) and \( B \) of the two molecules,

\[
K_{AB}^{cross} = \frac{(1 - \cos(\theta_c^{\theta-1}))^2}{4} \sigma_{c-3}^3 r_c^{\theta-1} - 1.
\]  

(7-10)

Finally, \( F_{AB}^{cross} \) is the Mayer function for the attractive part of the potential:

\[
F_{AB}^{cross} = \exp(\beta \epsilon_{c0}) - 1,
\]  

(7-11)

and \( \beta = 1/kT \), where \( k \) is Boltzmann’s constant and \( T \) is the absolute temperature of the system.

For the solvent molecules, we have an expression for fraction of spheres not bonded at a site \( A \)

\[
x_{sp(A)} = \frac{1}{1 + 2\rho_{sp}x_{sp(\theta)}\Delta^{self}},
\]  

(7-12)

where \( x_{sp(\theta)} \), the fraction of solvent molecules not bonded at a site \( B \) is
\[
x_{sp(\beta)} = \frac{1}{1 + 2 \rho_{sp} x_{sp(\beta)} \Delta_{self} + 2 \rho_{ch} x_{ch(\beta)} \Delta_{cross}}
\]  
(7-13)

where \( \rho_{ch} \) is the number density of chain molecules, and \( \Delta_{self} \) is (similarly as in Eqs. 7-9 through 7-11):

\[
\Delta_{self} = 4 \pi g_{HS}(\sigma_1) K_{AB}^{self} F_{AB}^{self}
\]
(7-14)

with

\[
K_{AB}^{self} = \frac{(1 - \cos \theta)^2}{4} \sigma_1^3 (r_c - 1)
\]
(7-15)

and

\[
F_{AB}^{self} = \exp(\beta \varepsilon_{sol}) - 1.
\]
(7-16)

The fraction of monomers can now be expressed according to Wertheim’s theory as

\[
x_{o}^{ch} = x_{ch(\beta)}^2
\]
(7-17)

for the chains and

\[
x_{o}^{sp} = x_{sp(\beta)}^2 x_{sp(\beta)}^2
\]
(7-18)

for the solvent molecules.

We can rewrite Eqs. 7-8 and 7-9 as:

\[
x_{sp(\beta)} + 2 \rho_{sp} x_{sp(\beta)} x_{sp(\beta)} \Delta_{self} = 1
\]
(7-19)
where $2\rho_{sp}x_{sp(A)}x_{sp(B)}\Delta^{self}$ and $2\rho_{ch}x_{ch(A)}x_{sp(B)}\Delta^{cross}$ can be identified as the fraction of spheres bonded at a site $A$ to another solvent molecule and to a chain molecule, respectively.

An interesting ratio derived from these expressions is:

$$\frac{x_{sp(A)} - x_{sp(B)}}{1 - x_{sp(B)}} = \frac{2\rho_{ch}x_{ch(A)}x_{sp(B)}\Delta^{cross}}{2\rho_{sp}x_{sp(A)}x_{sp(B)}\Delta^{self} + 2\rho_{ch}x_{ch(A)}x_{sp(B)}\Delta^{cross}}$$  (7-21)

which is the fraction of cross bonds that form relative to the total number of bonds (cross plus self bonds).

7.3.2 Three Association Sites

In the case of the second model with three bonding sites on the chain molecules, most of the equations in the previous section hold with the following exceptions.

Eq. 7-17 is now

$$x_{o}^{ch} = x_{ch(A)}$$  (7-22)

Eq. 7-13 becomes

$$x_{sp(B)} = \frac{1}{1 + 2\rho_{sp}x_{sp(A)}\Delta^{self} + 3\rho_{ch}x_{ch(A)}\Delta^{cross}}$$  (7-23)

and Eqs. 7-20 and 7-21:

$$x_{sp(B)} + 2\rho_{sp}x_{sp(A)}x_{sp(B)}\Delta^{self} + 3\rho_{ch}x_{ch(A)}x_{sp(B)}\Delta^{cross} = 1$$  (7-24)
and
\[
\frac{x_{sp(a)} - x_{sp(b)}}{1 - x_{sp(b)}} = \frac{3\rho_{ch} x_{ch(a)} x_{sp(b)} \Delta^{cross}}{2\rho_{sp} x_{sp(a)} x_{sp(b)} \Delta^{self} + 3\rho_{ch} x_{ch(a)} x_{sp(b)} \Delta^{cross}}. \tag{7-25}
\]

### 7.3.3 Thermodynamics

The derivation presented in Chapter 3 for Wertheim's theory and the general expression for the contribution due to association to the residual Helmholtz free energy for mixtures is applicable in this case and the reader is referred to it. The expression is:

\[
a^{assoc} = \sum_{i=1}^{k} x^{(i)} \sum_{A \in i} \left\{ \ln x^{(i)}_{A} - \frac{x^{(i)}_{A}}{2} \right\} + \frac{M^{(i)}}{2}, \tag{3-15}
\]

and in terms of our particular case:

\[
a^{assoc} = x_{sp} \left[ \ln(x_{sp}^{p}) - x_{sp(a)} - x_{sp(b)} + 2 \right] + x_{ch} \left[ \ln(x_{ch}^{p}) - \frac{M}{2} (x_{ch(a)} - 1) \right]. \tag{7-26}
\]

Here \( x_{sp} \) and \( x_{ch} \) are, respectively, the solvent and chain mole fractions. \( M \) is the number of association sites on the chain molecules (\( M = 2, 3 \)).

The changes in configurational internal energy and in compressibility factor due to association are determined by thermodynamic differentiation, the first expression being:

\[
\frac{U}{N} = \frac{\partial (a^{assoc})}{\partial \beta}. \tag{7-27}
\]

The compressibility factor of the nonassociating, hard chain reference fluid can be written as [73],
\[ Z^{\text{ref}} = \frac{1 + \eta + \eta^2 - \eta^3}{(1-\eta)^3} \left( x_{sp} + x_{eh} m \right) - \left( m - 1 \right) \left( 1 + \eta \frac{5 - 2\eta}{(1-\eta)(2-\eta)} \right) x_{eh}. \] (7-28)

The first term on the right hand side of Eq. 7-28 is the Carnahan-Starling equation of state [2, 113] and the packing fraction, \( \eta \), is given by

\[ \eta = \frac{\pi}{6} \rho \left( x_{sp} \sigma_s^3 + m x_{eh} \sigma_e^3 \right) \] (7-29)

where \( \rho \) is the total molecule number density, \( m \) is the number of segments in a chain molecule; in this work \( m=6 \).

The compressibility factor of the fluid mixture is then,

\[ Z = Z^{\text{assoc}} + Z^{\text{ref}} \] (7-30)

where \( Z^{\text{assoc}} \), the change in compressibility factor due to association is \( \rho \frac{\partial (a^{\text{assoc}})}{\partial \rho} \).

### 7.4 Results and Discussion

The simulations in this study were run at two packing fractions, \( \eta = .35 \) and \( .15 \), and two reduced bonding energies, \( \beta \epsilon = \epsilon_s^* = 5 \) and \( 7 \) (for all simulations \( \epsilon_{\text{cross}} = \epsilon_{\text{solv}} = \epsilon \)). The solvent mole fractions were \( x_{sp} = .3, .5 \) and \( .8 \). For the two site model, the NVT simulation results appear in Table 7.1 and the NpT simulation results in Table 7.3. Similarly, for the three site model the reader should refer to Tables 7.2 and 7.4 for the NVT and NpT simulation results, respectively. Tables 7.5 and 7.6 show the results for the fraction of cross bonds on spheres for the two and three site models, respectively.
Table 7.1 Two site model NVT simulation results for average fraction of unbonded chain, \(<x_{ch}^o>\), and solvent molecules, \(<x_{sp}^o>\), and for average reduced configurational energy, \(<U/N\epsilon>\), with their respective standard deviations (S. D.) at different packing fractions, \(\eta\), bonding energies, \(\epsilon^*\), and solvent mole fractions, \(x_{sp}\).

<table>
<thead>
<tr>
<th>(\eta)</th>
<th>(\epsilon^*)</th>
<th>(x_{sp})</th>
<th>(-&lt;U/N\epsilon&gt;)</th>
<th>S.D.</th>
<th>(&lt;x_{sp}^o&gt;)</th>
<th>S.D.</th>
<th>(&lt;x_{ch}^o&gt;)</th>
<th>S.D.</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.35</td>
<td>5 0.3034</td>
<td>1.972e-01</td>
<td>2.421e-04</td>
<td>3.716e-01</td>
<td>1.835e-03</td>
<td>8.080e-01</td>
<td>3.457e-04</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>0.7990</td>
<td>6.844e-01</td>
<td>1.738e-04</td>
<td>1.407e-01</td>
<td>4.255e-05</td>
<td>4.137e-01</td>
<td>1.550e-03</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>0.5000</td>
<td>6.941e-01</td>
<td>6.470e-05</td>
<td>3.723e-02</td>
<td>1.322e-04</td>
<td>3.762e-01</td>
<td>1.441e-04</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>0.7990</td>
<td>1.215e+00</td>
<td>3.689e-04</td>
<td>8.203e-03</td>
<td>1.136e-05</td>
<td>1.204e-01</td>
<td>2.173e-03</td>
<td></td>
</tr>
<tr>
<td>0.15</td>
<td>5 0.3034</td>
<td>5.730e-02</td>
<td>2.691e-05</td>
<td>7.689e-01</td>
<td>3.662e-04</td>
<td>9.449e-01</td>
<td>3.753e-05</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>0.5000</td>
<td>1.169e-01</td>
<td>4.773e-05</td>
<td>6.881e-01</td>
<td>1.139e-04</td>
<td>8.932e-01</td>
<td>6.355e-05</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>0.7990</td>
<td>2.863e-01</td>
<td>8.480e-05</td>
<td>4.889e-01</td>
<td>9.061e-05</td>
<td>7.739e-01</td>
<td>4.400e-04</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>0.3034</td>
<td>2.504e-01</td>
<td>7.143e-04</td>
<td>2.398e-01</td>
<td>2.053e-03</td>
<td>7.840e-01</td>
<td>6.464e-04</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>0.5000</td>
<td>4.672e-01</td>
<td>1.444e-03</td>
<td>1.752e-01</td>
<td>5.302e-04</td>
<td>6.531e-01</td>
<td>1.250e-03</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>0.7990</td>
<td>9.078e-01</td>
<td>7.374e-04</td>
<td>7.194e-02</td>
<td>1.081e-04</td>
<td>4.644e-01</td>
<td>1.990e-03</td>
<td></td>
</tr>
</tbody>
</table>
Table 7.2 Three site model $NVT$ simulation results for average fraction of unbonded chain, $\langle x_{\alpha}^{\text{ub}} \rangle$, and solvent molecules, $\langle x_{\alpha}^{\text{sp}} \rangle$, and for average reduced configurational energy, $\langle U / NC \rangle$, with their respective standard deviations (S. D.) at different packing fractions, $\eta$, bonding energies, $\varepsilon^*$, and solvent mole fractions, $x_{sp}$.

<table>
<thead>
<tr>
<th>$\eta$</th>
<th>$\varepsilon^*$</th>
<th>$x_{sp}$</th>
<th>$-\langle U / NC \rangle$</th>
<th>S.D.</th>
<th>$\langle x_{\alpha}^{\text{sp}} \rangle$</th>
<th>S.D.</th>
<th>$\langle x_{\alpha}^{\text{ub}} \rangle$</th>
<th>S.D.</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.35</td>
<td>5</td>
<td>0.3034</td>
<td>2.231e-01</td>
<td>2.583e-04</td>
<td>3.206e-01</td>
<td>8.390e-04</td>
<td>7.702e-01</td>
<td>4.166e-04</td>
</tr>
<tr>
<td>5</td>
<td>0.5000</td>
<td>3.894e-01</td>
<td>2.050e-04</td>
<td>2.461e-01</td>
<td>2.948e-04</td>
<td>6.489e-01</td>
<td>3.745e-04</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>0.7990</td>
<td>7.223e-01</td>
<td>4.190e-04</td>
<td>1.336e-01</td>
<td>7.622e-05</td>
<td>3.324e-01</td>
<td>1.694e-03</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>0.3034</td>
<td>4.934e-01</td>
<td>6.329e-04</td>
<td>2.255e-02</td>
<td>2.570e-04</td>
<td>5.383e-01</td>
<td>2.158e-04</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>0.5000</td>
<td>7.737e-01</td>
<td>1.279e-04</td>
<td>2.007e-02</td>
<td>6.568e-05</td>
<td>3.407e-01</td>
<td>1.066e-04</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>0.7990</td>
<td>1.230e+00</td>
<td>3.418e-04</td>
<td>9.164e-03</td>
<td>2.391e-05</td>
<td>7.418e-02</td>
<td>2.026e-04</td>
<td></td>
</tr>
<tr>
<td>0.15</td>
<td>5</td>
<td>0.3034</td>
<td>7.052e-02</td>
<td>5.748e-05</td>
<td>7.339e-01</td>
<td>6.025e-04</td>
<td>9.261e-01</td>
<td>8.494e-05</td>
</tr>
<tr>
<td>5</td>
<td>0.5000</td>
<td>1.370e-01</td>
<td>6.249e-05</td>
<td>6.561e-01</td>
<td>2.458e-04</td>
<td>8.579e-01</td>
<td>1.186e-04</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>0.7990</td>
<td>3.093e-01</td>
<td>8.963e-05</td>
<td>4.756e-01</td>
<td>1.182e-04</td>
<td>5.703e-01</td>
<td>1.479e-04</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>0.3034</td>
<td>2.831e-01</td>
<td>3.157e-04</td>
<td>2.189e-01</td>
<td>1.233e-03</td>
<td>7.340e-01</td>
<td>8.576e-04</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>0.5000</td>
<td>5.091e-01</td>
<td>2.181e-04</td>
<td>1.558e-01</td>
<td>8.151e-05</td>
<td>5.519e-01</td>
<td>1.626e-03</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>0.7990</td>
<td>8.997e-01</td>
<td>2.568e-04</td>
<td>6.053e-02</td>
<td>8.865e-05</td>
<td>2.560e-01</td>
<td>1.037e-03</td>
<td></td>
</tr>
</tbody>
</table>
Table 7.3 Two site model NpT simulation results for average fraction of unbonded chain, $\langle x_{o}^{ch} \rangle$, and solvent molecules, $\langle x_{o}^{sp} \rangle$.

and for average reduced configurational energy, $\langle U/N\varepsilon \rangle$ and average compressibility factor, $\langle Z \rangle$, with their respective standard deviations (S. D.) at different packing fractions, $\eta$, bonding energies, $\varepsilon^*$, and solvent mole fractions, $x_{sp}$.

<table>
<thead>
<tr>
<th>$\eta$</th>
<th>$\varepsilon^*$</th>
<th>$x_{sp}$</th>
<th>$-\langle U/N\varepsilon \rangle$</th>
<th>S.D.</th>
<th>$\langle Z \rangle$</th>
<th>S.D.</th>
<th>$\langle x_{o}^{sp} \rangle$</th>
<th>S.D.</th>
<th>$\langle x_{o}^{ch} \rangle$</th>
<th>S.D.</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.35</td>
<td>5</td>
<td>0.3034</td>
<td>1.875e-01</td>
<td>2.009e-04</td>
<td>1.430e+01</td>
<td>2.391e-02</td>
<td>3.788e-01</td>
<td>1.102e-03</td>
<td>8.333e-01</td>
<td>2.337e-04</td>
</tr>
<tr>
<td>7</td>
<td>0.7990</td>
<td>1.243e+00</td>
<td>7.266e-05</td>
<td>5.123e+00</td>
<td>5.660e-04</td>
<td>5.812e-03</td>
<td>4.084e-06</td>
<td>1.367e-01</td>
<td>5.450e-04</td>
<td>6.485e-04</td>
</tr>
<tr>
<td>0.15</td>
<td>5</td>
<td>0.3034</td>
<td>9.666e-02</td>
<td>4.125e-05</td>
<td>3.261e+00</td>
<td>5.888e-03</td>
<td>7.566e-01</td>
<td>3.130e-04</td>
<td>9.465e-01</td>
<td>5.522e-05</td>
</tr>
<tr>
<td>5</td>
<td>0.7990</td>
<td>2.937e-01</td>
<td>7.824e-05</td>
<td>1.938e+00</td>
<td>1.007e-03</td>
<td>4.826e-01</td>
<td>1.488e-04</td>
<td>7.511e-01</td>
<td>1.510e-04</td>
<td>6.485e-04</td>
</tr>
</tbody>
</table>
Table 7.4 Three site model $NpT$ simulation results for average fraction of unbonded chain, $\langle x^c \rangle$, and solvent molecules, $\langle x^{sp} \rangle$, average reduced configurational energy, $\langle U / N \varepsilon \rangle$ and average compressibility factor, $\langle Z \rangle$, with their respective standard deviations (S. D.) at different packing fractions, $\eta$, bonding energies, $\varepsilon^*$, and solvent mole fractions, $x_{sp}$.

<table>
<thead>
<tr>
<th>$\eta$</th>
<th>$\varepsilon^*$</th>
<th>$x_{sp}$</th>
<th>$-\langle U / N \varepsilon \rangle$</th>
<th>S.D.</th>
<th>$\langle Z \rangle$</th>
<th>S.D.</th>
<th>$\langle x^{sp} \rangle$</th>
<th>S.D.</th>
<th>$\langle x^c \rangle$</th>
<th>S.D.</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.35</td>
<td>5</td>
<td>0.3034</td>
<td>2.417e-01</td>
<td>2.535e-04</td>
<td>1.400e+01</td>
<td>1.055e-02</td>
<td>3.041e-01</td>
<td>9.832e-04</td>
<td>7.652e-01</td>
<td>3.071e-04</td>
</tr>
<tr>
<td>5</td>
<td>0.7990</td>
<td>7.362e-01</td>
<td>1.418e-04</td>
<td>6.197e+00</td>
<td>1.385e-03</td>
<td>1.295e-01</td>
<td>2.822e-05</td>
<td>3.278e-01</td>
<td>4.760e-04</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>0.3034</td>
<td>4.702e-01</td>
<td>2.778e-04</td>
<td>1.360e+01</td>
<td>2.290e-02</td>
<td>3.156e-02</td>
<td>1.536e-04</td>
<td>5.587e-01</td>
<td>7.162e-04</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>0.5000</td>
<td>7.967e-01</td>
<td>2.851e-04</td>
<td>1.005e+01</td>
<td>5.195e-03</td>
<td>1.627e-02</td>
<td>7.113e-05</td>
<td>3.204e-01</td>
<td>4.110e-04</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>0.7990</td>
<td>1.246e+00</td>
<td>2.477e-04</td>
<td>4.931e+00</td>
<td>1.421e-03</td>
<td>5.656e-03</td>
<td>5.336e-06</td>
<td>7.704e-02</td>
<td>6.627e-04</td>
<td></td>
</tr>
<tr>
<td>0.15</td>
<td>5</td>
<td>0.3034</td>
<td>7.792e-02</td>
<td>5.412e-05</td>
<td>3.233e+00</td>
<td>4.387e-03</td>
<td>7.165e-01</td>
<td>6.875e-04</td>
<td>9.192e-01</td>
<td>6.927e-05</td>
</tr>
<tr>
<td>5</td>
<td>0.5000</td>
<td>1.485e-01</td>
<td>1.142e-04</td>
<td>2.749e+00</td>
<td>1.107e-03</td>
<td>6.366e-01</td>
<td>3.519e-04</td>
<td>8.439e-01</td>
<td>1.389e-04</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>0.7990</td>
<td>3.349e-01</td>
<td>2.326e-04</td>
<td>1.783e+00</td>
<td>5.629e-03</td>
<td>4.419e-01</td>
<td>3.143e-04</td>
<td>6.637e-01</td>
<td>6.625e-04</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>0.3034</td>
<td>2.691e-01</td>
<td>3.662e-04</td>
<td>2.916e+00</td>
<td>4.700e-03</td>
<td>2.263e-01</td>
<td>7.093e-04</td>
<td>7.330e-01</td>
<td>2.796e-04</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>0.5000</td>
<td>5.373e-01</td>
<td>3.284e-04</td>
<td>2.162e+00</td>
<td>3.068e-03</td>
<td>1.213e-01</td>
<td>2.628e-04</td>
<td>5.379e-01</td>
<td>9.413e-04</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>0.7990</td>
<td>8.884e-01</td>
<td>3.318e-04</td>
<td>1.047e+00</td>
<td>3.686e-04</td>
<td>6.259e-02</td>
<td>1.113e-04</td>
<td>2.691e-01</td>
<td>1.394e-03</td>
<td></td>
</tr>
</tbody>
</table>
Two site model \(NVT\) simulation results for the average ratio of cross bonds to total bonds formed by the solvent molecules, \(\langle \text{cross/total} \rangle\) with the respective standard deviations (S. D.) at different packing fractions, \(\eta\), bonding energies, \(\tilde{\varepsilon}\), and solvent mole fractions, \(x_{sp}\).

<table>
<thead>
<tr>
<th>(\eta)</th>
<th>(\tilde{\varepsilon})</th>
<th>(x_{sp})</th>
<th>(\langle \text{cross/total} \rangle)</th>
<th>S.D.</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.35</td>
<td>5</td>
<td>0.3034</td>
<td>7.133e-01</td>
<td>1.869e-01</td>
</tr>
<tr>
<td>5</td>
<td>0.5000</td>
<td>2.145e-01</td>
<td>1.850e-02</td>
<td>3.941e-04</td>
</tr>
<tr>
<td>5</td>
<td>0.7990</td>
<td>5.993e-01</td>
<td>1.264e-01</td>
<td>5.849e-03</td>
</tr>
<tr>
<td>7</td>
<td>0.3034</td>
<td>2.069e-01</td>
<td>2.474e-04</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>0.5000</td>
<td>4.539e-01</td>
<td>1.110e-02</td>
<td>4.046e-04</td>
</tr>
<tr>
<td>7</td>
<td>0.7990</td>
<td>6.812e-01</td>
<td>9.428e-02</td>
<td>1.794e-01</td>
</tr>
<tr>
<td>0.15</td>
<td>5</td>
<td>0.3034</td>
<td>6.812e-01</td>
<td>9.428e-02</td>
</tr>
<tr>
<td>5</td>
<td>0.5000</td>
<td>1.687e-01</td>
<td>4.046e-04</td>
<td>2.798e-04</td>
</tr>
<tr>
<td>7</td>
<td>0.3034</td>
<td>6.567e-01</td>
<td>1.794e-01</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>0.5000</td>
<td>4.151e-01</td>
<td>9.849e-03</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>0.7990</td>
<td>1.407e-01</td>
<td>2.798e-04</td>
<td></td>
</tr>
</tbody>
</table>

### 7.4.1 Results for Chains with Two Association Sites

Figure 7.4 shows the average configurational internal energy, the average fraction of solvent molecules not bonded, and average fraction of unbonded chains versus solvent fraction. The solid curves represent the theory prediction and the symbols the simulation results. The plots show the results for \(\eta = .35\) (a liquid density) and \(\tilde{\varepsilon} = 5\) and 7 (approximately room temperature for water). For configurational energy, as the concentration of solvent molecules increases more bonding occurs and \(-U/N\tilde{\varepsilon}\),
Figure 7.4 Two association site model NVT results for average configurational internal energy and fraction of unbonded chain and solvent molecules as a function of solvent mole fraction for reduced energies $\epsilon^* = 5$ and 7 and packing fraction $\eta = .35$. Results are from theory (curves) and molecular simulation (symbols).
Table 7.6 Three site model *NVT* simulation results for the average ratio of cross bonds to total bonds formed by the solvent molecules, \( \langle \text{cross/total} \rangle \) with the respective standard deviations (S. D.) at different packing fractions, \( \eta \), bonding energies, \( \varepsilon^* \), and solvent mole fractions, \( x_m \).

<table>
<thead>
<tr>
<th>( \eta )</th>
<th>( \varepsilon^* )</th>
<th>( x_m )</th>
<th>( \langle \text{cross/total} \rangle )</th>
<th>S.D.</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.35</td>
<td>5</td>
<td>0.3034</td>
<td>7.688E-01</td>
<td>3.080E-01</td>
</tr>
<tr>
<td>5</td>
<td>0.5000</td>
<td>5.334E-01</td>
<td>1.783E-02</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>0.7990</td>
<td>2.568E-01</td>
<td>9.360E-04</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>0.3034</td>
<td>7.821E-01</td>
<td>8.139E-02</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>0.5000</td>
<td>6.069E-01</td>
<td>7.822E-03</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>0.7990</td>
<td>2.619E-01</td>
<td>1.555E-04</td>
<td></td>
</tr>
<tr>
<td>0.15</td>
<td>5</td>
<td>0.3034</td>
<td>7.488E-01</td>
<td>9.808E-02</td>
</tr>
<tr>
<td>5</td>
<td>0.5000</td>
<td>5.537E-01</td>
<td>2.122E-02</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>0.7990</td>
<td>2.458E-01</td>
<td>4.771E-04</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>0.3034</td>
<td>7.517E-01</td>
<td>4.971E-01</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>0.5000</td>
<td>5.788E-01</td>
<td>9.245E-02</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>0.7990</td>
<td>2.502E-01</td>
<td>1.887E-04</td>
<td></td>
</tr>
</tbody>
</table>

therefore, also increases. For the higher bonding energy this property is 50% higher at the pure solvent limit. The fraction of unbonded spheres and chains decreases as the solvent concentration increases, i.e., as more bonding sites are available for bonding.

The effect of bonding energy is more severe for the case of the spheres, where for the higher energy, \( \varepsilon^*=7 \), the fraction of monomer solvent molecules is less than 8% for the whole concentration range, and for pure spheres the fraction of monomers is less than 0.5%. Theory agrees very well with simulation results.
The results for the lower packing fraction, $\eta = .15$, are shown in Fig. 7.5. At this lower density, comparably less bonding occurs, but the trends remain the same. Good agreement between simulation and theory is observed.

The ratio of cross bonds to total bonds on a solvent molecules a function of solvent mole fraction appears in Fig. 7.6. Theory predicts that bonding energy and packing fraction have no effect on this parameter. The simulation results agree reasonably well (within statistical error) with this prediction. In the limit of infinite dilution of spheres ($x_{sp} \rightarrow 0$) all bonds on spheres are formed with a chain (cross bond) and for pure spheres ($x_{sp} = 1$), all bonds are formed with a solvent molecule (self bond).

Figs. 7-7 and 7-8 show the $NpT$ simulation results for $\eta = .35$ and .15, respectively. In these cases, besides configurational internal energy and monomer fractions, the average compressibility factor is obtained and plotted as well. Agreement between simulation and theory is excellent.

### 7.4.2 Results for Chains with Three Association Sites

For the model chain molecule with three association sites, the availability of more bonding sites to form bonds causes more pronounced effects on configurational internal energy and fraction of monomers as is shown in Fig. 7-9. The trends are the same as in Fig. 7-5 (showing results at the same packing fraction, $\eta = .35$, but for the two site model), however the fraction of monomer spheres is approximately 40% for the low bonding energy ($\varepsilon' = 5$) and less than 4% for the higher energy ($\varepsilon' = 7$) for the case of
Figure 7.5 Two association site model NVT results for average configurational internal energy and fraction of unbonded chain and solvent molecules as a function of solvent mole fraction for reduced energies $\epsilon^* = 5$ and $7$ and packing fraction $\eta = .15$. Results are from theory (curves) and molecular simulation (symbols).
Figure 7.6 Two association site model NVT results for average ratio of cross bonds of solvent molecules to total bonds as a function of solvent mole fraction for $\epsilon^* = 5$ and $\eta = .35$ (exes), $\epsilon^* = 7$ and $\eta = .35$ (circles), $\epsilon^* = 5$ and $\eta = .15$ (crosses), and $\epsilon^* = 7$ and $\eta = .15$ (stars).
Figure 7.7 Two association site model \( NpT \) results for average configurational internal energy, compressibility factor, and fraction of unbonded chain and solvent molecules as a function of solvent mole fraction for reduced energies \( \varepsilon^* = 5 \) and 7 and packing fraction \( \eta \) = .35. Results are from theory (curves) and molecular simulation (symbols).
Figure 7.8 Two association site model $NpT$ results for average configurational internal energy, compressibility factor, and fraction of unbonded chain and solvent molecules as a function of solvent mole fraction for reduced energies $\epsilon' = 5$ and $7$ and packing fraction $\eta = .15$. Results are from theory (curves) and molecular simulation (symbols).
Figure 7.9 Three association site model NVT results for average configurational internal energy and fraction of unbonded chain and solvent molecules as a function of solvent mole fraction for reduced energies $\epsilon' = 5$ and $7$ and packing fraction $\eta = .35$. Results are from theory (curves) and molecular simulation (symbols).
infinite dilution of spheres. Theory predictions agree well with molecular simulation results.

For the lower packing fraction, \( \eta = .15 \), we observe good agreement between theory and simulation (Fig. 7-10) and comparing with the two site model, the configurational internal energy and fraction of monomers all show a greater amount of bond formation for the three site model, as expected.

The ratio of cross bonds to total bonds on the spheres is shown in Fig. 7-11. The theory prediction for the three bonding site model is larger than for the two bonding site chain, and the simulation results show this type of behavior as well.

Results for \( NpT \) simulations appear in Figs. 7-12 and 7-13. Compressibility factor for the various concentrations and bonding energies are plotted for packing fractions, \( \eta = .35 \) and .15. Excellent agreement between theory and simulation was obtained.

### 7.5 Conclusions

We have presented molecular simulation results and a theory to predict thermodynamic properties and bonding distributions of hexamer chain molecules with two and three association sites in a hydrogen bonding solvent. Agreement between theory and simulation is very good for a wide range of state conditions. The effect of density of bonding sites is slight but may become more important as it is further increased due to steric hindrance.
Figure 7.10 Three association site model NVT results for average configurational internal energy and fraction of unbonded chain and solvent molecules as a function of solvent mole fraction for reduced energies $\epsilon^* = 5$ and 7 and packing fraction $\eta = .15$. Results are from theory (curves) and molecular simulation (symbols).
Figure 7.11 Three association site model NVT results for average ratio of cross bonds of solvent molecules to total bonds as a function of solvent mole fraction for $\varepsilon' = 5$ and $\eta = .35$ (exes), $\varepsilon' = 7$ and $\eta = .35$ (circles), $\varepsilon' = 5$ and $\eta = .15$ (crosses), and $\varepsilon' = 7$ and $\eta = .15$ (stars).
Figure 7.12 Three association site model $NpT$ results for average configurational internal energy, compressibility factor, and fraction of unbonded chain and solvent molecules as a function of solvent mole fraction for reduced energies $\epsilon^* = 5$ and 7 and packing fraction $\eta = .35$. Results are from theory (curves) and molecular simulation (symbols).
Figure 7.13 Three association site model $NpT$ results for average configurational internal energy, compressibility factor, and fraction of unbonded chain and solvent molecules as a function of solvent mole fraction for reduced energies $\epsilon^* = 5$ and $7$ and packing fraction $\eta = .15$. Results are from theory (curves) and molecular simulation (symbols).
CONCLUSIONS AND FUTURE WORK

In the previous chapters various systems of associating molecules have been studied. These systems consisted of very different types of molecules, from spheres to chains to cyclics. Wertheim's theory of association and a theory of intramolecular association were tested using molecular simulation techniques.

The framework provided by perturbation theory allows us to make systematic improvements over an idealized model. In this way, it is possible to go from the ideal gas to hard spheres to chains and cyclics, and additional interactions can be considered, e.g., association.

In Chapter 5 a telechelic polymer in an associating solvent was modeled. The results included the effect of solvent concentration in the ability of the telechelic to bond inter- and intramolecularly. The proposed theory explained the complex bonding distributions accurately.

Chapter 6 presented a study of associating cyclic molecules. Taking the limit of complete bonding for the theory of intramolecular association, results in an equation of state for cyclics. Using the perturbation theory approach, the effect of association was added to the analysis to account for cluster formation of the cyclics. These ideas could result in theories useful in studying dendritic structures, polynuclear aromatics, and polymers containing ring structures or crosslinking.
In Chapter 7, chain molecules with multiple bonding sites were used as models to examine the effect of association site density on bonding distributions and thermodynamic properties. The system studied also included an associating solvent in various concentrations.

Future work should deal with the effect of bond cooperativity that is responsible for bridging of molecules between sites. A sound theoretical approach should be developed to explain the phenomenon. Wertheim’s theory is limited in this area because it does not account for bonding site position or orientation on a molecule. Cases where the theory breaks down are of interest, especially cases where bond cooperativity is important, and this could be studied using molecular simulation.

Some future applications of this work include biochemical systems, where the complexity of the equilibrium structures of protein folding, for example, can be studied with this type of approach to determine the importance of the competition between inter- and intramolecular hydrogen bonding and the effect of bond cooperativity.

Important also are industrial applications, as in equipment design and in polymer processing, especially in the \textit{a priori} determination of water solubility from molecular and structural formulas. This is based on the molecular interactions and therefore, progress in this area is of the utmost importance.

More molecular simulations, in particular simulations that calculate structural quantities would provide invaluable information for achieving the previous goals.
The experimental component of these thermodynamic studies should always be part of the picture. Experiments provide information necessary to reconcile models with real fluids. They reveal interesting phenomena and present new challenges to theorists.
REFERENCES


75. Perez Carassai, V., M. S. Thesis, Rice University, Houston, Texas (1997)


