INTEGRAL EQUATION THEORIES FOR COMPLEX
FLUIDS

by

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Submitted to the Department of Chemical Engineering
on May 5, 1994, in partial fulfillment of the
requirements for the degree of
Doctor of Philosophy in Chemical Engineering

Abstract

The prediction of thermodynamic properties of fluids is of central importance to the chemical engineer. For fluid systems composed of molecules modeled using interaction site potentials, the structural and bulk thermodynamic properties can be determined "exactly" using Monte Carlo or molecular dynamics simulations. However, these techniques have several shortcomings, including limitations in the length and time scales that can be examined, and the computational expense.

On the other hand, integral equation theories do not suffer from such limitations. These equations, when combined with an approximate closure relation, yield the intermolecular site-site correlation functions, which provide physical insight into the underlying structure of the fluid. From these correlation functions, the thermodynamic behavior of the system can be computed. The primary goal of this thesis is to bring integral equation theories for molecular fluids to a level where they can provide a useful computational tool for the chemical engineer. This involves assessing the applicability of existing integral equations and improving their predictive capabilities as needed. For this purpose, two integral equations for interaction site fluids, the site-site Ornstein-Zernike (SSOZ) equation and the Chandler-Silbey-Ladanyi (CSL) equations, were examined for various complex fluids.

For water, the SSOZ equation was solved for several different potential models at ambient conditions. The SSOZ equation captured the short-ranged correlations in water properly, however, for the second coordination shell and beyond, the predicted pair correlation functions deviated significantly from those found using computer simulations and experimental measurements. The predictions for the thermodynamic properties of water were found to be reasonable.

For hydrocarbons at infinite dilution in water, the SSOZ equation was solved under a variety of different closure relations in order to compare their quantitative predictive capabilities. When used with certain approximate closures, the SSOZ equation yielded reasonable predictions of the structural and bulk thermodynamic properties of the hydrocarbon-water systems examined. In addition, the chain conformations of hydrocarbons in vacuum and at infinite dilution in water were computed. While
all the closure relations which were examined predicted that the hydrocarbon chain becomes more collapsed when placed in water, which is what is physically expected due to the hydrophobic effect, the magnitude of this effect was found to depend on the particular closure used.

The SSOZ equation was then applied to a model surfactant-water system, in which micellar aggregates can form, and was found to yield several unphysical results. In particular, it yielded large negative regions in the predicted surfactant-surfactant pair correlation functions. In addition, no solutions to the SSOZ-PY equation were found over a large region in the temperature-surfactant concentration plane. When the HNC closure was employed, no solutions were found except at very high temperatures and low surfactant densities, which is unphysical. The disparate and unphysical behavior of the SSOZ equation with different simple fluid closures suggests that this equation may not be sufficiently accurate to adequately model self-assembling systems.

Although the SSOZ equation has been fairly successful in predicting the behavior of interaction site fluids such as water and hydrocarbons in water, it has several limitations. The major limitation is that when the known approximate closures fail to provide physically reasonable results, such as in the case of the Lennard-Jones surfactant model system discussed above, no straightforward method exists to improve their accuracy. This led to the use of a new set of integral equations, known as the Chandler-Silbey-Ladanyi (CSL) equations, the primary advantage of which is that, in principle, their accuracy can be systematically improved using diagrammatic methods. In spite of this appealing aspect of the CSL equations, they have found limited application in the past. Accordingly, in this thesis, expressions for the free energy for the CSL equations were developed, and various computational aspects of these equations were analyzed.

Comparisons have been made between the capabilities of the CSL and SSOZ equations to predict the structure of homonuclear and heteronuclear diatomic Lennard-Jones molecules at various temperatures, densities, and bond lengths. In general, the CSL-HNC equations were found to be in better agreement with the computer simulation results as the bond length increases or as the density decreases, while temperature was found to have little effect. A method was developed for computing the low-order corrections to the correlation functions. The addition of the zeroth-order corrections was found to have little effect on the predictions of the CSL equations, while the addition of the first-order corrections resulted in a significant improvement in the predictive capabilities of the CSL equations.

Finally, the CSL equations and the SSOZ equation were applied to several different potential models of water. The predictions for the pair correlation functions and the thermodynamic properties of the CSL equations were found to be in slightly better agreement with computer simulation results than those of the SSOZ equation. The phase behavior of water was also predicted using these integral equations, and found to be in fair agreement with results from computer simulations and experimental measurements.

Thesis Supervisor: Daniel Blankschtein
Title: Associate Professor
Acknowledgments

To begin, I would like to thank my advisor, Professor Daniel Blankschtein, who has been more than just an advisor to me. From the day I joined his group, he has continually provided me both scientific guidance and moral support. With his help, I feel I have grown tremendously as a scientist and, more importantly, as a person. I will always be indebted to him and hope someday to make him proud.

I would also like to thank Professors Robert Armstrong, Sow-Hsin Chen, and Jonathan Harris for serving on my thesis committee. In particular, I owe a great debt to Professor Harris who, no matter how busy, always made time for me to discuss ideas.

I thank Xinjin Zhao for being a true friend since the day I met him. Xinjin is a person whom I could always rely on, both extremely patient and understanding, helping me through all my troubled times. I look up to him as the older brother I never had. I wish him, his wife, Luhong Bo, and their son, Daniel, the best of luck.

I consider myself lucky to call Reza Mehrabi a friend. His interests in cooking, modern dance, painting, and art in general greatly broadened me as a person. Whenever I needed anything, he was always willing to help. Reza is a person I greatly admire and deeply respect. I wish him and his wife the best.

I would like to thank the Ehh!!! gang, Stathis Avgoustiniatos, Abdul Barakat, Brian Laffey, and Joy Mendoza, with whom I spent most of my time here at MIT, either eating dinner, watching all night movie marathons in 66-110, or talking in the lab till 4am. To each of them, I owe a special debt which I can never repay: Stathis for sharing his quest for truth and knowledge, Abdul for showing me dedication and perseverance, Brian for opening my ears to music and my mind to social responsibility, and Joy for teaching me to accept people as they are. They are the closest friends I have ever known in my life. I thank them for keeping life interesting and fun. I will always remember the times we have spent together.

I am grateful to the other members of the group. In my initial years at MIT, Sudhakar Puvvada, as Blankschtein’s first student, served as a mentor for me, always
there to offer guidance. I want to thank him and let him know that I missed him greatly when he graduated. I want to thank Ayal Naor (SPORE rules!) and Pak Yuet for being around late at night to bounce ideas off of, for all their help, encouragement, as well as advice, and for their friendship. I would like to thank my UROP Denise Ciotti and wish her good luck at BU. I thank Nick Abbott, Giuseppe Briganti, Teresa Carale, Chia-li Liu, Mark Johnson, Yvonne Nikas, and Claudia Sarmoria for all their help and the times we have spend together. I also want to wish the newer students, Crist Clark, Samir Mitragotri, Anat Shiloach, Ginger Tse, and Nancy Zoeller, well and the best of luck on their research.

Thanks to the Friday night Basketball Crew for the many enjoyable hours on the court: Davy Chang, Alex “Koulalex” Koulouris, Mike Kwan, Dave “College Boy” Lathrop, Nelson Lin, Marc Moran, Gokaraju Raju, Bruce Scruggs, Hiroshi Saito, and “I wanna be like” Mike Thompson.

I also owe thanks to the guys down on the second floor in Brown’s crystal growth group: Howard Covert, Angelos Kyrilidis, John Lee, and Dimitri Maroudas. They were always willing to discuss anything from numerical methods to music theory and from statistical physics to life in general. Thanks for all the help.

Thanks to all my other friends in the department, who made each day enjoyable: Elaine Aufiero-Peters, Arline Benford, Diane Burke, Alex Diaz (Hey Alex,...BANG!), Barbara Driscoll, Janet Fischer, Dave Oda, Sujatha Karoor, Nancy Masley, Sandeep Patel, Costas Patrikios (Ehh, man!), Gerald Prioleau, Mike Pomianek, and Gordon Smith.

I would also like to thank the National Science Foundation and the National Institute of Health for financial support through their fellowship programs.

Finally, I thank my parents, to whom I owe everything.
Contents

1 Introduction and Objectives ............................................. 23
  1.1 Motivation .......................................................... 23
  1.2 Models for Intermolecular Interactions ......................... 24
  1.3 Liquid State Theory ............................................... 27
    1.3.1 Computer Simulation Methods .............................. 28
    1.3.2 Integral Equation Theories ................................ 29
  1.4 Thesis Objectives ................................................ 30

2 The Site-Site Ornstein-Zernike Equation ......................... 32
  2.1 Description of the Formalism .................................... 32
    2.1.1 Simple Fluids .............................................. 32
    2.1.2 Molecular Fluids ........................................... 35
  2.2 Thermodynamic Properties ....................................... 37
    2.2.1 Expressions for Various Thermodynamic Properties .... 38
    2.2.2 Chemical Potential .......................................... 40
  2.3 Previous Applications of the SSOZ Equation .................... 42

3 The Site-Site Ornstein-Zernike Equation: Application to Water ... 44
  3.1 Introduction and Overview ....................................... 44
  3.2 Potential Models for Water ....................................... 45
  3.3 Structural Properties of Water .................................. 47
  3.4 Bulk Thermodynamic Properties of Water ....................... 50
  3.5 Concluding Remarks ............................................... 53
4 The Site-Site Ornstein-Zernike Equation: Application to Hydrocarbons in Water

4.1 Introduction and Overview .................................. 55
4.2 Potential Models for Hydrocarbons .......................... 56
4.3 Methane in Water ........................................... 57
4.4 Ethane in Water .............................................. 60
4.5 Propane in Water ............................................. 63
4.6 Medium Length n-Alkanes ................................... 70
  4.6.1 Challenges Resulting from Chain Flexibility ............. 70
  4.6.2 The Conformations of n-Butane ........................ 71
  4.6.3 Results for Longer n-Alkanes ......................... 73
4.7 Concluding Remarks ......................................... 75

5 The Site-Site Ornstein-Zernike Equation: Application to a Lennard-Jones Surfactant Model

5.1 Introduction and Overview ................................... 78
5.2 Description of the Potential Functions ....................... 79
5.3 Results from Computer Simulations .......................... 81
5.4 Application of the SSOZ Equation ........................... 81
  5.4.1 The HT-Solvent System ................................. 82
  5.4.2 The H_2T_5-Solvent System ............................ 85
5.5 Concluding Remarks ......................................... 90

6 The Chandler-Silbey-Ladanyi Equations

6.1 The Need for a New Integral Equation ......................... 92
6.2 Description of the New Formalism ............................ 94
6.3 Formulae for Thermodynamic Properties ...................... 102
  6.3.1 Residual Helmholtz Free Energy ........................ 102
  6.3.2 The Variational Principle .............................. 104
  6.3.3 Residual Chemical Potential ............................ 107
6.4 Previous Applications of the CSL Equations .................. 108
6.5 Analysis of the CSL Equations .................................. 110
   6.5.1 The Exact Closure Relations .............................. 111
   6.5.2 The Hypernetted-Chain Closure .......................... 116
   6.5.3 Auxiliary Sites ........................................... 122
6.6 Concluding Remarks ............................................. 130

7 The Chandler-Silbey-Ladanyi Equations: Application to Diatomic Molecules 132
   7.1 Introduction and Overview .................................. 132
   7.2 The Bridge Functions ....................................... 133
   7.3 Homonuclear Diatomic Lennard-Jones Molecules ............... 143
   7.4 Heteronuclear Diatomic Lennard-Jones Molecules ............. 153
      7.4.1 Nonpolar Molecules .................................... 155
      7.4.2 Polar Molecules ....................................... 159
   7.5 Concluding Remarks ......................................... 166

8 The Chandler-Silbey-Ladanyi Equations: Application to Water 168
   8.1 Introduction and Overview .................................. 168
   8.2 The Bridge Functions for Water ............................ 169
   8.3 The Structure of Water ...................................... 174
   8.4 The Thermodynamics of Water ................................ 178
   8.5 Phase Behavior ............................................. 182
   8.6 Concluding Remarks ......................................... 188

9 Concluding Remarks ................................................. 190
   9.1 Summary of Salient Findings ................................ 190
   9.2 Recommendations for Future Work ........................... 194
   9.3 Final Remarks ................................................ 196

A Derivation of Eq. (2.25) ........................................... 198
B Coupling Constant Integrations in Eqs. (6.41) and (6.55) 200

B.1 Integral for the Residual Helmholtz Free Energy ........................................... 203

B.2 Integral for the Residual Chemical Potential ........................................ 203

C Numerical Methods 205

C.1 Introduction .................................................. 205

C.2 Gillan Method .................................................. 207

C.3 The SSOZ Equation ............................................ 209
  C.3.1 Equivalent Sites ........................................ 209
  C.3.2 Development of the Residual .................................. 210
  C.3.3 Development of the Jacobian .................................... 211
  C.3.4 Long-Ranged Correlations ..................................... 213

C.4 The CSL Equations ........................................... 214
  C.4.1 Equivalent Sites ........................................ 215
  C.4.2 Development of the Residual .................................... 217
  C.4.3 Development of the Jacobian .................................... 219
  C.4.4 Long-Range Correlations ..................................... 221

C.5 Fourier Transforms ........................................ 222

Bibliography 225
List of Figures

3-1 Oxygen-oxygen pair correlation functions, $g_{oo}(r)$, as a function of the site-site separation, $r$, for SPC water at 25°C and 0.997 g/cm$^3$: (i) predicted using the SSOZ equation with the HNC closure (solid line), (ii) predicted from Monte Carlo simulations of Jorgensen et al.\textsuperscript{15} (dashed line), and (iii) deduced from neutron-scattering measurements of Soper and Phillips\textsuperscript{84} (dotted line). ........................................... 48

3-2 Hydrogen-hydrogen pair correlation functions, $g_{HH}(r)$, as a function of the site-site separation, $r$, for SPC water at 25°C and 0.997 g/cm$^3$. The notation is the same as that in Figure 3-1 ........................................... 49

3-3 Oxygen-hydrogen pair correlation functions, $g_{OH}(r)$, as a function of the site-site separation, $r$, for SPC water at 25°C and 0.997 g/cm$^3$. The notation is the same as that in Figure 3-1 ........................................... 49

4-1 Methane-water pair correlation functions (a, CH$_4$-O; b, CH$_4$-H) as a function of $r$ for methane at infinite dilution in water at 25°C and 0.997 g/cm$^3$: (i) SSOZ equation with HNC closure (solid line), (ii) SSOZ equation with MaS closure (dashed line), and (iii) SSOZ equation with BPGG closure, $s = 1.79$ (dotted line). ........................................... 58
4-2 Residual chemical potential of methane at infinite dilution in water as a function of temperature: (i) predictions of the SSOZ equation with the MaS closure (dashed line), (ii) predictions of the SSOZ equation with the BPGG closure, \( s = 1.79 \) (solid line), (iii) data of Morrison and Billett\(^{94} \) (circles), (iv) data of Wen and Hung\(^{102} \) (squares), and (v) data of Yaacobi and Ben-Naim\(^{103} \) (triangles).

4-3 Ethane-water pair correlation functions (a, CH\(_3\)-O; b, CH\(_3\)-H) as a function of \( r \) for ethane at infinite dilution in water at 25\(^\circ\)C and 0.997 g/cm\(^3\): (i) SSOZ equation with HNC closure (solid line), (ii) SSOZ equation with MaS closure (dashed line), and (iii) SSOZ equation with BPGG closure, \( s = 1.79 \) (dotted line). Note that the predictions of the MaS and BPGG closures are almost identical.

4-4 Residual chemical potential of ethane at infinite dilution in water as a function of temperature: (i) predictions of the SSOZ equation with the MaS closure (dashed line), (ii) predictions of the SSOZ equation with the BPGG closure, \( s = 1.96 \) (solid line), (iii) data of Morrison and Billett\(^{94} \) (circles), (iv) data of Wen and Hung\(^{102} \) (squares), and (v) data of Yaacobi and Ben-Naim\(^{103} \) (triangles).

4-5 Propane-water pair correlation functions (a, CH\(_2\)-O; b, CH\(_3\)-O; c, CH\(_2\)-H; d, CH\(_3\)-H) as a function of \( r \) for propane at infinite dilution in water at 25\(^\circ\)C and 0.997 g/cm\(^3\): (i) SSOZ equation with HNC closure (solid line), (ii) SSOZ equation with MaS closure (dashed line), and (iii) SSOZ equation with BPGG closure, \( s = 1.79 \) (dotted line). Note that the predictions of the MaS and BPGG closures are almost identical.

4-6 Propane-water pair correlation functions (CH\(_3\)-O) as a function of \( r \) for propane at infinite dilution in water at 25\(^\circ\)C and 0.997 g/cm\(^3\) using the potential model of Ichiye and Chandler: (i) SSOZ equation with HNC closure (solid line), (ii) SSOZ equation with MaS closure (dashed line), and (iii) molecular dynamics simulation of Ichiye and Chandler\(^{61} \) (dotted line).
4-7 Residual chemical potential of propane at infinite dilution in water as a function of temperature: (i) predictions of the SSOZ equation with the MaS closure (dashed line), (ii) predictions of the SSOZ equation with the BP GG closure, $s = 2.05$ (solid line), (iii) data of Morrison and Billett\textsuperscript{94} (circles), and (iv) data of Wen and Hung\textsuperscript{102} (squares).  

4-8 Application of the equivalent-site approximation (ESA) to propane in water. (a) Propane-water oxygen pair correlation functions: (i) CH\textsubscript{2}-O, full potential (thin dashed line); (ii) CH\textsubscript{3}-O, full potential (thick dashed line); (iii) CH\textsubscript{2}-O, modified potential (thin dotted line); (iv) CH\textsubscript{3}-O, modified potential (thick dotted line); and (v) CH\textsubscript{n}-O, equivalent-site approximation (solid line). (b) Propane-water hydrogen pair correlation functions: (i) CH\textsubscript{2}-H, full potential (thin dashed line); (ii) CH\textsubscript{3}-H, full potential (thick dashed line); (iii) CH\textsubscript{2}-H, modified potential (thin dotted line); (iv) CH\textsubscript{3}-H, modified potential (thick dotted line); and (v) CH\textsubscript{n}-H, equivalent site approximation (solid line).  

4-9 Dihedral angle distribution of n-butane in water: (i) predictions of the SSOZ equation with the HNC closure, (ii) predictions of the SSOZ equation with the MaS closure, and (iii) ideal-gas phase predictions.  

4-10 Carbon number dependence of the residual chemical potential of n-alkanes ($1 \leq n \leq 7$) at infinite dilution in water: (i) predictions of the SSOZ equation with the HNC closure (circles), (ii) predictions of the SSOZ equation with the MaS closure (triangles), and (iii) experimental measurements of Abraham\textsuperscript{96} (squares). Note that the various lines are drawn to guide the eye.  

4-11 Carbon number dependence of the root-mean-square end-to-end distance of n-alkanes ($1 \leq n \leq 7$) at infinite dilution in water: (i) predictions of the SSOZ equation with the HNC closure (circles), (ii) predictions of the SSOZ equation with the MaS closure (triangles), and (iii) ideal-gas phase predictions (squares). Note that the various lines are drawn to guide the eye.
5-1 Lennard-Jones potential model for surfactant-oil-water systems. . . . 80
5-2 Predicted pair correlation functions for a HT surfactant at infinite
dilution in a Lennard-Jones solvent at $T^* = 1.0$ and $\rho^*_s = 0.7$: (i) solvent-solvent (solid line), (ii) solvent-head (dashed line), and (iii) solvent-tail (dotted line). ................................. 83
5-3 Predicted pair correlation functions for a HT surfactant at infinite
dilution in a Lennard-Jones solvent at $T^* = 1.0$ and $\rho^*_s = 0.7$: (i) head-head (solid line), (ii) tail-tail (dashed line), and (iii) head-tail (dotted line). ................................. 83
5-4 Schematic behavior of the osmotic compressibility as a function of so-
lute concentration for different types of solutions: (i) ideal solution
(solid line), (ii) regular solution (dotted lines), and (iii) micellar solu-
tion (dashed line) ................................. 85
5-5 Dependence of the osmotic compressibility on the HT surfactant con-
centration. .......................................... 86
5-6 Predicted pair correlation functions for a $\text{H}_2\text{T}_5$ surfactant at infinite
dilution in a Lennard-Jones solvent at $T^* = 1.0$ and $\rho^*_s = 0.7$: (i) solvent-solvent (solid line), (ii) solvent-head (dashed line), and (iii) solvent-tail (dotted line). ................................. 87
5-7 Predicted pair correlation functions for a $\text{H}_2\text{T}_5$ surfactant at infinite
dilution in a Lennard-Jones solvent at $T^* = 1.0$ and $\rho^*_s = 0.7$: (i) head-
head (solid line), (ii) tail-tail (dashed line), and (iii) head-tail (dotted
d line). .................................................. 88
5-8 Predicted pair correlation functions for a $\text{H}_2\text{T}_5$ surfactant at infinite
dilution in a Lennard-Jones solvent at $T^* = 1.26$ and $\rho^*_s = 0.7$: (i) head-head (solid line), (ii) tail-tail (dashed line), and (iii) head-tail (dotted line). ................................. 88
5-9 Regions of solution of the SSOZ-PY equation in the temperature-
surfactant concentration plane for the H₂T₅ surfactant system. The
SSOZ-PY equation predicts physically reasonable surfactant-surfact-
ant pair correlation functions in Region 1, and unphysical surfactant-
surfactant pair correlation functions in Region 2. No solutions are
found between these two regions. ................................. 89

6-1 The interaction site diagrams contributing at zeroth-order in the den-
sity to $h$ for a diatomic fluid. The straight lines represent Mayer $f$-
bonds, and the wavy lines represent $s$-bonds. The white circles are
root sites, and the black circles are field sites. The diagram on the first
line contributes to $h^o$. The two diagrams on the second line contribute
to $h^l$, the two diagrams on the third line contribute to $h^r$, and the
remaining ten diagrams contribute to $h^b$. ................................. 96

6-2 Example of an unallowed diagram. The notation is the same as that
in Figure 6-1. ...................................................... 96

6-3 Diagrams contributing to $\hat{h}_{AA}(0)$ at zero density for a diatomic fluid. 117
6-4 Diagrams contributing to $\hat{h}_{AB}(0)$ at zero density for a diatomic fluid. 118
6-5 Diagrams contributing to $\hat{h}_{BB}(0)$ at zero density for a diatomic fluid. 119

7-1 The dependence of the molecular $e$-bond on the site-site $e$-bonds for
a system of diatomic molecules. The thick dashed line represents the
molecular $e$-bond, the thin dashed lines represent the site-site $e$-bonds,
and the wavy lines represent $s$-bonds (see Eq. 6.10). The large white
circles represent molecular root sites, and the small white circles rep-
resent interaction site root sites. ................................. 138

7-2 Illustration of the procedure involved in obtaining an interaction site
diagram from a molecular diagram. The notation is the same as that
in Figure 7-1. ...................................................... 138
7-3 Diagrams contributing to the zeroth-order molecular pair correlation function, $g^{(0)}(R_1, R_2)$, and the zeroth-order indirect correlation functions. The thick dashed line represents a molecular $e$-bond, the thin dashed lines represent site-site $e$-bonds, and the wavy lines represent $s$-bonds. The white circles represent root sites, and the black circles represent field sites.

7-4 Diagrams contributing to the first-order molecular pair correlation function, $g^{(1)}(R_1, R_2)$, and the first-order indirect correlation functions. The notation is the same as that in Figure 7-3.

7-5 Diagrams contributing to the zeroth order chain functions for diatomic molecules. The solid lines represent Mayer $f$-bonds, the dashed lines represent $e$-bonds, and the wavy lines represent $s$-bonds. The white circles represent root sites, and the black circles represent field sites.

7-6 Diagrams contributing to the first-order chain functions for diatomic molecules. The notation is the same as that in Figure 7-5.

7-7 Predicted site-site pair correlation function for homonuclear diatomic Lennard-Jones molecules at $T^* = 3.0$, $\rho^* = 0.1$, and $l^* = 0.603$: (i) predicted using the CSL-HNC equations (solid line), (ii) predicted using the SSOZ-PY equation (dashed line), and (iii) predicted from Monte Carlo simulations (circles).

7-8 Predicted site-site pair correlation function for homonuclear diatomic Lennard-Jones molecules at $T^* = 3.0$, $\rho^* = 0.2$, and $l^* = 0.603$. The notation is the same as that in Figure 7-7.

7-9 Predicted site-site pair correlation function for homonuclear diatomic Lennard-Jones molecules at $T^* = 3.0$, $\rho^* = 0.3$, and $l^* = 0.603$. The notation is the same as that in Figure 7-7.

7-10 Predicted site-site pair correlation function for homonuclear diatomic Lennard-Jones molecules at $T^* = 3.0$, $\rho^* = 0.4$, and $l^* = 0.603$. The notation is the same as that in Figure 7-7.
7-11 Predicted site-site pair correlation function for homonuclear diatomic Lennard-Jones molecules at $T^* = 3.0$, $\rho^* = 0.5$, and $l^* = 0.603$. The notation is the same as that in Figure 7-7. ............... 147

7-12 Predicted site-site pair correlation function for homonuclear diatomic Lennard-Jones molecules at $T^* = 3.0$, $\rho^* = 0.55$, and $l^* = 0.329$. The notation is the same as that in Figure 7-7. ............... 148

7-13 Predicted site-site pair correlation function for homonuclear diatomic Lennard-Jones molecules at $T^* = 2.0$, $\rho^* = 0.5$, and $l^* = 0.793$. The notation is the same as that in Figure 7-7. ............... 149

7-14 Predicted site-site pair correlation function for homonuclear diatomic Lennard-Jones molecules at $T^* = 4.0$, $\rho^* = 0.5$, and $l^* = 0.603$. The notation is the same as that in Figure 7-7. ............... 149

7-15 Predicted site-site pair correlation function for homonuclear diatomic Lennard-Jones molecules at $T^* = 5.0$, $\rho^* = 0.5$, and $l^* = 0.603$. The notation is the same as that in Figure 7-7. ............... 150

7-16 Predicted bridge functions for homonuclear diatomic Lennard-Jones molecules at $T^* = 3.0$, $\rho^* = 0.5$, and $l^* = 0.603$: (i) $b^{(0)}(r)$ (solid line), (ii) $b^{(1)}(r)$ (dashed line), (iii) $b^{(1)}(r)$ (dotted line), and $b^{(1)}(r)$ (dash-dotted line). ............... 151

7-17 Predicted site-site pair correlation function for homonuclear diatomic Lennard-Jones molecules at $T^* = 3.0$, $\rho^* = 0.5$, and $l^* = 0.603$: predictions of the (i) CSL-HNC (solid line), (ii) CSL-HNC+$B^{(0)}$ (dashed line), (iii) CSL-HNC+$B^{(1)}$ (dotted line), (iv) SSOZ-PY (dash-dotted line) equations, and (v) Monte Carlo simulation (circles). Note that the predictions of the CSL-HNC and CSL-HNC+$B^{(0)}$ equations are almost identical. ............... 152

7-18 Predicted site-site pair correlation function for homonuclear diatomic Lennard-Jones molecules at $T^* = 3.0$, $\rho^* = 0.55$, and $l^* = 0.329$. The notation is the same as that in Figure 7-17. ............... 153

7-19 Schematic drawing of the model HCl molecule. ............... 154
7-20 Predicted hydrogen-hydrogen pair correlation function for uncharged HCl at $T = 210$ K and $\rho = 0.018$ Å$^{-3}$: (i) predicted using the CSL-HNC equations (solid line), (ii) predicted using the CSL-HNC+$B^{(0)}$ equations (dashed line), (iii) predicted using the CSL-HNC+$B^{(1)}$ equations (dotted line), (iv) predicted using the SSOZ-PY equation (dash-dotted line), and (v) predicted from molecular dynamics simulations of Hirata et al.$^{50}$ (circles).

7-21 Predicted hydrogen-chlorine pair correlation function for uncharged HCl at $T = 210$ K and $\rho = 0.018$ Å$^{-3}$. The notation is the same as that in Figure 7-20.

7-22 Predicted chlorine-chlorine pair correlation function for uncharged HCl at $T = 210$ K and $\rho = 0.018$ Å$^{-3}$. The notation is the same as that in Figure 7-20.

7-23 Predictions of the CSL-HNC equations for uncharged HCl for $h^o$: (i) $h^o_{HH}(r)$ (solid line), (ii) $h^o_{HCl}(r)$ (dashed line), and (iii) $h^o_{ClCl}(r)$ (dotted line).

7-24 Predictions of the CSL-HNC equations for uncharged HCl for $h^1$: (i) $h^1_{HH}(r)$ (solid line), (ii) $h^1_{HCl}(r)$ (dashed line), (iii) $h^1_{ClCl}(r)$ (dotted line), and (iv) $h^1_{ClH}(r)$ (dash-dotted line). Note that $h^1_{ClH}(r)$ is nearly equal to zero.

7-25 Predictions of the CSL-HNC equations for uncharged HCl for $h^b$: (i) $h^b_{HH}(r)$ (solid line), (ii) $h^b_{HCl}(r)$ (dashed line), and (iii) $h^b_{ClCl}(r)$ (dotted line). Note that $h^b_{HCl}(r)$ and $h^b_{ClCl}(r)$ are essentially equal to zero.

7-26 Predicted zeroth-order bridge functions for uncharged HCl at $T = 210$ K and $\rho = 0.018$ Å$^{-3}$: (i) $b_{HH}^{b(0)}(r)$ (solid line), (ii) $b_{HCl}^{b(0)}(r)$ (dashed line), and (iii) $b_{ClCl}^{b(0)}(r)$ (dotted line). Note that $b_{HCl}^{b(0)}(r)$ and $b_{ClCl}^{b(0)}(r)$ are essentially equal to zero.
7-27 Predicted first-order bridge functions for uncharged HCl at $T = 210$ K and $\rho = 0.018 \ \text{Å}^{-3}$: (i) $\rho_{HH}^{b(1)}(r)$ (solid line), (ii) $\rho_{HCl}^{b(1)}(r)$ (dashed line), and (iii) $\rho_{ClCl}^{b(1)}$ (dotted line). Note that $\rho_{HH}^{o(1)}(r)$ and $\rho_{HCl}^{o(1)}(r)$ are essentially equal to zero. ........................................... 160

7-28 Predicted first-order bridge functions for uncharged HCl at $T = 210$ K and $\rho = 0.018 \ \text{Å}^{-3}$: (i) $\rho_{HH}^{b(1)}(r)$ (solid line), (ii) $\rho_{HCl}^{b(1)}(r)$ (dashed line), (iii) $\rho_{ClCl}^{b(1)}$ (dotted line), and (iv) $\rho_{CIH}^{b(1)}$ (dash-dotted). Note that $\rho_{HH}^{b(1)}(r)$ and $\rho_{HCl}^{b(1)}(r)$ are essentially equal to zero. ......................... 161

7-29 Predicted first-order bridge functions for uncharged HCl at $T = 210$ K and $\rho = 0.018 \ \text{Å}^{-3}$: (i) $\rho_{HH}^{b(1)}(r)$ (solid line), (ii) $\rho_{HCl}^{b(1)}(r)$ (dashed line), and (iii) $\rho_{ClCl}^{b(1)}$ (dotted line) ......................... 161

7-30 Predicted hydrogen-hydrogen pair correlation function for charged HCl at $T = 210$ K and $\rho = 0.018 \ \text{Å}^{-3}$. The notation is the same as that in Figure 7-20. ........................................... 162

7-31 Predicted hydrogen-chlorine pair correlation function for charged HCl at $T = 210$ K and $\rho = 0.018 \ \text{Å}^{-3}$. The notation is the same as that in Figure 7-20. ........................................... 163

7-32 Predicted chlorine-chlorine pair correlation function for charged HCl at $T = 210$ K and $\rho = 0.018 \ \text{Å}^{-3}$; The notation is the same as that in Figure 7-20. ........................................... 163

7-33 Predictions of the CSL-HNC equations for charged HCl at $T = 210$ K and $\rho = 0.018 \ \text{Å}^{-3}$ for $h^o$: (i) $h_{HH}^{o}(r)$ (solid line), (ii) $h_{HCl}^{o}(r)$ (dashed line), and (iii) $h_{ClCl}^{o}(r)$ (dotted line). .............. 164

7-34 Predictions of the CSL-HNC equations for charged HCl at $T = 210$ K and $\rho = 0.018 \ \text{Å}^{-3}$ for $h^l$: (i) $h_{HH}^{l}(r)$ (solid line), (ii) $h_{HCl}^{l}(r)$ (dashed line), (iii) $h_{ClCl}^{l}(r)$ (dotted line), and (iv) $h_{CIH}^{l}(r)$ (dash-dotted line). 164

7-35 Predictions of the CSL-HNC equations for charged HCl at $T = 210$ K and $\rho = 0.018 \ \text{Å}^{-3}$ for $h^b$: (i) $h_{HH}^{b}(r)$ (solid line), (ii) $h_{HCl}^{b}(r)$ (dashed line), and (iii) $h_{ClCl}^{b}(r)$ (dotted line). .............................. 165
8-1 Diagrams contributing to the indirect correlation functions for water at zeroth-order in the density. The white circles represent root sites, and the black circles represent field sites. A dashed line represents an e-bond (or a $g^0$-bond, where $g^0 = 1 + h^0$). The shaded triangle represents a three-body intramolecular distribution function, which is analogous to an $s$-bond in the case of two-body intramolecular interactions.

8-2 Diagrams contributing to the chain correlation functions for water at zeroth-order in the density. The white circles represent root sites, and the black circles represent field sites. A dashed line represents an e-bond (or a $g^0$-bond), a solid line represents an $f$-bond (or an $h^0$-bond), and a wavy line represents an $s$-bond. A shaded triangle represents a three-body intramolecular distribution function.

8-3 Mayer $f$-function associated with the oxygen-hydrogen interaction for SPC water at 25°C. Note that $f_{OH}(r) < 0$ for $r < 1.5$ Å, and is therefore not plotted in this region because of the use of a log scale.

8-4 Oxygen-oxygen pair correlation functions, $g_{OO}(r)$, as a function of the site-site separation, $r$, for SPC water at 25°C and 0.997 g/cm$^3$: (i) predicted using the CSL-HNC equations (solid line), (ii) predicted using the CSL-HNC+$B^{(0)}$ equations (dashed line), (iii) predicted using the SSOZ-HNC equation (dotted line), and (iv) predicted from the Monte Carlo simulations of Jorgensen et al. (circles).

8-5 Oxygen-hydrogen pair correlation functions, $g_{OH}(r)$, as a function of the site-site separation, $r$, for SPC water at 25°C and 0.997 g/cm$^3$. The notation is the same as that in Figure 8-4.

8-6 Hydrogen-hydrogen pair correlation functions, $g_{HH}(r)$, as a function of the site-site separation, $r$, for SPC water at 25°C and 0.997 g/cm$^3$. The notation is the same as that in Figure 8-4.

8-7 CSL-HNC predictions for the $h^0$-functions for SPC water at $T = 25°C$ and $\rho = 0.997$ g/cm$^3$: (i) $h^0_{OO}(r)$ (solid line), (ii) $h^0_{OH}(r)$ (dashed line), and (iii) $h^0_{HH}(r)$ (dotted line).
8-8 Predicted second virial coefficient of water: (i) SPC model (solid line), and (ii) experimental measurements (dashed line) ............... 185

8-9 Predicted pressure versus chemical potential for SPC water at \( T = 298.15 \text{ K} \): (i) truncated virial expansion for the vapor phase (solid line), (ii) ideal-gas approximation for the vapor phase (dashed line), (iii) CSL-HNC equations for the liquid phase (dotted line), and (iv) SSOZ-HNC equation for the liquid phase (dash-dotted line) ............... 186

8-10 Predicted \( T - \rho \) phase diagram of SPC water: (i) predictions of the CSL-HNC equations (open squares), (ii) predictions of the SSOZ-HNC equation (open triangles), (iii) results of Monte Carlo simulations of de Pablo et al.\(^{93}\) (solid circles), and (iv) experimental measurements\(^1\) (solid line) .................. 188

8-11 Predicted vapor pressure of water as a function of temperature: (i) predictions of the CSL-HNC equations for SPC water (squares), predictions of the SSOZ-HNC equation for SPC water (triangles), and (iii) experimental data\(^1\) (solid line) .................. 189

C-1 Flow diagram of the Gillan method .................. 208
List of Tables

3.1 Characteristic Properties of a Water Molecule ................................ 45
3.2 Interaction Parameters of the Potential Models for Water$^a$ .................. 46
3.3 Predictions (Bolded Entry in Each Cell) of the SSOZ-HNC Equation for Water at 25°C and 0.997 g/cm$^3$, and Comparison with Computer Simulations and Experimental Values ............................................ 51

4.1 Interaction Parameters of Various Hydrocarbons$^a$ .......................... 57
4.2 Coefficients for Intramolecular Rotational Potential Functions$^a$ ..... 57
4.3 OPLS for Methane at Infinite Dilution in SPC Water at $T = 25^\circ$C and $\rho = 0.997$ g/cm$^3$ ......................................................... 59
4.4 OPLS for Ethane at Infinite Dilution in SPC Water at $T = 25^\circ$C and $\rho = 0.997$ g/cm$^3$ ......................................................... 63
4.5 OPLS for Propane at Infinite Dilution in SPC Water at $T = 25^\circ$C and $\rho = 0.997$ g/cm$^3$ ......................................................... 67
4.6 Propane in SPC Water (MaS Closure) at $T = 25^\circ$C and $\rho = 0.997$ g/cm$^3$: A Test of the Equivalent-Site Approximation .................. 69

8.1 Predicted Values of the Residual Internal Energy, $U^{\text{res}}$, Residual Helmholtz Free Energy, $A^{\text{res}}$, Residual Chemical Potential, $\mu^{\text{res}}$, Isothermal Compressibility, $\kappa$, and Pressure, $p$, using the CSL-HNC and SSOZ-HNC Equations for SPC Water at 25°C and 0.997 g/cm$^3$, and Comparison with Computer Simulations and Experimental Values. ........ 179
8.2 Predictions of the CSL-HNC and SSOZ-HNC Equations for SPC/E Water at 25°C and 0.997 g/cm³ and Comparison with Computer Simulations Values. The notation is the same as that in Figure 8.1. . . . 181

8.3 Predictions of the CSL-HNC and SSOZ-HNC Equations for TIP3P Water at 25°C and 0.997 g/cm³ and Comparison with Computer Simulations Values. The notation is the same as that in Figure 8.1. . . . 182

8.4 Predictions of the CSL-HNC and SSOZ-HNC Equations for MCY Water at 25°C and 0.997 g/cm³ and Comparison with Computer Simulations Values. The notation is the same as that in Figure 8.1. . . . . . . 183
Chapter 1

Introduction and Objectives

1.1 Motivation

Understanding the thermodynamic behavior of fluids is of central importance to the field of chemical engineering. Indeed, the design of flow processes, power cycles, refrigeration cycles, chemical reactors, and separation processes all involve thermodynamic calculations of the fluid phases involved. These calculations include predicting heat capacities, vapor-liquid coexistence curves, and activity coefficients. In order to perform meaningful calculations, the chemical engineer needs accurate estimations of the thermodynamic properties of fluids. Although, in principle, these properties can be obtained from experimental measurements, in practice, such measurements are typically time consuming and may require expensive equipment.

This situation clearly highlights the need to develop theoretical methodologies that can be utilized to predict the thermodynamic properties of fluids. Ideally, one would like to be able to predict the bulk thermodynamic properties of a fluid given only the chemical identity of the molecules which comprise the fluid. This would involve understanding the nature of the relevant intermolecular interactions, as well as the various modes by which these interactions lead to the observed behavior of the bulk fluid under consideration. Therefore, not only is the problem at hand one of significant practical importance, but it is also one of considerable scientific relevance. For these reasons, considerable effort has been devoted throughout the history of
science to achieve this important goal.

The general problem of predicting the thermodynamic behavior of fluids can be divided into two broad areas. The first one deals with determining the interactions which occur between the molecules comprising the fluid. In Section 1.2, I will provide a brief overview of this area, as well as describe the interaction potential models which will be utilized in this thesis. The second area involves determining the bulk thermodynamic properties of the fluid given the form for the intermolecular potentials. In Section 1.3, I will briefly discuss some of the techniques that have been developed to deal with this issue.

### 1.2 Models for Intermolecular Interactions

Generally speaking, the interactions between molecules can be extremely complex. In practice, the total interaction energy of a system, $U$, depends on the relative positions and orientations of all the molecules comprising the system. As such, $U$ can be modeled\(^2\) as the sum of two-body, three-body, and higher-order multibody interactions. Specifically,

$$U(R_1, R_2, ..., R_N) = u^{(2)}(R_i, R_j) + u^{(3)}(R_i, R_j, R_k) + ...$$  \hspace{1cm} (1.1)

where $R_i$ refers to both the position and orientation of molecule $i$, $u^{(2)}$ is the two-body interaction potential, $u^{(3)}$ is the three-body interaction potential, and so on.

In order to make the model in Eq. (1.1) computationally tractable, it is necessary to make approximations, while retaining the most important contributions. In general, the most important contribution to $U$ results from the two-body terms in Eq. (1.1). In dealing with molecular interactions, therefore, the first approximation involves assuming pairwise additivity. In other words, the total interaction energy of the system, $U$, is approximated as

$$U(R_1, R_2, ..., R_N) = \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} u(R_i, R_j)$$  \hspace{1cm} (1.2)
where \( u(R_i, R_j) \) is an effective pairwise interaction potential between molecules \( i \) and \( j \). Note that the effective pair potential, \( u \), is not necessarily the same as the two-body interaction potential, \( u^{(2)} \), because in deriving Eq. (1.2) higher-body interactions have been incorporated indirectly.

A variety of models are currently available to describe the effective pairwise interaction potential between two molecules, \( u \). Among these, the interaction site model (ISM)\(^3\) has been used extensively to describe the interactions between the molecules comprising a fluid. In the ISM, sites having spherically symmetric interaction potentials are located at various positions within a molecule, typically on atoms or groups of atoms which make up the molecule. For example, in the case of a hydrocarbon chain, \( \text{CH}_3(\text{CH}_2)_{n-2}\text{CH}_3 \), the interaction sites are located on the carbon atoms. The interaction energy between a molecule at position \( R_1 \) and another molecule at position \( R_2 \), \( u(R_1, R_2) \), is taken to be the pairwise sum of the interaction energies between the sites in each molecule, that is,

\[
u(R_1, R_2) = \sum_{\alpha\gamma} u_{\alpha\gamma}(|r_1^\alpha - r_2^\gamma|) \tag{1.3}\]

where \( r_1^\alpha \) is the position of site \( \alpha \) in molecule 1, \( r_2^\gamma \) is the position of site \( \gamma \) in molecule 2, and \( u_{\alpha\gamma} \) is the interaction potential between sites \( \alpha \) and \( \gamma \). Note that the function, \( u_{\alpha\gamma} \), depends solely on the distance between sites \( \alpha \) and \( \gamma \).

Jorgensen and coworkers have developed ISM's for several different molecular species. In their models, the bond lengths and bond angles of the molecules are held fixed, and the site-site interaction potentials are fitted to a sum of Lennard-Jones and Coulomb potentials. Specifically,

\[
u_{\alpha\gamma}(r) = \frac{q_{\alpha} q_{\gamma}}{r} + \frac{A_{\alpha} A_{\gamma}}{r^{12}} - \frac{C_{\alpha} C_{\gamma}}{r^6} \tag{1.4}\]

where \( r \) is the distance between sites \( \alpha \) and \( \gamma \), and \( u_{\alpha\gamma}(r) \) is the corresponding interaction potential. The parameters which enter into the site-site potential functions (namely, \( q, A, \) and \( C \)) have been tabulated for different atoms and groups of atoms. Therefore, these potentials are transferable among different molecules, and as such,
are referred to as transferable intermolecular potential functions (TIPS). The TIPS have been tested against empirical data for water,\(^5\) methanol,\(^6\) and ethanol\(^7\) using Monte Carlo simulations. The parameters for these functions have also been tested for hydrocarbons,\(^8\) sulfur compounds,\(^9\) as well as for various ions.\(^10\)

Although the bond lengths and bond angles are held fixed in these models, the molecules can still alter their conformations by rotations of their dihedral angle, \(\phi\). Associated with the rotation of each dihedral angle one can introduce a potential function, \(V(\phi)\). An extensively used expression for \(V(\phi)\) is given by\(^8\)

\[
V(\phi) = V_0 + \frac{1}{2}V_1(1 + \cos \phi) + \frac{1}{2}V_2(1 - \cos 2\phi) + \frac{1}{2}V_3(1 + \cos 3\phi)
\]

where the parameters \(V_0\), \(V_1\), \(V_2\), and \(V_3\) have been tabulated for various groups of atoms.\(^8\)

Water plays a central role in many systems of practical importance, and will therefore be considered at length in this thesis. In the case of water, two main classes of potential models have been introduced. In the first class, the two hydrogen atoms in a water molecule are always bonded to the oxygen atom. This implies that the water molecules are not allowed to exchange hydrogens. An example of this class of potential models is the TIPS model developed by Jorgensen.\(^5\) Berendsen has also developed an interaction potential model for water called the simple-point charge (SPC) model.\(^11\) The SPC model has the same form as Jorgensen's TIPS model, but utilizes different parameter values. Berendsen later modified the SPC model to include the effects of water polarizability, which resulted in the so called SPC/E model.\(^12\) The second class of potential models for water, referred to as central-force models, treats the hydrogen and oxygen atoms in liquid water as independent atoms. An example is the central-force model developed by Stillinger et al.\(^13,14\) A comparison of the predictions of several different interaction potential models for water has been performed by Jorgensen et al.,\(^15\) who concluded that all the tested models predict results to a comparable accuracy when compared to experimental measurements.
1.3 Liquid State Theory

The central goal of statistical mechanics is to predict the bulk properties of a system given a description of the intermolecular interactions between the molecules which comprise the system.

In general, when modeling a molecular system, one is concerned with the importance of quantum-mechanical effects. Quantum effects, however, are known to be unimportant when the following two conditions are satisfied

\[ \rho^{1/3} \lambda = \rho^{1/3} \sqrt{\frac{\beta h^2}{2\pi m}} \ll 1 \]

\[ \frac{\beta h^2}{8\pi^2 I} \ll 1 \]

(1.6)

where \( \rho \) is the density, \( h \) is Planck's constant, \( \beta = (kT_B)^{-1} \), with \( k_B \) the Boltzmann constant and \( T \) the absolute temperature, \( m \) and \( I \) are the mass and the moment of inertia of the molecule, respectively, and \( \lambda \) is the de Broglie wavelength. The first condition states that the de Broglie wavelength of a molecule, \( \lambda \), which is associated with the translational momentum of the molecule, is much smaller than the typical separation between two molecules, \( \rho^{-1/3} \). The second condition states that the characteristic thermal energy of a molecule, \( \beta^{-1} \), must be larger than the typical spacing between rotational energy levels of the molecule, \( h^2/(8\pi^2 I) \). For most fluid systems at temperatures above or around room temperature, these two conditions are satisfied, and consequently these systems can be treated classically.

Given a description of the intermolecular interactions between molecules, and the fact that the system can be treated classically, one can then employ the principles of classical statistical mechanics. In order to calculate the thermodynamic properties of a fluid, there are two principal theoretical methodologies that can be utilized: (i) computer simulation methods, and (ii) integral equation methods. These will be discussed separately in the following two sections.
1.3.1 Computer Simulation Methods

Given the intermolecular interaction potentials between the various species which are present in the system, one can determine the thermodynamic properties of the system through either Monte Carlo or molecular dynamics simulations.\textsuperscript{17} If the simulations are performed accurately, the results will be essentially exact for the given interaction potential models.

Although computer simulations constitute a powerful tool to analyze molecular systems, they possess several limitations. The most important limitations involve (i) the time scales that can be analyzed, and (ii) the computational expense required.

To illustrate this point, I will consider a surfactant-water system. First, in general, typical simulation times are very short (about $10^{-10}$ s). Micelles are dynamic entities which assemble, exchange monomers, and eventually break apart. The time scale\textsuperscript{18} for monomer exchange between micelles is approximately $10^{-5}$ s, and the time scale\textsuperscript{18} for micelle dissociation is about $10^{-3}$ s. Both of these time scales are orders of magnitude longer than the duration of a typical simulation. Therefore, current simulations cannot capture the dynamic nature of the micellar aggregates. Another problem with simulations is that there is a practical limit\textsuperscript{17} on the number of interaction sites that can be simulated (about $10^4$). A typical surfactant has about 10 interaction sites, and water has three or four interaction sites depending on the particular potential model utilized. At a surfactant concentration of about 1.0 M, there are approximately 50 water molecules for each surfactant molecule. Accordingly, there are 200 interaction sites associated with the water molecules per simulated surfactant molecule. A typical micelle consists of about 50 surfactant molecules, which implies that there are $10^4$ interaction sites per micelle. This implies that if the water molecules are explicitly taken into account at surfactant concentrations less than 1.0 M, only one micelle can be simulated. For many practical applications, the surfactant concentration is of the order of $10^{-3}$ M, in which case the situation is even worse due to the abundance of water molecules. In the arguments presented above, the micelles were assumed to be monodisperse. By using periodic boundary conditions, the simulations are able to mimic the properties of the bulk fluid. However, if the micelles exhibit polydispers-
sity, which is a commonly encountered case, then using periodic boundary conditions on a single micelle will not accurately describe the actual physical system. Instead, more than one micelle will have to be simulated. At the present time, this constitutes an extremely difficult computational problem. Consequently, it appears that current computer simulations alone may be insufficient to examine the full range of phenomena occurring in molecular fluids.

1.3.2 Integral Equation Theories

Integral equation theories, although less accurate than computer simulations, provide a powerful means to analyze the behavior of molecular systems. One major advantage is that they do not run into the computational difficulties encountered by simulations. Instead, they offer a tradeoff between accuracy and computational expense. In addition, these theories offer a means to calculate the thermodynamic properties of the system, both mechanical and thermal. Therefore, it appears very challenging and important to examine in detail the extent of applicability of integral equation theories.

Early in the development of integral equation theories for fluids, the field was highly abstract. Almost all the work was confined to fluids characterized by rather simplistic intermolecular potentials, including hard-sphere and Lennard-Jones potentials. However, over the last twenty years, due to the development of better formalisms and the increase in computational power, integral equation theories have advanced to a high level of sophistication. In fact, theories of this type have been applied to systems which are highly relevant to the chemical engineer, including polar and polymeric fluids.

Two potentially useful integral equations which have been developed for molecular fluids are the site-site Ornstein-Zernike (SSOZ) equation and the Chandler-Silbey Ladanyi (CSL) equations. The utilization of these equations to describe the behavior of complex fluids is still limited, and considerable work needs to be done to explore their range of validity and predictive capabilities.
1.4 Thesis Objectives

The central goal of this thesis is to bring integral equation theories for molecular fluids to a level where they can provide a useful tool for the chemical engineer to predict structural and bulk thermodynamic properties of complex fluids. In order to achieve this goal, this thesis focuses on two main aspects.

The first one involves assessing the applicability of the currently available integral equations for molecular fluids to a variety of systems which are relevant to the chemical engineer. This will entail applying these equations to complex realistic fluids such as water, hydrocarbons in water, and a surfactant-water model system based on the Lennard-Jones potential. The resulting predictions of these equations will then be compared with those from computer simulations and experimental measurements to assess their range of validity and applicability.

In cases where the integral equations considered do not provide accurate predictions, the second aspect of this thesis will come into play. Specifically, an attempt will be made to rationalize the reasons for the observed inaccuracies, as well as to propose methods to correct the existing integral equations for molecular fluids. The inexactness of the integral equations arise from the neglect of certain physical pathways via which molecules in a system can interact with one another. In order to construct better approximations, an attempt will be made to identify these physical pathways as well as to develop methods for numerically evaluating their contribution.

The thesis is organized as follows. Chapter 2 presents an overview of the Ornstein-Zernike (OZ) and the site-site Ornstein-Zernike (SSOZ) equations. In addition, approximate closure relations as well as the formulae for computing the thermodynamic properties from the correlation functions are presented. In Chapter 3, the SSOZ equation is utilized to predict the structural and bulk thermodynamic properties of pure water, and the predictions are compared with results from computer simulations and experimental measurements. In Chapter 4, a similar analysis is carried out for n-alkanes at infinite dilution in water. In Chapter 5, a surfactant-water model system is analyzed in the context of the SSOZ equation to determine if the formalism
can describe the spontaneous formation of self-assembled micellar microstructures. In Chapter 6, the limitations of the SSOZ equation are discussed, and a new set of integral equations for ISM fluids, known as the Chandler-Silbey-Ladanyi (CSL) equations is presented. In addition, expressions for the Helmholtz free energy and the chemical potential are developed, and various aspects of the CSL equations are analyzed. In Chapter 7, the CSL equations are applied to homonuclear and heteronuclear diatomic Lennard-Jones fluids, and the theoretical predictions for the fluid structure are compared against those from the SSOZ equation and computer simulations. In Chapter 8, the CSL equations are utilized to predict the structure, thermodynamics, and phase behavior of water. These theoretical predictions are compared with those from the SSOZ equation and computer simulations, as well as with experimental measurements. Finally, Chapter 9 presents a summary of the salient findings of this thesis, as well as a discussion of possible directions for future work.
Chapter 2

The Site-Site Ornstein-Zernike Equation

2.1 Description of the Formalism

2.1.1 Simple Fluids

One of the simplest potential models of a fluid assumes that the interaction potential between molecules is spherically symmetric and pairwise additive. A system which is composed of molecules of this type is referred\textsuperscript{16} to as a simple fluid. An integral equation which has had a great deal of success\textsuperscript{16} for simple fluids is the Ornstein-Zernike (OZ) equation. It is written below in matrix form and in $k$ space

$$K(k) = c(k) + (k)p(k)$$

where $h$ is the total correlation function matrix, $c$ is the direct correlation function matrix, and $\rho$ is the density matrix. Note that each term in Eq. (2.1) is a $N \times N$ matrix, where $N$ is the number of components in the system. The element, $h_{MM'}$ (or $c_{MM'}$), of the matrix, $h$ (or $c$), represents the total (or direct) correlation function between molecules of type $M$ and $M'$. The matrix, $\rho$, is diagonal, and the matrix element, $\rho_{MM}$, is equal to the number density of molecules of type $M$ in the system.
The symbol indicates the Fourier transform of a function.

Neither the total correlation function, \( h \), nor the direct correlation function, \( c \), is known a priori. Therefore, in order to solve for these quantities, another relation, known as the closure relation, is needed to complement Eq. (2.1). For simple fluids, the exact form of the closure relation is given by

\[
1 + h_{MM}(r) = \exp[-\beta u_{MM}(r) + h_{MM}(r) - c_{MM}(r) + b_{MM}(r)]
\]

(2.2)

where \( b_{MM}(r) \) are the bridge functions, which are complex functionals of the total correlation functions, and \( \beta = 1/(k_B T) \), where \( k_B \) is the Boltzmann constant and \( T \) is the absolute temperature. Approximations enter the theory when a form for the bridge functions, \( b_{MM}(r) \), is chosen. In general, the total correlation function can be represented as an infinite sum of diagrams, and the bridge functions are an infinite sum of graphs which are a subset of these diagrams.

The bridge diagrams are highly connected, and, therefore, are shorter ranged than the other diagrams which contribute to the total correlation functions. If the bridge diagrams are neglected, that is, if one sets

\[
b_{MM}(r) = 0
\]

(2.3)

in Eq. (2.2), then one obtains the hypernetted-chain (HNC) closure. The HNC closure has been found to work well for fluids characterized by long-ranged interactions, for example, the restricted primitive model.

There are several approximations to the bridge functions of the form \( b = b(t(r)) \), where \( t(r) = h(r) - c(r) \), which have proven successful for simple fluids. If the bridge functions are approximated by

\[
b_{MM}(r) = \ln[1 + t_{MM}(r)] - t_{MM}(r)
\]

(2.4)

then one obtains the Percus-Yevick (PY) closure, which has been found to work well for systems characterized solely by short-ranged forces, such as, the hard-sphere and
Lennard-Jones systems. Note that the PY closure sums over fewer diagrams than the HNC closure.

The Martynov-Sarkisov (MaS) closure was proposed as an improvement to the PY closure. It approximates the bridge functions by

\[ b_{MM'}(r) = \left[ 1 + 2t_{MM'}(r) \right]^{1/2} - t_{MM'}(r) - 1 \]  

(2.5)

For the case of hard-spheres, the MaS closure predictions of thermodynamic properties, such as the pressure, as well as of the pair correlation functions, are in better agreement with computer simulations than the corresponding PY closure predictions.

The Ballone-Pastore-Galli-Gazzillo (BPGG) closure was introduced as a generalization of the MaS closure and has an adjustable parameter, s. Its bridge functions are given by

\[ b_{MM'}(r) = \left[ 1 + s t_{MM'}(r) \right]^{1/s} - t_{MM'}(r) - 1 \]  

(2.6)

It is interesting to point out that when \( s = 1 \), the BPGG closure reduces to the HNC closure, and when \( s = 2 \), it reduces to the MaS closure. In previous applications, \( s \) was fixed by enforcing the equality of pressures obtained from the virial and compressibility equations.

The Rogers-Young (RY) closure has an adjustable function, \( f(r) \). Its bridge functions are given by

\[ b_{MM'}(r) = \ln \left\{ 1 + \frac{\exp[f(r)t_{MM'}(r)] - 1}{f(r)} \right\} - t_{MM'}(r) \]  

(2.7)

The only restrictions on the function, \( f(r) \), are that it should satisfy the boundary conditions: \( f(0) = 0 \) and \( f(\infty) = 1 \). Therefore, as can be seen by comparing Eq. (2.7) with Eqs. (2.4) and (2.3) in the limits \( r \to 0 \) and \( r \to \infty \), respectively, the RY closure mimics the PY closure at short distances, while it mimics the HNC closure at long distances. Typically, the function, \( f(r) \), is chosen to be of the form, \( f(r) = 1 - \exp(-\alpha r) \). The parameter, \( \alpha \), is chosen such that the pressures calculated using
the virial and compressibility equations are equal. The RY closure has been found to work much better than the PY closure for systems characterized by purely repulsive interactions, such as, $1/r^n$ potential fluids.\textsuperscript{23}

One approximate closure for simple fluids which is not of the form given in Eq. (2.2) is the soft mean-spherical approximation (SMSA) closure.\textsuperscript{24} The SMSA requires that the potential function, $u_{MM'}(r)$, be divided into a repulsive contribution, $u_{MM'}^{(0)}(r)$, and an attractive contribution, $u_{MM'}^{(1)}(r)$, that is,

$$u_{MM'}(r) = u_{MM'}^{(0)}(r) + u_{MM'}^{(1)}(r) \quad (2.8)$$

This division is typically done using the Weeks-Chandler-Andersen (WCA) criterion.\textsuperscript{25, 26} The SMSA closure is then given by\textsuperscript{24}

$$1 + h_{MM'}(r) = e^{-\beta u_{MM'}^{(0)}(r)}[1 + h_{MM'}(r) - c_{MM'}(r) - \beta u_{MM'}^{(1)}(r)] \quad (2.9)$$

The SMSA closure has been found to work extremely well for Lennard-Jones fluids, and provides a significant improvement over the HNC and PY closures for liquid metals.\textsuperscript{24}

### 2.1.2 Molecular Fluids

Simple fluid models become\textsuperscript{16} inadequate when the molecules are “highly” nonspherical. The OZ equation must then be extended to take into account the anisotropies of the molecular interaction potential. For fluids which consist of molecules characterized by nonspherical interaction potentials, the OZ equation can be generalized as follows\textsuperscript{3, 16}

$$h(R_1, R_2) = c(R_1, R_2) + \int dR_3 c(R_1, R_3) \rho h(R_3, R_2) \quad (2.10)$$

where $R_i$ refers to both the position and orientation of molecule $i$. Equation (2.10) is referred to as the Molecular Ornstein-Zernike (MOZ) equation. The correlation functions are now not only functions of the distance between molecules, but also depend on the relative orientation of the molecules, as well as on their conformation.
in the case of flexible molecules.

The fact that the correlation functions depend on many variables, makes the numerical solution of the MOZ equation difficult for rigid molecules and intractable for large flexible molecules. As will be shown later, the function \( h_{MM}(R_1, R_2) \) actually contains more information than is needed to compute the thermodynamic properties of the system. A more convenient function to work with is the site-site total correlation function, \( h_{aM \alpha' M'}(r) \), which is only a function of the site-site separation, \( r \).

The site-site total correlation function can be obtained from the molecular total correlation function as follows:

\[
h_{aM \alpha' M'}(r) = \int dR_1 dR_2 h_{MM}(R_1, R_2) \delta(\tau_{1M}^{aM}) \delta(|\tau_{2M}^{\alpha'M'} - r|)
\]

where \( \tau_{1M}^{aM} \) is the position of site \( \alpha \) on molecule 1 (which is of type \( M \)). Note that \( R_1 = (\tau_{1M}^{1M}, \tau_{2M}^{2M}, ..., \tau_{1M}^{\alpha'M}, ...) \). Since the site-site total correlation function is an integral over the molecular total correlation function, it contains less information. However, as will be shown later, knowledge of the site-site total correlation function is sufficient to compute the thermodynamic properties of a fluid.

Chandler and Andersen were able to derive an integral equation for the site-site total correlation function for interaction site fluids by making the assumption that the direct correlation function can be written as

\[
c_{MM'}(R_1, R_2) \approx \sum_{\alpha \alpha'} c_{aM \alpha' M'}(\tau_{1M}^{\alpha M} - r_{2M}^{\alpha' M'})
\]

Substituting Eq. (2.12) into the MOZ equation (see Eq. (2.10)), and integrating both sides over all molecular orientations, one obtains the site-site Ornstein-Zernike (SSOZ) equation, which is written below in matrix form in momentum \( (k) \) space

\[
\hat{h}(k) = \hat{\omega}(k)\hat{c}(k)\hat{w}(k) + \hat{\omega}(k)\hat{c}(k)p\hat{h}(k)
\]

where \( h \) is the site-site total correlation function, \( c \) is the site-site direct correlation...
function, \( w \) describes the intramolecular correlations (that is, correlations between sites belonging to the same molecule), and \( \rho \) is the density of sites of the system.

The elements of the matrix, \( w \), are given by

\[
\hat{w}_{\alpha M \alpha' M'}(k) = \delta_{MM'} \frac{\sin kl_{\alpha \alpha' M}}{kl_{\alpha \alpha' M}}
\]  

(2.14)

where \( l_{\alpha \alpha' M} \) is the distance between sites \( \alpha \) and \( \alpha' \) in a molecule of type \( M \). Note that \( \hat{w}_{\alpha M \alpha' M'}(k) = 0 \) for molecules of different types (that is, if \( M \neq M' \)). Note also that the SSOZ equation reduces to the OZ equation when \( \hat{w}(k) \) is equal to the identity matrix. This corresponds to dissociating all the sites within the molecules.

As in the case of the simple fluids, a closure relation is needed to complement Eq. (2.13). Hirata and Rossky suggested\(^29\) using the closure relations for simple fluids, in the context of the SSOZ equation, to describe interaction site fluids. Note, however, that in the case of polyatomic molecules, using closures intended for simple fluids is in itself an approximation. Indeed, this will generate\(^30\) an infinite number of diagrams which are unallowed in the exact theory of interaction site fluids at every level of the density. Approximations of this type lead to a theory with known deficiencies which will be discussed later in Chapter 6. In spite of these limitations, theories which employ the SSOZ equation with a simple fluid closure have been found to perform well for a wide variety of molecular systems. These theories have been found to yield pair correlation functions in qualitative agreement with the results of computer simulations. In fact, the SSOZ equation is the most extensively used approach to model interaction site fluids. Accordingly, the SSOZ equation offers a good starting point for analyzing interaction site fluids.

### 2.2 Thermodynamic Properties

As stated in Section 1.3.2, the thermodynamic properties of a system can be computed from knowledge of the site-site pair correlation functions. For completeness, expressions for a variety of thermodynamic properties will be presented in Section
2.2.1. In addition, I have developed an analytical expression for the residual chemical potential, appropriate for interaction site fluids, in terms of pair and direct correlation functions at full coupling for various closures. To date, an expression of this type was only available for the HNC closure. This new expression facilitates the calculation of the residual chemical potential by eliminating the previous need to perform a numerical integration over the coupling constant, thus making the computation of the chemical potential simpler and more efficient. This new development will be described in Section 2.2.2.

2.2.1 Expressions for Various Thermodynamic Properties

Below, I present expressions for various thermodynamic properties in terms of the site-site pair correlation functions.

The residual internal energy, $U^{\text{res}}$, is given by

$$\frac{U^{\text{res}}}{V} = \frac{1}{2} \sum_{\alpha M, \alpha' M'} \rho_{\alpha M} \rho_{\alpha' M'} \int d^3 r \ u_{\alpha M, \alpha' M'}(r) g_{\alpha M, \alpha' M'}(r)$$  \hspace{1cm} (2.15)

where $g_{\alpha M, \alpha' M'}(r) = 1 + h_{\alpha M, \alpha' M'}(r)$, $V$ is the system volume, $\rho_{\alpha M}$ (or $\rho_{\alpha' M'}$) is the density of the sites of type $\alpha$ (or $\alpha'$) on molecules of type $M$ (or $M'$), $M$ and $M'$ run over all molecular species, and $\alpha$ and $\alpha'$ run over all the sites in each molecule. Here, the residual of a property is defined as the difference in the value of a particular system property from that corresponding to an ideal gas at the same temperature, composition, and total volume. Note that this definition of the residual is slightly different from that typically used in classical thermodynamics, where the residual is defined with respect to an ideal gas at the same temperature, composition, and pressure.\(^1\)

For a one-component system, the isothermal compressibility, $\kappa_T$, is given by

$$\kappa_T = \frac{\beta}{\rho} [1 + \rho \hbar(0)]$$ \hspace{1cm} (2.16)

where $\rho$ is the system density.
For a two-component system, the solute partial molar volume, $\bar{V}_u$, is given by

$$\bar{V}_u = \frac{1 + [\hat{h}_{uv} - \hat{h}_{uv}(0)]\rho_v}{\rho_u + \rho_v + \rho_u\rho_v[\hat{h}_{uv}(0) + \hat{h}_{uv}(0) - 2\hat{h}_{uv}(0)]}$$ (2.17)

where $\rho_u$ is the solute density, and $\rho_v$ is the solvent density. The index $u$ refers to the solute, and the index $v$ refers to the solvent.

The heat capacity at constant volume, $C_V$, is given by

$$C_V = \sum_M C_{V,M}^{\text{ideal}} + \left( \frac{\partial U^{\text{res}}}{\partial T} \right)_{V,N_i}$$ (2.18)

where $C_{V,M}^{\text{ideal}}$ is the ideal gas heat capacity for molecules of type $M$, which depends only on temperature. Values of $C_{V,M}^{\text{ideal}}$ for various molecules can be found in the literature.

The residual Helmholtz free energy, $A^{\text{res}}$, can be calculated as follows

$$\frac{A^{\text{res}}}{V} = \int_0^1 d\zeta < U^{\text{res}} >_\zeta$$

$$= \frac{1}{2} \sum_{\alpha M \alpha' M'} \rho_{\alpha M} \rho_{\alpha' M'} \int d^3 r \int_0^1 d\zeta \frac{\partial u_{\alpha M \alpha' M'}(r;\zeta)}{\partial \zeta} g_{\alpha M \alpha' M'}(r;\zeta)$$ (2.19)

where the parameter, $\zeta$, couples the interactions of all the molecules with one another, and $< U^{\text{res}} >_\zeta$ is the residual internal energy of the system at a coupling constant strength, $\zeta$. When $\zeta = 1$, all the molecules in the system interact fully with one another, that is, $u_{\alpha M \alpha' M'}(r;\zeta) = u_{\alpha M \alpha' M'}(r)$ for all $\alpha, \alpha', M,$ and $M'$. On the other hand, when $\zeta = 0$, there are no intermolecular interactions present in the system; that is, $u_{\alpha M \alpha' M'}(r;\zeta) = 0$, and the system behaves like an ideal gas. Note that the integration with respect to $\zeta$ in Eq. (2.19) is performed at constant temperature, composition, and total volume.

For simple fluids, Morita and Hiroike were able to express $A^{\text{res}}$ in terms of integrals over the pair correlation functions. Singer and Chandler generalized this result for the SSOZ equation under the HNC closure. I have extended both of these expressions in the context of the SSOZ equation with a general simple fluid closure.
The resulting expression for $A^{res}$ is given by

$$\frac{\beta A^{res}}{V} = \frac{1}{2} \sum_{a_{\alpha \alpha}^M} \rho_{a_{\alpha} M} \rho_{a'_{\alpha'} M'} \int d^3 r \left\{ \frac{1}{2} h_{a_{\alpha} M} (r) - c_{a_{\alpha} M} (r) + b_{a_{\alpha} M} (r) \right\}$$

$$+ \frac{1}{2} \int d^3 k \left\{ \ln |\text{det}[1 - \rho \hat{w}(k) \hat{c}(k)] + Tr \rho \hat{w}(k) \hat{c}(k)| \right\}$$

$$+ \frac{1}{2} \int d^3 r \int_0^1 d \zeta \sum_{a_{\alpha} M} \rho_{a_{\alpha} M} h_{a_{\alpha} M} (r) \rho_{a'_{\alpha'} M} \frac{\partial b_{a_{\alpha} M} (r; \zeta)}{\partial \zeta}$$

(2.20)

For the HNC closure, where $b(r) = 0$, Eq. (2.20) yields an expression for $A^{res}$ which is only a functional of the correlation functions at full coupling.

The enthalpy of solution of molecules of type $M$, $\Delta H_M$, is given by

$$\Delta H_M = H_M^\infty - H_M^{\text{ideal}}$$

$$= \mu_M^{res} - T \left( \frac{\partial \mu_M^{res}}{\partial T} \right)_{N,V}$$

$$= \mu_M^{res} - T \left( \frac{\partial \mu_M^{res}}{\partial T} \right)_{N,V} + k_B T \left( \frac{\alpha_p V_M}{\kappa T k_B} - 1 \right)$$

(2.21)

where $H_M^{\text{ideal}}$ is the partial molar enthalpy of $M$ in the ideal gas state, $H_M^\infty$ is the partial molar enthalpy of $M$ at infinite dilution, and $\alpha_p$ is the coefficient of thermal expansion of the solution.

### 2.2.2 Chemical Potential

In this section, I present the derivation of a new analytical expression for the residual chemical potential, appropriate for interaction site fluids, in terms of the pair and direct correlation functions at full coupling for closure relations characterized by bridge functions of the form $b = b(t(r))$.

The residual chemical potential of a molecule of type $M$, $\mu_M^{res}$, is given by

$$\mu_M^{res} = \int_0^1 d \zeta' < E_{\omega} > \zeta'$$

$$= \sum_{a_{\alpha} M} \rho_{a_{\alpha}'} \int d^3 r \int_0^1 d \zeta' \frac{\partial u_{a_{\alpha} M} (r; \zeta')}{\partial \zeta'} g_{a_{\alpha} M} (r; \zeta')$$

(2.22)
where $\zeta'$ couples the interaction of a single molecule of type $M$ with the rest of the molecules in the system, $\alpha$ runs over the interaction sites of a molecule of type $M$, $M'$ runs over all the molecular types, $\alpha'$ runs over the interaction sites of molecules of type $M'$, and $<\epsilon_{uu}>_{\zeta'}$ is the interaction energy of a single molecule of type $M$ with the rest of the system. Note that at infinite dilution, the solute-solvent interaction energy, $\epsilon_{uu}$, is given by

$$\epsilon_{uu} = \sum_{\alpha \alpha' M'} \rho_{\alpha' M'} \int d^3 r u_{\alpha M \alpha' M'}(r) g_{\alpha M \alpha' M'}(r)$$  \hspace{1cm} (2.23)

where $\alpha$ runs over all the interaction sites of the solute molecule (which is of type $M$), $M'$ runs over all the molecular species in the system, and $\alpha'$ runs over the interaction sites of molecules of type $M'$.

The only restrictions on the integration path in Eq. (2.22) are that:
(1) $u_{\alpha M \alpha' M'}(r; \zeta' = 1) = u_{\alpha M \alpha' M'}(r)$, and (2) $u_{\alpha M \alpha' M'}(r; \zeta' = 0) = 0$. Note that the integration with respect to $\zeta'$ is performed at constant $T$, $\rho_M$, and $V$. In principle, the expression in Eq. (2.22) can be used to calculate the residual chemical potential by (a) solving the SSOZ equation for different values of the coupling constant, $\zeta'$, (b) calculating the solute-solvent interaction energy, $<\epsilon_{uu}>_{\zeta'}$, via Eq. (2.23), and (c) performing the coupling constant integration numerically.

Clearly, it would be much more efficient if one had access to an expression for $\mu_{uu}^{res}$ which is only a function of the correlation functions at $\zeta' = 1$. To this end, I have generalized the derivation of Morita and Hiroike, 33 which applies only to simple fluids, to the case of interaction site fluids. If a closure relation of the form given in Eq. (2.2) is used, then a generalization of the arguments of Morita and Hiroike leads to the following expression for $\mu_{uu}^{res}$

$$\beta \mu_{uu}^{res} = \sum_{\alpha \alpha' M'} \int d^3 r \left\{ \frac{1}{2} h_{\alpha M \alpha' M'}(r) - \frac{1}{2} h_{\alpha M \alpha' M'}(r) c_{\alpha M \alpha' M'}(r) \right\}$$
$$- c_{\alpha M \alpha' M'}(r) + b_{\alpha M \alpha' M'}(r)$$
$$+ \sum_{\alpha \alpha' M'} \rho_{\alpha' M'} \int d^3 r \int_0^1 d\zeta' h_{\alpha M \alpha' M'}(r) \frac{\partial b_{\alpha M \alpha' M'}(r; \zeta')}{\partial \zeta'}$$ \hspace{1cm} (2.24)
For the HNC closure, where $b(r) = 0$, Eq. (2.24) reduces to the expression obtained by Singer and Chandler\(^{34}\) for interaction site fluids. For other closures, however, the last term in Eq. (2.24), which requires the integration of the bridge functions over $\zeta'$, poses a computational problem. Note that for an approximate closure, the residual chemical potential is, in general, dependent on the path of integration chosen to evaluate the last term in Eq. (2.24). For one-component simple fluids, Kjellander and Sarman were able to find\(^{37}\) an analytical expression for this integral for a closure of the form $b = b(t(r))$, using a path along which $h(r; \zeta') = \zeta' h(r)$. Their evaluation of the last term in Eq. (2.24) can be extended directly to interaction site fluids (see Appendix A) to yield the following result

\[
\int_0^1 d\zeta' h_{\alpha M} \frac{\partial b_{\alpha M}^{\zeta'}(r)}{\partial \zeta'} = h_{\alpha M} \int_0^{t_{\alpha M}^{\zeta'}} dt' \frac{\partial b_{\alpha M}^{\zeta'}(t')}{\partial t'} \tag{2.25}
\]

Substituting Eq. (2.25) into Eq. (2.24), one obtains an expression for $\mu_M^{\text{res}}$ which depends only on the correlation functions at full coupling.

### 2.3 Previous Applications of the SSOZ Equation

The SSOZ equation was used initially with the PY closure to predict the structure of diatomic fused hard-sphere fluids.\(^{38, 39}\) Analytical solutions to these equations were obtained later for hard dumbbells,\(^{40, 41, 42, 43, 44, 45}\) polar hard dumbbells,\(^{46, 47}\) and mixtures of the two.\(^{48}\)

The SSOZ equation has also been used to predict the structure of more "realistic" fluid models. These include bromine,\(^{49, 50}\) hydrogen chloride,\(^{50}\) nitrogen,\(^{51, 49}\) oxygen,\(^{49}\) benzene,\(^{52}\) benzene-hexafluorobenzene mixtures,\(^{53, 54}\) n-butane,\(^{55}\) butane in water,\(^{55}\) sulfur dioxide,\(^{56}\) methanol,\(^{57}\) water,\(^{58}\) salt-water mixtures,\(^{59, 60}\) and propane in water.\(^{61}\) In general, the predictions of the SSOZ equation are in qualitative agreement with the pair correlation functions obtained from computer simulations and experimental scattering studies.

The SSOZ equation has not only been applied to "small" molecules, but it has
also been applied to systems composed of macromolecules. For example, Schweizer and coworkers have used the SSOZ equation to determine the structure of polymer systems. When dealing with systems composed of large chain-like molecules, two problems arise. First, the number of correlation functions which need to be solved increases rapidly with the number of interaction sites on the chain. In view of this, to simplify the analysis, Curro and Schweizer developed a perturbation scheme to reduce the number of equations that need to be solved. At the zeroth level, all the site-site correlation functions are considered to be equivalent. The second problem involves determining the average conformation of the molecules in the system. While for a "small" molecule this is typically known beforehand since the molecule is rigid, the conformations of long molecules are not known a priori. These conformations not only depend on interactions within the molecule, but they also depend on the environment of the molecule. The initial studies for linear polymer chains assumed a form for the chain structure (for example, Gaussian, Freely Jointed, etc.) and the solvent effect on the polymer conformations was neglected. Subsequently, methods were developed to self-consistently determine the intramolecular structure in order to study the conformations of polymer chains in bulk solution.

In all the previously mentioned applications of the SSOZ equation, the main point of concern was the ability of the theory to yield structural information about the fluid. However, this formalism is also able to provide thermodynamic information about the fluid. As an example, Karplus and coworkers studied the thermodynamics of various ions in water using the SSOZ-HNC equation. In addition, Schweizer and Curro studied the thermodynamics of polymer melts and alloys, and were able to obtain an effective \( \chi \) parameter.

In the following chapters, I apply the SSOZ equation with several different simple fluid closures to study pure water (Chapter 3), hydrocarbon-water systems (Chapter 4), and a model surfactant-water system (Chapter 5). These studies involve predicting structural as well as thermodynamic properties of these systems using the SSOZ equation, and comparing the theoretical predictions with those of computer simulations and experimental measurements.
Chapter 3

The Site-Site Ornstein-Zernike Equation: Application to Water

3.1 Introduction and Overview

Water plays a central role in many systems of both scientific and practical interest. It also displays many unusual properties, due to the extremely anisotropic interactions between water molecules and their ability to form strong hydrogen bonds. Consequently, water appears to be an ideal fluid to test the accuracy of integral equation theories.

The structural properties of water have been studied in the past by Pettitt and Rossky\textsuperscript{58} in the context of the SSOZ-HNC equation. In this thesis, I have significantly extended\textsuperscript{80} this work by predicting both the thermodynamic behavior and the structural properties of water for various potential models for water. Specifically, I have solved the SSOZ equation with the HNC and SMSA closures for several potential models of water at ambient conditions ($T = 25^\circ\text{C}$ and $\rho = 0.997 \text{ g/cm}^3$).

This chapter is organized as follows. In Section 3.2, I describe the potential models used to characterize the interactions between water molecules. In Section 3.3, the computation of the pair correlation functions computed using the SSOZ equation is presented. The theoretical predictions are then compared with pair correlation functions obtained through computer simulations and neutron scattering measurements.
Table 3.1: Characteristic Properties of a Water Molecule

<table>
<thead>
<tr>
<th></th>
<th>$r_{OH}$, Å</th>
<th>$\theta_{HOH}$, Degrees</th>
<th>$d$, D</th>
<th>$\alpha$, Å$^3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Expt.</td>
<td>0.95718$^a$</td>
<td>104.523$^a$</td>
<td>1.85$^b$</td>
<td>1.444$^a$</td>
</tr>
<tr>
<td>SPC$^c$</td>
<td>1</td>
<td>109.47</td>
<td>2.274</td>
<td>0</td>
</tr>
<tr>
<td>MCY$^d$</td>
<td>0.9572</td>
<td>104.5</td>
<td>2.19 (2.448)$^g$</td>
<td>0</td>
</tr>
<tr>
<td>SPC/E$^e$</td>
<td>1</td>
<td>109.47</td>
<td>2.351</td>
<td>0</td>
</tr>
<tr>
<td>TIP3P$^f$</td>
<td>0.9572</td>
<td>104.52</td>
<td>2.347</td>
<td>0</td>
</tr>
</tbody>
</table>

$^a$See Ref. 82. $^b$See Ref. 83. $^c$See Ref. 11. $^d$See Refs. 81 and 58. $^e$See Ref. 12. $^f$See Ref. 15. $^g$Value for the fitted 12-6-1 potential 3-site model, see text.

In Section 3.4, I present predictions of several thermodynamic properties of water using the SSOZ equation. In addition, a comparison of the theoretical predictions with results from computer simulations and experimental measurements is presented. Finally, in Section 3.5, I summarize the salient points of this chapter.

3.2 Potential Models for Water

The SPC,$^{11}$ MCY,$^{81}$ SPC/E,$^{12}$ and TIP3P$^{15}$ potentials were used to model water. Some characteristic properties associated with these four potential models are listed in Table 3.1, along with the corresponding experimentally determined$^{82,83}$ values for isolated water molecules. In Table 3.1, $r_{OH}$ is the oxygen-hydrogen bond length, $\theta_{HOH}$ is the hydrogen-oxygen-hydrogen bond angle, $d$ is the dipole moment, and $\alpha_{pol}$ is the polarizability. Note that the quoted experimental values correspond to water molecules in vacuo. The parameters, $z$, $A$, and $C$ (see Eq. (1.4) in Chapter 1) corresponding to these four potential models of water are listed in Table 3.2.

Note that the original MCY model has four interaction sites, that is, one on each of the three atoms in the water molecule and a fourth site located at the center of the molecule, directly below the oxygen atom. Furthermore, the site-site interaction potentials are complicated functions of the site-site separations. In view of these
Table 3.2: Interaction Parameters of the Potential Models for Water\textsuperscript{a}

<table>
<thead>
<tr>
<th></th>
<th>$z_H$</th>
<th>$A_{OO}$, kcal/mol Å\textsuperscript{12}</th>
<th>$A_{OH}$, kcal/mol Å\textsuperscript{12}</th>
<th>$A_{HH}$, kcal/mol Å\textsuperscript{12}</th>
<th>$C_{OO}$, kcal/mol Å\textsuperscript{6}</th>
</tr>
</thead>
<tbody>
<tr>
<td>SPC\textsuperscript{b}</td>
<td>0.41</td>
<td>629,400</td>
<td>0</td>
<td>0</td>
<td>625.5</td>
</tr>
<tr>
<td>MCY\textsuperscript{c}</td>
<td>0.43304</td>
<td>309,408</td>
<td>689.348</td>
<td>610.455</td>
<td>-262.566</td>
</tr>
<tr>
<td>SPC/Ed\textsuperscript{d}</td>
<td>0.4238</td>
<td>629,400</td>
<td>0</td>
<td>0</td>
<td>625.5</td>
</tr>
<tr>
<td>TIP3Pe\textsuperscript{e}</td>
<td>0.417</td>
<td>582,000</td>
<td>0</td>
<td>0</td>
<td>595.0</td>
</tr>
</tbody>
</table>

\textsuperscript{a} $C_{OH}$ and $C_{HH}$ are equal to zero. \textsuperscript{b}See Ref. 11. \textsuperscript{c}See Ref. 58. \textsuperscript{d}See Ref. 12. \textsuperscript{e}See Ref. 15.

complexities, Pettitt and Rossky have fitted\textsuperscript{58} the MCY energy surface to a three-site model, thus obtaining a modified MCY model which is similar in mathematical structure to the other three potential models for water. This is the form of the MCY model which I have used.

In each of the potential models for water, with the exception of the MCY model, there is no oxygen-hydrogen repulsion but only a Coulombic attraction ($A_{OH} = 0$, see Table 3.2). This will lead to a "catastrophic overlap" of the oxygen and hydrogen sites of different water molecules. This phenomenon is not observed in simulation studies because there is a large energy barrier of about $10^6$ kcal/mol that must be overcome in order to bring together the oxygen and hydrogen sites of two different water molecules. The simulation is set up initially such that all the water molecules are located sufficiently far away from each other, and are therefore outside this "collapse barrier". Since the typical kinetic energy of a simulated water molecule at room temperature is about 1 kcal/mol, the region of phase space where the oxygen and hydrogen sites overlap has a low probability of being sampled within a limited-time simulation. Note, however, that if a simulation were started with the water molecules located sufficiently close to each other such that they were inside the energy barrier, then this collapse would be observed. In the case of the SSOZ equation, which in effect samples all of phase space, this collapse of the water molecules would occur in the absence of an oxygen-hydrogen repulsion. To prevent this, I have added a $1/r^{12}$
repulsive term having a magnitude, $A_{OH}$, chosen so as to reproduce the experimentally observed value of $U^{**}$. Specifically, I find that for the SPC model, $A_{OH} = 900 \text{ Å}^{12} \text{ kcal/mol}$, for the SPC/E model, $A_{OH} = 800 \text{ Å}^{12} \text{ kcal/mol}$, and for the TIP3P model, $A_{OH} = 1030 \text{ Å}^{12} \text{ kcal/mol}$. These values are of the same order of magnitude as the value chosen by Pettitt and Rossky (AOH = 226 Å$^{12}$ kcal/mol).

### 3.3 Structural Properties of Water

I have solved the SSOZ equations with the HNC closure and SMSA closure for the SPC, MCY, SPC/E, and TIP3P potential models for water (see Tables 3.1 and 3.2 for a listing of the appropriate potential parameters) at ambient conditions ($T = 25^\circ \text{C}$, and $\rho = 0.997 \text{ g/cm}^3$). I have utilized the HNC and SMSA closures because they have been found to work well for simple fluids characterized by long-ranged interactions.

Plots of the site-site pair correlation functions, $g_{OO}(r)$, $g_{HH}(r)$, and $g_{OH}(r)$, for the SPC potential model for water are presented in Figures 3-1–3-3. The solid lines are the predictions of the SSOZ equation with the HNC closure. The dashed lines are the results from Monte Carlo simulations performed by Jorgensen et al. The dotted lines are the $g(r)$'s deduced from neutron scattering measurements performed by Soper and Phillips. I have found that the SMSA closure predicts a negative region in both the hydrogen-hydrogen and oxygen-hydrogen pair correlation functions. This is unphysical, and therefore, I do not report the predictions based on this closure. I have also obtained the pair correlation functions for the MCY, SPC/E, and TIP3P models for water. The $g(r)$'s for these water models were found to be very similar to those for the SPC model, and therefore, are also not reported.

The agreement between the $g_{OO}(r)$ predicted by the SSOZ-HNC equation (full line) and that predicted by the simulation data (dashed line) is rather poor; see Figure 3-1. The position of the first peak is approximately correct, but the positions of the other peaks are shifted. There is an indication of a peak in the predictions of the SSOZ-HNC equation at the location of the second peak in the experimental and simulated $g_{OO}(r)$'s. Overall, the predicted structure is reminiscent to that of a
Figure 3-1: Oxygen-oxygen pair correlation functions, $g_{oo}(r)$, as a function of the site-site separation, $r$, for SPC water at 25°C and 0.997 g/cm$^3$: (i) predicted using the SSOZ equation with the HNC closure (solid line), (ii) predicted from Monte Carlo simulations of Jorgensen et al.$^{15}$ (dashed line), and (iii) deduced from neutron-scattering measurements of Soper and Phillips$^{84}$ (dotted line).
Figure 3-2: Hydrogen-hydrogen pair correlation functions, $g_{HH}(r)$, as a function of the site-site separation, $r$, for SPC water at 25°C and 0.997 g/cm$^3$. The notation is the same as that in Figure 3-1.

Figure 3-3: Oxygen-hydrogen pair correlation functions, $g_{OH}(r)$, as a function of the site-site separation, $r$, for SPC water at 25°C and 0.997 g/cm$^3$. The notation is the same as that in Figure 3-1.
Lennard-Jones fluid, a hexagonally closed-packed structure. Recall, however, that water is actually tetrahedral in structure. The agreement of the predicted $g_{HH}(r)$ and $g_{OH}(r)$ with the simulation and experimental results is fair; see Figures 3-2 and 3-3. The peaks which are shown for the HH and OH $g(r)$'s are due to correlations between sites located on adjacent water molecules, that is, they reflect interactions between a water molecule and its first coordination shell. It appears, therefore, that correlations between water molecules at short range are captured fairly well by the SSOZ-HNC equation.

The incorrect prediction of the “long-ranged structure” (see Figure 3-1) is possibly due to the known defects of the SSOZ equation, in particular, the inability to predict nontrivial angular correlation factors. These angular correlations are important in water because of its highly directional hydrogen-bonded structure.

3.4 Bulk Thermodynamic Properties of Water

Table 3.3 lists the predicted values of the residual internal energy, $U^{res}$, the residual Helmholtz free energy, $A^{res}$, the residual chemical potential, $\mu^{res}$, the isothermal compressibility, $\kappa_T$, and the heat capacity at constant volume, $C_V$, for water at 25°C and 0.997 g/cm$^3$ using the SSOZ-HNC equation for the various potential models for water. Also listed are the values of these properties obtained from experimental measurements$^{85, 86, 87, 1}$ and computer simulations.$^{88, 89, 90, 91, 92, 93}$ In Table 3.3, the first column contains the experimentally measured values of each property. Each of the four remaining columns corresponds to predictions of these properties for various potential models for water. For each property, the bolded entry in each cell corresponds to my predictions based on the SSOZ-HNC equation, and the remaining entries correspond to reported values from various computer simulations.

In the four potential models for water described above, the molecules cannot alter their dipole moments and consequently $\alpha_{pol} = 0$ (see Table 3.1). From Table 3.1, one can also see that each of the dipole moments of the model water molecules is larger that the actual (experimental) dipole moment of an isolated water molecule.
Table 3.3: Predictions (Bolded Entry in Each Cell) of the SSOZ-HNC Equation for Water at 25°C and 0.997 g/cm³, and Comparison with Computer Simulations and Experimental Values

<table>
<thead>
<tr>
<th></th>
<th>Expt.</th>
<th>MCY</th>
<th>SPC</th>
<th>SPC/E</th>
<th>TIP3P</th>
</tr>
</thead>
<tbody>
<tr>
<td>$-U^{res}$, kcal/mol</td>
<td>9.90	extsuperscript{a}</td>
<td>8.80</td>
<td>9.90</td>
<td>9.90 (11.1)</td>
<td>9.91</td>
</tr>
<tr>
<td></td>
<td></td>
<td>8.58,	extsuperscript{e} 8.51	extsuperscript{f}</td>
<td>10.18,	extsuperscript{g} 9.01,	extsuperscript{i}</td>
<td></td>
<td>9.86	extsuperscript{g}</td>
</tr>
<tr>
<td>$-A^{res}$, kcal/mol</td>
<td>5.74	extsuperscript{a}</td>
<td>3.74</td>
<td>5.15</td>
<td>4.93 (6.18)</td>
<td>5.22</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4.31	extsuperscript{e}</td>
<td>5.8	extsuperscript{e}</td>
<td>5.5 (6.4)	extsuperscript{e}</td>
<td>5.4	extsuperscript{e}</td>
</tr>
<tr>
<td>$-\mu^{res}$, kcal/mol</td>
<td>6.324	extsuperscript{b}</td>
<td>2.03</td>
<td>2.50</td>
<td>2.52 (3.77)</td>
<td>2.70</td>
</tr>
<tr>
<td>$10^6\kappa_T$, atm	extsuperscript{-1}</td>
<td>45.2472	extsuperscript{c}</td>
<td>30.3</td>
<td>55.6</td>
<td>57.1</td>
<td>58.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>53	extsuperscript{f}</td>
<td>27	extsuperscript{g}</td>
<td>41.41	extsuperscript{h}</td>
<td>18	extsuperscript{g}</td>
</tr>
<tr>
<td>$C_V$, cal g	extsuperscript{-1} K	extsuperscript{-1}</td>
<td>0.9899	extsuperscript{d}</td>
<td>0.932</td>
<td>0.889</td>
<td>0.911</td>
<td>0.859</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.999	extsuperscript{f}</td>
<td>1.03,	extsuperscript{i} 0.909	extsuperscript{i}</td>
<td>1.14	extsuperscript{i}</td>
<td></td>
</tr>
</tbody>
</table>

	extsuperscript{a}See Ref. 86. 	extsuperscript{b}See Ref. 87. 	extsuperscript{c}See Ref. 85. 	extsuperscript{d}See Ref. 1. 	extsuperscript{e}NVT Monte Carlo simulation with $T = 25^\circ$C and $\rho = 1$ g/cm³. See Ref. 88. 	extsuperscript{f}NVT Monte Carlo simulation with $T = 25^\circ$C and $\rho = 0.997$ g/cm³. See Ref. 90. 	extsuperscript{g}NPT Monte Carlo simulation with $p = 1$ atm and $T = 25^\circ$C. See Ref. 15. 	extsuperscript{h}NPT molecular dynamics simulation with $p = 1$ atm and $T = 25^\circ$C. See Ref. 94. 	extsuperscript{i}See Ref. 92. 	extsuperscript{j}See Ref. 93. For an explanation of the entries in parentheses for the SPC/E model, see text.
For the SPC/E model, Berendsen et al. attribute this to the polarization of a water molecule by its environment. Using simple arguments, they find that the energy associated with polarizing a water molecule, $E_{\text{pol}}$, is given by

$$E_{\text{pol}} = \frac{(d - d^0)^2}{2\alpha_{\text{pol}}}$$

(3.1)

where $d$ is the dipole moment of a model water molecule, $d^0$ is the dipole moment of an isolated water molecule, and $\alpha_{\text{pol}}$ is its polarizability, both taken to be equal to their experimental values in vacuo. This offers a method to correct for the polarizability of the SPC/E water molecules. In Table 3.3, the bolded entries in parentheses for the SPC/E model correspond to values predicted without the polarization correction, $E_{\text{pol}}$.

As explained earlier, in the case of the SPC, SPC/E, and TIP3P water potential models, a repulsive term was added to prevent the overlap of oxygen and hydrogen sites. The magnitude of this repulsive term was estimated by requiring that the predicted value of $U_{\text{rea}}$ be equal to the experimentally measured one. This is clearly represented in the bolded entry values of $U_{\text{rea}}$ ($-9.90 \text{ kcal/mol}$) for these three water models. Note, however, that the prediction of $U_{\text{rea}}$ for the MCY water model ($-8.80 \text{ kcal/mol}$) is an independent one.

The major difficulty in simulating water is in handling the long-ranged interactions. The variation in the reported simulation valued presented in Table 3.3 is due mainly to the different ways in which these long-ranged interactions are treated. For example, the values $-9.01 \text{ kcal/mol}$ and $-10.8 \text{ kcal/mol}$ for $U_{\text{rea}}$ of SPC water are a result of employing two different smoothing functions to truncate the interaction potential. Using Ewald summation yields, $U_{\text{rea}} = -9.82 \text{ kcal/mol}$. This variation in the simulation values should be kept in mind when comparing the results of the simulations with the predictions of the SSOZ equation.

Overall, an examination of Table 3.3 indicates fair agreement between the predictions of the SSOZ-HNC equation and the experimental results, with the exception of $\mu_{\text{rea}}$. The fact that the prediction for $A_{\text{rea}}$ is good and that $\mu = A/N + p$ for a one-
component system (where $\mu$ is the chemical potential, $A$ is the Helmholtz free energy, $N$ is the number of moles, and $p$ is the pressure) suggests that the poor prediction of the residual chemical potential may be related to the fact that the pressure is very sensitive to the approximations make in liquid-state theory. The residual Helmholtz free energy was computed using Eq. (2.20), as well as by numerical integration as specified by Eq. (2.19) (see Chapter 2). By using an eight-point Gauss-Laguerre quadrature, the two methods yielded predictions within 1% of each other. This is a reflection of the accuracy of our numerical methods. Mezei et al. computed $A^{\text{res}}$ for MCY water by performing a Monte Carlo simulation at each value of the coupling parameter, $\zeta$, to obtain $<\mathcal{U}_{\text{res}}>$, and subsequently utilized an eight-point Gauss-Legendre quadrature to perform the integration with respect to the coupling constant (see Eq. (2.19)). When I used an eight-point Gauss-Legendre quadrature, I obtained $A^{\text{res}} = -4.46$ kcal/mol, close to their value of $-4.31$ kcal/mol. However, I found that if I increased the number of quadrature points, the computed value of $A^{\text{res}}$ slowly increased to $-3.74$ kcal/mol, the value reported in Table 3.3. Therefore, I feel that the results of Mezei et al. would be closer to my results if they had used more quadrature points.

3.5 Concluding Remarks

The SSOZ equation was solved using the HNC and SMSA closures for several different potential models for water at ambient conditions. A comparison of the predictions of structural and thermodynamic properties was made with results of computer simulations and experimental measurements. The SSOZ-HNC equation seems to capture the short-ranged correlations in water properly. However, the distribution of water molecules in the second coordination shell and beyond, as predicted by the SSOZ-HNC equation, was found to deviate significantly from that found experimentally (see Figure 3-1). The predictions for the pressure were found to be rather poor. However, in general, the predictions for the other thermodynamic properties were found to be reasonable (see Table 3.3).
In the next chapter, I will apply the SSOZ equation to hydrocarbons at infinite dilution in water to predict structural and thermodynamic properties of these complex fluids. Since water-hydrocarbon interactions are short-ranged, the hydrocarbon molecules are not expected to interact significantly with water molecules beyond the first coordination shell. Accordingly, for these systems, the inability of the SSOZ equation to properly predict the long-range correlations in water discussed in this chapter should not pose a major problem.
Chapter 4

The Site-Site Ornstein-Zernike Equation: Application to Hydrocarbons in Water

4.1 Introduction and Overview

The quantitative prediction of structural and bulk thermodynamic properties of hydrocarbon-water systems represents a challenging problem in liquid-state theory. These systems are particularly interesting because they are the simplest to exhibit the hydrophobic effect. In the previous chapter, I computed the structural and bulk thermodynamic properties of pure water using the SSOZ equation. The central goal of this chapter is to examine the ability of various closure relations, when combined with the SSOZ equation, to provide accurate quantitative predictions of structural and bulk thermodynamic properties of hydrocarbons in water from knowledge of their interaction potential only.

The application of the SSOZ equation to these systems poses several interesting challenges. First, one needs to determine an appropriate closure relation that can be used in conjunction with the SSOZ equation to yield accurate quantitative predictions of the structural and bulk thermodynamic properties of these systems. In this respect, it is noteworthy, that previous attempts to predict the bulk thermodynamic properties
of interaction site fluids have utilized almost exclusively the hypernetted-chain (HNC) closure (see Section 2.1.1). For this reason, I will also examine two recently developed closures: (i) the Martynov-Sarkisov (MaS) closure, and (ii) the Ballone-Pastore-Galli-Gazzillo (BPGG) closure. Specifically, I will compare the predictions of the SSOZ equation with these two new closures against results of computer simulations and experimental measurements.

A second challenge involves dealing with molecules possessing a large number of interaction sites. To deal with this issue, I will test the equivalent-site approximation (see Section 2.3) developed by Curro and Schweizer. In addition, when treating larger molecules, one needs to account for their flexibility, since the conformations of such molecules depend not only on their intramolecular interaction potential, but also on their environment. In this respect, I will present a simple way to deal with this issue as well as to predict the average conformations of various hydrocarbons in vacuo and in water.

The remainder of this chapter is organized as follows. In Section 4.2, I will describe the potential models for the hydrocarbons considered. Sections 4.3, 4.4, and 4.5 describe the application of the theory to methane, ethane, and propane in water, respectively. Specifically, I will present predictions of the SSOZ equation with various closures for the structural and thermodynamic properties of these systems, and compare them with results from computer simulations and experimental measurements. In Section 4.6, I will consider the challenging problem of chain flexibility for longer hydrocarbon chains, from n-butane to n-heptane, and will predict the average conformations of these molecules in vacuo and in water. Finally, in Section 4.7, I will summarize the salient features of this chapter.

4.2 Potential Models for Hydrocarbons

In the calculations of the structural and bulk thermodynamic properties of hydrocarbons in water, I have used the simple point charge (SPC) potential model for water (see Section 3.2 for details).
Table 4.1: Interaction Parameters of Various Hydrocarbons

<table>
<thead>
<tr>
<th>Molecule</th>
<th>( z_{aM} )</th>
<th>( 10^{-3} A_{aM'\alpha'M'} ) kcal mol(^{-1}) Å(^{12} )</th>
<th>( C_{aM'\alpha'M'} ) kcal mol(^{-1}) Å(^6 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH(_4)</td>
<td>0</td>
<td>8529</td>
<td>3167</td>
</tr>
<tr>
<td>CH(_3)</td>
<td>0</td>
<td>6935</td>
<td>2396</td>
</tr>
<tr>
<td>CH(_2)</td>
<td>0</td>
<td>5935</td>
<td>1674</td>
</tr>
</tbody>
</table>

\( ^a \)See Ref. 8.

Table 4.2: Coefficients for Intramolecular Rotational Potential Functions

<table>
<thead>
<tr>
<th>Molecule</th>
<th>( V_0 )</th>
<th>( V_1 )</th>
<th>( V_2 )</th>
<th>( V_3 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-Butane</td>
<td>0.0</td>
<td>1.522</td>
<td>-0.315</td>
<td>3.207</td>
</tr>
<tr>
<td>Other n-Alkanes</td>
<td>0.0</td>
<td>1.411</td>
<td>-0.271</td>
<td>3.145</td>
</tr>
</tbody>
</table>

\( ^a \)Units for the various \( V \)'s are in kcal/mol. See Ref. 8.

To model the hydrocarbons, I have utilized the optimized potentials for liquid simulation (OPLS) developed\(^8\) by Jorgensen et al. The interaction parameters \( z, A, \) and \( C \) (see Eq. (1.4)) associated with this model for CH\(_4\), CH\(_3\), and CH\(_2\) are listed in Table 4.1. For the OPLS, the carbon-carbon bond length is 1.53 Å, and the CH\(_3\)-CH\(_2\)-CH\(_3\) bond angle is 112°. The coefficients for the barrier to rotating the dihedral angles (see Eq. (1.5)) are listed in Table 4.2.

4.3 Methane in Water

The SSOZ equation was solved for methane at infinite dilution in water with the HNC, PY, RY, MaS, and BPGG closures for the methane-water correlation functions and the HNC closure for the water-water pair correlation functions (for details on this closure, see Section 2.1.1). The CH\(_4\)-O pair correlation functions are shown in Figure 4-1a, and the CH\(_4\)-H pair correlation functions are shown in Figure 4-1b. The solid lines are the predictions of the SSOZ equation with the HNC closure, the dashed...
Figure 4-1: Methane-water pair correlation functions (a, \( \text{CH}_4\cdot\text{O} \); b, \( \text{CH}_4\cdot\text{H} \)) as a function of \( r \) for methane at infinite dilution in water at 25°C and 0.997 g/cm\(^3\): (i) SSOZ equation with HNC closure (solid line), (ii) SSOZ equation with MaS closure (dashed line), and (iii) SSOZ equation with BPGG closure, \( s = 1.79 \) (dotted line).

lines are the predictions of the SSOZ equation with the MaS closure, and the dotted lines are the predictions of the SSOZ equation with the BPGG closure for \( s = 1.79 \). This \( s \) value was chosen such that the predicted \( \mu_{M}^{\text{ex}} \) fits the experimental value at \( T = 25^\circ\text{C} \) and \( \rho = 0.997 \text{ g/cm}^3 \). Note that I have found that the SSOZ equation with the RY and PY closures predicts a negative region in the \( \text{CH}_4\cdot\text{H} \) pair correlation function. This is unphysical and reflects the well-known limitations of these closures when describing systems exhibiting strong attractive interactions. Accordingly, I have not reported the results for these two closures. Note that I was unable to find methane-water pair correlation functions from simulations that utilized potentials similar to mine. In addition, to the best of my knowledge, no scattering experiments have been performed on methane-water systems. Consequently, no comparison of the theoretical predictions shown in Figure 4-1 could be made.

Predictions for the enthalpy of solution, \( \Delta H_M \) (see Eq. (2.21)), the residual chemical potential, \( \mu_{M}^{\text{ex}} \) (see Eq. (2.22)), the solute partial molar volume, \( V_u \) (see Eq. (2.17)), the solute-solvent interaction energy, \( \epsilon_{uv} \) (see Eq. (2.23)), and the hydration number, \( N_{\text{hyd}} \), of methane in water at \( T = 25^\circ\text{C} \) and \( \rho = 0.997 \text{ g/cm}^3 \) are listed in Table 4.3. Note that following Jorgensen et al., the hydration number, \( N_{\text{hyd}} \), of methane is taken to be the number of water oxygen sites within 5.35 Å of the center of a methane molecule. In Table 4.3, the predicted values are compared with results
Table 4.3: OPLS for Methane at Infinite Dilution in SPC Water at $T = 25^\circ C$ and $\rho = 0.997 \text{ g/cm}^3$

<table>
<thead>
<tr>
<th></th>
<th>$\Delta H_M$, kcal/mol</th>
<th>$\mu_M^{\text{res}}$, kcal/mol</th>
<th>$V_M$, $\text{Å}^3$</th>
<th>$\epsilon_{uv}^M$, kcal/mol</th>
<th>$N_{hyd}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Expt.</td>
<td>-3.30,$^a$ -3.15$^f$</td>
<td>2.01$^a$</td>
<td>57.3$^b$ 61.44$^c$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Comp. Simul.</td>
<td>-5.02$^d$</td>
<td>2.3$^e$</td>
<td></td>
<td>-2.89$^d$</td>
<td>19,$^g$ 20.3$^d$</td>
</tr>
<tr>
<td>HNC</td>
<td>1.56</td>
<td>8.72 (8.71)</td>
<td>53.6</td>
<td>-1.75</td>
<td>19.0</td>
</tr>
<tr>
<td>MaS</td>
<td>-2.27</td>
<td>1.21 (4.64)</td>
<td>64.2</td>
<td>-2.60</td>
<td>18.7</td>
</tr>
<tr>
<td>BPGG ($s = 1.79$)</td>
<td>-1.98</td>
<td>2.02 (5.15)</td>
<td>63.1</td>
<td>-2.50</td>
<td>18.7</td>
</tr>
</tbody>
</table>

$^a$See Ref. 96. $^b$See Ref. 97. $^c$See Ref. 98. $^d$See Ref. 95. $^e$See Ref. 100. $^f$See Ref. 99. $^g$See Ref. 101.

from experiments$^{96, 97, 98, 99}$ and computer simulations.$^{95, 100, 101}$ To demonstrate the path dependence of $\mu_M^{\text{res}}$, I calculated this quantity using two different integration paths: (1) $h(r; \zeta') = \zeta' h(r)$, and (2) $u(r; \zeta') = \zeta' u(r)$. The first entry in Table 4.3 for $\mu_M^{\text{res}}$ is the prediction using the first integration path, and the entry in parentheses is the prediction using the second integration path. In order to calculate $\mu_M^{\text{res}}$ using path 1, the SSOZ equation was solved at full coupling, and then Eq. (2.24) with Eq. (2.25) was utilized. Because no such formula exists for path 2, the integral with respect to $\zeta'$ had to be performed numerically. This involved solving the SSOZ equation at each value of $\zeta'$, determining $< \epsilon_{uv}^M >_{\zeta'}$, and then using numerical quadrature to compute the integral. Therefore, the calculations using path 1 were much less time consuming that those using path 2.

As can be seen from Table 4.3, the HNC closure shows no dependence on the path of integration, while for the MaS and BPGG closures the first path yields a lower value for $\mu_M^{\text{res}}$ than the second path. It is noteworthy that the first path, which is the more computationally efficient one, is in better agreement with the experimental and computer simulation values. If the closure relation were exact, the predicted value of $\mu_M^{\text{res}}$ should be independent of the integration path.$^{37}$ However, because of the approximations in the theory, this dependency arises. This path dependence is
analogous to the discrepancy which arises in the calculation of the pressure using the compressibility and the virial routes with an approximate closure.

In Figure 4-2, I present the predicted temperature variation of the residual chemical potential of methane at infinite dilution in water over the range 5 - 80°C. To generate these predictions, I utilized the OPLS for methane and the SPC potential for water. The HNC closure was used for the water-water pair correlation functions, and the variation of the density of water with temperature was taken from the data of Kell. The solid line is the prediction of the SSOZ equation with the BPGG closure with \( s = 1.79 \), and the dashed line is the prediction of the SSOZ equation with the MaS closure. The value of the free parameter, \( s \), of the BPGG closure was chosen to fit the experimental residual chemical potential at \( T = 25^\circ C \) and \( \rho = 0.997 \text{ g/cm}^3 \). The symbols correspond to experimentally measured values. As can be seen from Figure 4-2, the predictions of the BPGG closure are in very good agreement with the experimental data. The MaS closure shows the same trend as the BPGG closure but is shifted downward. It is noteworthy that, although not shown in the figure, the SSOZ-HNC equation grossly overpredicts (by more than 300%) the values of the residual chemical potential.

The same calculations were also repeated for methane in water using the TIP3P model for water (see Table 3.2). The difference in the methane-water correlation functions using the SPC and the TIP3P potential models for water is too small to be seen. In addition, I have found that the choice of water potential model does not have a significant effect on the predictions of the bulk thermodynamic properties listed in Table 4.3.

4.4 Ethane in Water

I have also solved the SSOZ equation with the HNC, PY, RY, MaS, and BPGG closures for ethane at infinite dilution in water. The CH\(_3\)-O pair correlation functions are shown in Figure 4-3a, and the CH\(_3\)-H pair correlation functions are shown in Figure 4-3b. The solid lines are the predictions of the SSOZ-HNC equation, the
Figure 4-2: Residual chemical potential of methane at infinite dilution in water as a function of temperature: (i) predictions of the SSOZ equation with the MaS closure (dashed line), (ii) predictions of the SSOZ equation with the BPGG closure, $s = 1.79$ (solid line), (iii) data of Morrison and Billett $^{94}$ (circles), (iv) data of Wen and Hung $^{102}$ (squares), and (v) data of Yaacobi and Ben-Naim $^{103}$ (triangles).
Figure 4-3: Ethane-water pair correlation functions (a, CH₃-O; b, CH₃-H) as a function of \( r \) for ethane at infinite dilution in water at 25°C and 0.997 g/cm³: (i) SSOZ equation with HNC closure (solid line), (ii) SSOZ equation with MaS closure (dashed line), and (iii) SSOZ equation with BPGG closure, \( s = 1.79 \) (dotted line). Note that the predictions of the MaS and BPGG closures are almost identical.

dashed lines are the predictions of the SSOZ-MaS equation, and the dotted lines are the predictions of the SSOZ-BPGG equation with \( s = 1.96 \). The parameter, \( s \), was chosen such that the predicted residual chemical potential is equal to the experimentally measure value at ambient conditions. Note that the predictions of the MaS closure (dashed lines) are almost identical to those of the BPGG closure (dotted lines). As for methane, the RY and PY closures yield negative regions in the CH₃-H correlation functions (for the same reason explained earlier), and therefore the results for these closures are not presented. I could not find pair correlation functions from either simulations or scattering experiments to compare with my predictions. Various predicted thermodynamic properties for ethane in water are listed in Table 4.4, along with the results available from experimental measurements\(^{96,98,99}\) and computer simulations.\(^{95}\)

The predicted temperature variation of the residual chemical potential of ethane at infinite dilution in water over the range 5-80°C is presented in Figure 4-4. As with methane in water, the predictions of the BPGG closure (with \( s = 1.96 \)) are in very good agreement with the experimental data for temperatures below about 50°C. However, at the higher temperatures (\( T > 50°C \)), the agreement begins to worsen. The dashed line is the prediction of the SSOZ equation with the MaS closure, and,
Table 4.4: OPLS for Ethane at Infinite Dilution in SPC Water at $T = 25^\circ C$ and $\rho = 0.997$ g/cm$^3$

<table>
<thead>
<tr>
<th></th>
<th>$\Delta H_M$ kcal/mol</th>
<th>$\mu_M^{\infty}$ kcal/mol</th>
<th>$V_M$ Å$^3$</th>
<th>$\tau_{uv}^M$ kcal/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Expt.</td>
<td>-4.72$^a$, -4.67$^d$</td>
<td>1.84$^a$</td>
<td>87.8$^b$</td>
<td></td>
</tr>
<tr>
<td>Comp. Simul.</td>
<td>-20$^c$</td>
<td></td>
<td></td>
<td>-4.80$^c$</td>
</tr>
<tr>
<td>HNC</td>
<td>1.33</td>
<td>12.3 (12.3)</td>
<td>69.8</td>
<td>-3.49</td>
</tr>
<tr>
<td>MaS</td>
<td>-4.19</td>
<td>1.62 (6.96)</td>
<td>82.0</td>
<td>-4.49</td>
</tr>
<tr>
<td>BPGG ($s = 1.96$)</td>
<td>-4.02</td>
<td>1.83 (7.08)</td>
<td>81.6</td>
<td>-4.47</td>
</tr>
</tbody>
</table>

$^a$See Ref. 96. $^b$See Ref. 98. $^c$See Ref. 95. $^d$See Ref. 99.

as in the case of methane, it is displaced downward from that of the BPGG closure. As with methane, the SSOZ-HNC equation *grossly overpredicts* (by more than 600%) the values of the residual chemical potential.

### 4.5 Propane in Water

The SSOZ equation with the HNC, PY, RY, MaS, and BPGG closures were also solved to predict the propane-water pair correlation functions. The CH$_2$-O, CH$_3$-O, CH$_2$-H, and CH$_3$-H pair correlation functions are shown in parts a-d of Figure 4-5. The solid lines are the predictions of the HNC closure, the dashed lines are the predictions of the MaS closure, and the dotted lines are the predictions of the BPGG closure with $s = 2.05$. As before, the parameter, $s$, was chosen such that the predicted residual chemical potential is equal the the experimentally measured value at ambient conditions. Note that the predictions of the MaS closure (dashed lines) are almost identical to those of the BPGG closure (dotted lines). The results of the RY and PY closures are not reported because, as explained earlier, they yield negative regions in the CH$_2$-H and CH$_3$-H pair correlation functions.

Ichiye and Chandler solved$^{61}$ the SSOZ equation with the HNC closure for propane at infinite dilution in water and also performed molecular dynamics simulations to compare their predictions. In their work, they utilized$^{61}$ potentials which are different.
Figure 4-4: Residual chemical potential of ethane at infinite dilution in water as a function of temperature: (i) predictions of the SSOZ equation with the MaS closure (dashed line), (ii) predictions of the SSOZ equation with the BPGG closure, \( s = 1.96 \) (solid line), (iii) data of Morrison and Billett\(^94\) (circles), (iv) data of Wen and Hung\(^102\) (squares), and (v) data of Yaacobi and Ben-Naim\(^103\) (triangles).
Figure 4-5: Propane-water pair correlation functions (a, CH₂-O; b, CH₃-O; c, CH₂-H; d, CH₃-H) as a function of $r$ for propane at infinite dilution in water at 25°C and 0.997 g/cm³: (i) SSOZ equation with HNC closure (solid line), (ii) SSOZ equation with MaS closure (dashed line), and (iii) SSOZ equation with BPGG closure, $s = 1.79$ (dotted line). Note that the predictions of the MaS and BPGG closures are almost identical.
Figure 4-6: Propane-water pair correlation functions (CH$_2$-O) as a function of $r$ for propane at infinite dilution in water at 25°C and 0.997 g/cm$^3$ using the potential model of Ichiye and Chandler: (i) SSOZ equation with HNC closure (solid line), (ii) SSOZ equation with MaS closure (dashed line), and (iii) molecular dynamics simulation of Ichiye and Chandler$^{61}$ (dotted line).

from mine. Accordingly, to compare my predictions with their simulation work, I solved the SSOZ equation with the MaS closure for propane in water using the same potential models$^{61}$ that they utilized. The predictions of the MaS and the HNC closures for all the propane-water correlation functions are very similar, with the MaS closure yielding slightly better agreement with the molecular dynamics simulation data. As an illustration, in Figure 4-6, I show a comparison of the predicted CH$_2$-O pair correlation functions with the molecular dynamics simulation data. The solid lines are the predictions of the HNC closure, the dashed lines are the predictions of the MaS closure, and the dotted lines are the molecular dynamics simulation results. The other propane-water $g(r)$'s exhibit similar trends and are therefore not reported.

Predictions for $\Delta H_M$, $\mu_M^{ru}$, $\bar{V}_M$, and $\epsilon_{uu}^M$ are listed in Table 4.5 along with the results from experimental measurements$^{96, 98, 99}$ and computer simulations.$^{95}$ Figure 4-7 shows the predicted temperature variation of the residual chemical potential of
Table 4.5: OPLS for Propane at Infinite Dilution in SPC Water at $T = 25^\circ C$ and $
abla = 0.997 g/cm^3$

<table>
<thead>
<tr>
<th></th>
<th>$\Delta H_M$</th>
<th>$\mu_{M}^{res}$</th>
<th>$V_M$</th>
<th>$\xi_{uu}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>kcal/mol</td>
<td>kcal/mol</td>
<td>Å³</td>
<td>kcal/mol</td>
</tr>
<tr>
<td>Expt.</td>
<td>-5.38, a</td>
<td>-5.56 d</td>
<td>1.96a</td>
<td>117.4 b</td>
</tr>
<tr>
<td>Comp. Simul.</td>
<td>13 c</td>
<td></td>
<td></td>
<td>-6.60 c</td>
</tr>
<tr>
<td>HNC</td>
<td>2.20</td>
<td>17.5 (17.4)</td>
<td>92.7</td>
<td>-4.46</td>
</tr>
<tr>
<td>MaS</td>
<td>-5.41</td>
<td>2.35 (10.2)</td>
<td>107.3</td>
<td>-5.76</td>
</tr>
<tr>
<td>BPGG ($s = 2.05$)</td>
<td>-5.61</td>
<td>1.98 (10.0)</td>
<td>107.8</td>
<td>-5.79</td>
</tr>
</tbody>
</table>

aSee Ref. 96. bSee Ref. 98. cSee Ref. 95. dSee Ref. 99.

Propane at infinite dilution in water over the range 5-80°C. The agreement between the predictions of the BPGG closure (with $s = 2.05$) and the experimental values is extremely good at the lower temperatures ($T < 40^\circ C$); however, the predictions worsen at the higher temperatures ($T > 40^\circ C$). Once again, the MaS predictions show the same variation with temperature as that of the BPGG closure, although it is shifted upward. As with methane and ethane, the SSOZ-HNC equation grossly overpredicts (by more that 800%) the values of the residual chemical potential.

The propane molecule has two nonequivalent interaction sites. I have analyzed the effect of the equivalent-site approximation (ESA) by solving the SSOZ equation with the MaS closure for three different scenarios. The first scenario treats the propane molecule as having two distinct sites using OPLS interaction parameters. The second scenario treats a propane molecule as having two distinct sites, but with the CH$_3$ groups treated as CH$_2$ groups. The third scenario employs the ESA, which treats the molecule as having sites which interact as CH$_2$ groups and are all equivalent. As before, the OPLS were used to model propane, and the SPC potential was utilized to model water.

The site-site pair correlation functions for each of these systems are shown in parts a and b of Figure 4-8. In each figure, the dashed lines represent the site-site pair correlation functions for the first scenario, the dotted lines are for the second scenario, and the solid lines are the results of the ESA (third scenario). The thin
Figure 4.7: Residual chemical potential of propane at infinite dilution in water as a function of temperature: (i) predictions of the SSOZ equation with the MaS closure (dashed line), (ii) predictions of the SSOZ equation with the BPYY closure, $s = 2.05$ (solid line), (iii) data of Morrison and Billett94 (circles), and (iv) data of Wen and Hung102 (squares).
Figure 4-8: Application of the equivalent-site approximation (ESA) to propane in water. (a) Propane-water oxygen pair correlation functions: (i) CH₂-O, full potential (thin dashed line); (ii) CH₃-O, full potential (thick dashed line); (iii) CH₂-O, modified potential (thin dotted line); (iv) CH₃-O, modified potential (thick dotted line); and (v) CHₙ-O, equivalent-site approximation (solid line). (b) Propane-water hydrogen pair correlation functions: (i) CH₂-H, full potential (thin dashed line); (ii) CH₃-H, full potential (thick dashed line); (iii) CH₂-H, modified potential (thin dotted line); (iv) CH₃-H, modified potential (thick dotted line); and (v) CHₙ-H, equivalent-site approximation (solid line).

Table 4.6: Propane in SPC Water (MaS Closure) at T = 25°C and ρ = 0.997 g/cm³: A Test of the Equivalent-Site Approximation

<table>
<thead>
<tr>
<th>Scenario</th>
<th>μ^{r^\infty}_M</th>
<th>V_M, Å³</th>
<th>ε^{M}_uv, kcal/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Scenario 1</td>
<td>2.35</td>
<td>107.3</td>
<td>-5.76</td>
</tr>
<tr>
<td>Scenario 2</td>
<td>3.32</td>
<td>108.1</td>
<td>-4.64</td>
</tr>
<tr>
<td>Scenario 3 (ESA)</td>
<td>3.42</td>
<td>104.9</td>
<td>-4.69</td>
</tr>
</tbody>
</table>

(dashed and dotted) lines are for the CH₂-water correlations, and the thick (dashed and dotted) lines are for the CH₃-water correlations. The predictions for μ^{r^\infty}_M, V_M, and ε^{M}_uv for each of these scenarios are compared in Table 4.6.
4.6 Medium Length n-Alkanes

4.6.1 Challenges Resulting from Chain Flexibility

Until now, I have only considered rigid hydrocarbons, for which the solution of the SSOZ equation has been relatively straightforward. However, hydrocarbons which are longer than propane are not rigid in the context of the OPLS, and therefore, to deal with such molecules, one must address the additional complications arising from the flexibility of these chain-like molecules.

Before the SSOZ equation can be solved, the \( w \) matrix needs to be specified (see Eq. (2.13)). This is equivalent to knowing the average conformation of the molecules in solution. Recall that for rigid molecules, this poses no special problems, since the distances between the sites within a molecule, \( l_{aa'M} \), are known, and, therefore, the \( w \) matrix can be easily computed using Eq. (2.14). However, for a flexible molecule, where the presence of other molecules may influence its conformation, the \( l_{aa'M} \) values are unknown. Accordingly, the definition of the \( w \) matrix given in Eq. (2.14) needs to be generalized. Specifically, one has

\[
\hat{w}_{a_a'M'}(k) = \delta_{MM'} \sum_{j_M} s_M(j_M) \frac{\sin kl_{aa'M}(j_M)}{kl_{aa'M}(j_M)}
\]

(4.1)

where \( j_M \) labels all possible conformations of a molecule of type \( M \), \( s_M(j_M) \) is the fraction of \( M \) molecules in the conformation \( j_M \), and \( l_{aa'M}(j_M) \) is the distance between sites \( a \) and \( a' \) in a molecule of type \( M \) when it is in conformation \( j_M \). In order to calculate the \( w \) matrix, it is necessary to find an expression for \( s_M(j_M) \). Note that a rigid molecule can only be in one conformation, in which case Eq. (4.1) reduces to Eq. (2.14).

Clearly, flexible molecules pose a problem because \( s_M(j_M) \) is not known a priori. Indeed, an additional set of equations is required to find \( s_M(j_M) \). Naumann suggested\textsuperscript{104} that a fluid composed of flexible molecules could be treated as a multicomponent chemically reactive mixture of rigid molecules. Each different conformation, \( i_M \), is considered to be a distinct chemical species, having a mole fraction, \( s_M(i_M) \).
From thermodynamics, one finds that

$$s_M(i_M) \propto e^{-\beta \mu_M(i_M)}$$  \hspace{1cm} (4.2)$$

where $\mu_M(i_M)$ is the chemical potential of a molecule of type $M$ in conformation, $i_M$. Summing Eq. (4.2) over all conformations, $i_M$, and noting that $\sum_{i_M} s_M(i_M) = 1$, yields

$$s_M(i_M) = \frac{1}{q^*_M} e^{-\beta u_M(i_M) - \beta \mu_M^{\text{res}}(i_M)}$$  \hspace{1cm} (4.3)$$

where

$$q^*_M = \sum_{i_M} e^{-\beta u_M(i_M) - \beta \mu_M^{\text{res}}(i_M)}$$  \hspace{1cm} (4.4)$$

where $u_M(i_M)$ is the energy of an isolated molecule of type $M$ when it is in the conformation, $i_M$, and $\mu_M^{\text{res}}(i_M)$ is the residual chemical potential of molecules of type $M$ in the conformation, $i_M$. Equations (4.3) and (4.4) are the set of additional equations which need to be solved to describe the chain conformations.

### 4.6.2 The Conformations of n-Butane

In the OPLS, the shortest linear hydrocarbon which is flexible is n-butane, and the only manner in which n-butane can alter its conformation is by a rotation of its dihedral angle, $\phi$. In order to compute $s(\phi)$ for n-butane at infinite dilution in water, I first solve the SSOZ equation to obtain the water-water and butane-water correlation functions for each possible value of the dihedral angle. From these correlation functions, I can then compute the residual chemical potential, $\mu^{\text{res}}(\phi)$. By inserting $\mu^{\text{res}}(\phi)$ and $u(\phi)$, the energetic barrier to rotation of the dihedral angle (see Table 4.1), into Eqs. (4.3) and (4.4), one obtains $s(\phi)$, the fraction of molecules having a dihedral angle, $\phi$.

In Figure 4-9, I plot the function $s(\phi)$ for n-butane at ambient conditions. The solid line is the prediction of the SSOZ-HNC equation for n-butane in water, the
Figure 4-9: Dihedral angle distribution of n-butane in water: (i) predictions of the SSOZ equation with the HNC closure, (ii) predictions of the SSOZ equation with the MaS closure, and (iii) ideal-gas phase predictions.

The dashed line is the prediction of the SSOZ-MaS equation for n-butane in water, and the dotted line corresponds to n-butane in the ideal-gas state.

By integrating over the middle peak, one can determine the fraction of butane molecules in the trans state, $\phi \approx 180^\circ$. In the ideal-gas state, 69.5% of the molecules are in the trans state. When the butane molecule is placed in water, the SSOZ-HNC equation predicts that only 27.6% are in the trans state, while the SSOZ-MaS equation predicts that 65.5% are in the trans state. These results are physically reasonable, since hydrocarbons tend to minimize contact with water, and therefore are expected to coil up in order to do so. This is indeed what is observed in Figure 4-9, as n-butane tends to populate the more extended trans state less frequently when it is placed in water.
4.6.3 Results for Longer n-Alkanes

As the length of the hydrocarbon chain increases, the number of possible conformations also increases. In order to keep this to a tractable number, I have utilized the rotational isomeric state (RIS) approximation to restrict the number of allowed conformations. In the RIS approximation, the dihedral angles can only take on three distinct values: (1) $\phi = 180^\circ$, the trans state, (2) $\phi = 60^\circ$, the gauche (+) state, and (3) $\phi = 300^\circ$, the gauche (-) state. Under the RIS approximation, specifying the state of each dihedral bond (trans-gauche sequence) uniquely determines the conformation of the molecule.

Another complication which arises for long chains, is that the number of correlation functions which need to be computed increases with the length of the chain. In order to keep this number to a minimum, I have employed the equivalent-site approximation, as discussed in Section 4.5.

Using these approximations, I was able to solve the SSOZ equation with the HNC and MaS closures for each conformation (that is, each distinct trans-gauche sequence) of n-pentane, n-hexane, and n-heptane at infinite dilution in water. From the resulting correlation functions, I was then able to compute the residual chemical potential, $\mu(i)$, of a particular conformation, $i$ (see Eqs. (2.24) and (2.25)). Using these along with the intramolecular interaction potential (see Table 4.1) in Eq. (4.3), one can then determine the fraction of molecules in each allowable conformation. From this, one can then determine the thermodynamic properties of the system. As an example, in Figure 4-10, I present the predicted residual chemical potential of n-alkanes (for $1 \leq n \leq 7$) at infinite dilution in water. The predictions of the SSOZ-HNC equation are shown as circles, the predictions of the SSOZ-MaS equation are shown as triangles, and the experimentally measured values are denoted by squares. As can be seen, the HNC closure clearly overestimates the magnitude of the residual chemical potential, while the MaS closure provides a more reasonable estimate.

In addition to thermodynamic properties, one can also compute chain conformational properties, such as the root-mean-square end-to-end distance, $< r^2 >^{1/2}$. This is shown in Figure 4-11. The circles represent the predictions of the SSOZ-
Figure 4-10: Carbon number dependence of the residual chemical potential of n-alkanes ($1 \leq n \leq 7$) at infinite dilution in water: (i) predictions of the SSOZ equation with the HNC closure (circles), (ii) predictions of the SSOZ equation with the MaS closure (triangles), and (iii) experimental measurements of Abraham$^{96}$ (squares). Note that the various lines are drawn to guide the eye.
Figure 4-11: Carbon number dependence of the root-mean-square end-to-end distance of n-alkanes (1 ≤ n ≤ 7) at infinite dilution in water: (i) predictions of the SSOZ equation with the HNC closure (circles), (ii) predictions of the SSOZ equation with the MaS closure (triangles), and (iii) ideal-gas phase predictions (squares). Note that the various lines are drawn to guide the eye.

HNC equation, the triangles are the predictions of the SSOZ-MaS equation, and the squares are the predictions for isolated hydrocarbons (that is, for the ideal-gas state). For methane, ethane, and propane, there is no predicted change in <r²>¹/² as the hydrocarbons are placed in water. This reflects the fact that these molecules are rigid for the potential models that I have utilized. As in the case of butane in water, both the HNC and MaS closures predict that the hydrocarbon chain becomes more collapsed in water, with the HNC closure predicting a more severe collapse than that predicted by the MaS closure.

4.7 Concluding Remarks

In this chapter, I have studied the structural and bulk thermodynamic properties of methane, ethane, and propane at infinite dilution in water using the site-site Ornstein-Zernike (SSOZ) equation under a variety of different closure relations for
the hydrocarbon-water correlation functions in order to compare the quantitative predictive capabilities of the various closures. The HNC closure, which is the closure that has been utilized almost exclusively to predict bulk thermodynamic properties of interaction site fluids, performs rather poorly. Specifically, it consistently underpredicts the magnitudes of both the solute partial molar volume and the solute-solvent interaction energy, grossly overpredicts the magnitude of the residual chemical potential, and gives the incorrect sign of the enthalpy of solution. On the other hand, two recently developed closures, the Martynov-Sarkisov (MaS) and Ballone-Pastore-Galli-Gazzillo (BPGG) closures, which have not been utilized so far in conjunction with the SSOZ equation, yield reasonable predictions of the structural and bulk thermodynamic properties of the hydrocarbon-water systems studied. In particular, utilizing the SSOZ-BPGG equation, the predicted temperature variation of the residual chemical potential over the relatively broad range 5 – 80°C was found to be in very good agreement with the experimental data.

I have also tested the accuracy of the equivalent-site approximation (ESA), a perturbation method which was developed by Curro and Schweizer to study long polymeric chains by treating all the sites in a given molecule as equivalent, on the predictions of the structural and bulk thermodynamic properties of propane at infinite dilution in water. Note that of all the n-alkanes, propane poses the most severe challenge to the ESA. Interestingly, already for propane, the ESA yields predictions of bulk thermodynamic properties which are within 5% of those obtained using the rigorous calculations.

In addition, for long-chain hydrocarbons (4 ≤ n ≤ 7), I have predicted the change in the chain conformations associated with transferring the molecules from vacuum to water at infinite dilution. Both the SSOZ-HNC and SSOZ-MaS equations predict that the hydrocarbon chain will become more collapsed when placed in water. However, the SSOZ-HNC equation predicts a more severe collapse than that predicted by the SSOZ-MaS equation. Finally, I have predicted the variation of the residual chemical potential of hydrocarbons at infinite dilution in water, \( \mu^{\text{res}} \), with hydrocarbon chain-length. The SSOZ-MaS equation predicts \( \mu^{\text{res}} \) values which are in fairly good
agreement with the available experimental values, while the SSOZ-HNC equation greatly overpredicts the \( \mu^{***} \) values.

In the next chapter, I will examine the applicability of the SSOZ equation in the case of a model surfactant-water system. This model system is much more complicated than any of those which have been studied in the past in the context of the SSOZ equation. This is due to the fact that the surfactant molecules can self-assemble to form relatively large, stable micellar aggregates in solution. Consequently, such a "complex fluid" poses a rather severe test to the SSOZ equation.
Chapter 5

The Site-Site Ornstein-Zernike
Equation: Application to a
Lennard-Jones Surfactant Model

5.1 Introduction and Overview

In this chapter, I analyze a model surfactant-water system in the context of the SSOZ formalism. This system offers an additional challenge beyond the pure water and hydrocarbon-water systems considered in Chapters 3 and 4 because the surfactant molecules can assemble spontaneously into stable microstructures known as micelles. The morphology and size of these micelles depend on the chemical structure of the surfactant molecules as well as on solution conditions. This unique dependence can have a profound effect on the thermodynamic behavior of these complex fluids.

To date, previous applications of liquid state theory to surfactant-water\textsuperscript{105, 106, 107, 108, 109} and surfactant-oil-water\textsuperscript{110} systems have treated the surfactant micelles as rigid entities, such as hard spheres. Previous treatments have therefore neglected the self-assembling, dynamic nature of the micelles, and consequently were not able to predict important micellar characteristics, such as, their size distribution.

On the other hand, simulations which explicitly account for the individual surfactant molecules comprising each micelle, can only describe a single micelle.\textsuperscript{111, 112, 113, 114}
Therefore, intermicellar interactions cannot be investigated. Furthermore, the typical duration of these types of simulations is orders of magnitude too short to observe the spontaneous formation of a micelle from individual monomers in solution.

Quite recently, Smit et al. performed\textsuperscript{115,116} simulations of a model micellar solution, which explicitly accounted for the surfactant and solvent molecules, and observed the spontaneous formation of micellar aggregates. However, questions exist as to whether the simulations were run long enough to ensure that the systems studied reached a true equilibrium state, and that the micelles were indeed stable. In order to verify the observed simulation results and to ascertain the applicability of current approximate integral equation theories to self-assembling systems, I have examined this model surfactant-water system using the SSOZ equation.

This chapter is organized as follows. In Section 5.2, I describe the potential functions for the surfactant-water model system. Previous simulation work on these model systems is summarized in Section 5.3. The application of the SSOZ equation to this system is presented in Section 5.4. Finally, a summary is given in Section 5.5.

5.2 Description of the Potential Functions

Smit et al. developed\textsuperscript{117} a simple model to mimic the basic elements of surfactant-oil-water systems. The molecules in this model are constructed from two types of particles: “water-like” and “oil-like”. The interactions between each of these particles is given by shifted truncated Lennard-Jones potentials. Specifically,

\[
\Phi_{ij}(r) = \begin{cases} 
\phi_{ij}(r) - \phi_{ij}(R_{ij}^c), & r \leq R_{ij}^c \\
0, & r > R_{ij}^c 
\end{cases} 
\tag{5.1}
\]

where \(R_{ij}^c\) is the cutoff length of the interaction between sites \(i\) and \(j\), and \(\phi_{ij}\) is the Lennard-Jones interaction potential, given by

\[
\phi_{ij}(r) = 4\epsilon_{ij} \left[ \left( \frac{\sigma_{ij}}{r} \right)^{12} - \left( \frac{\sigma_{ij}}{r} \right)^6 \right] 
\tag{5.2}
\]
where $\epsilon_{ij} = \epsilon$ and $\sigma_{ij} = \sigma$ for all types of particles $i$ and $j$. Note that particle $i$ and particle $j$ do not interact with each other when they are separated by distances greater than $R_{ij}$. Therefore, the potential function is short-ranged. For interactions between like particles, $R_{ij} = 2.5\sigma$, and therefore, the potential, $\Phi_{ij}(r)$, between two "oil-like" or two "water-like" particles has both a repulsive core and an attractive well. For unlike particles, $R_{ij} = 2^{1/6}\sigma$, so that the interactions between "oil-like" and "water-like" particles are purely repulsive.

The solvent corresponding to water consists of "water-like" particles. The solvent corresponding to oil consists of "oil-like" particles. The surfactant molecule consists of two chemically distinct moieties: a hydrophilic portion referred to as the head group, and a hydrophobic portion referred to as the tail group. The head group is built from "water-like" particles linked together, and the tail group is made up of "oil-like" particles linked together. The bond length between particles is equal to $\sigma$.

A schematic representation of the various molecules comprising the system is given in Figure 5-1.
5.3 Results from Computer Simulations

Smit et al. performed\textsuperscript{117, 118, 119, 116, 120} molecular dynamics simulations on the model surfactant-oil-water system described in Section 5.2. The initial investigations were aimed at computing the oil-water interfacial tension in the presence of surfactants. The interfacial tension was found to decrease with increasing surfactant concentration and with increasing length of the surfactant tail group, which is the behavior observed experimentally.

Later studies analyzed the morphology of the surfactant-oil-water system for a surfactant composed of one head segment and one tail segment (HT), as well as for a surfactant composed of two head segments and five tail segments (H\textsubscript{2}T\textsubscript{5}) at a reduced temperature, $T^{*} = 1.0$, and a solvent reduced density, $\rho_{c}^{*} = 0.7$. At these conditions, the “oil-like” and “water-like” particles phase separate and form a stable interface.\textsuperscript{117} Smit et al. claim that they identify the formation of micellar aggregates for solutions having 1.5% and 3.0% H\textsubscript{2}T\textsubscript{5} surfactant. In defining a micellar aggregate, two surfactant molecules are considered to be in the same aggregate if a tail segment from one of the surfactant molecules is found to be within a distance, $R_{cl} = 1.4\sigma$, from a tail segment from the other surfactant molecule. No stable aggregates were found for the HT surfactant. However, there still exist questions as to whether the simulations were run long enough to ensure that these aggregates were indeed stable.

5.4 Application of the SSOZ Equation

For systems having only short-ranged interactions, the SSOZ-PY equation has been found to work well.\textsuperscript{38, 39, 49, 50, 51} Therefore, the SSOZ-PY equation will be utilized here to study the surfactant-water (HT and H\textsubscript{2}T\textsubscript{5}) model systems described above. Note that no oil is present in the systems that I will examine. The results of this study are described in the following sections.
5.4.1 The HT-Solvent System

I solved the SSOZ-PY equation for a HT surfactant at several densities in a Lennard-Jones solvent at $T^* = 1.0$ and $\rho_o^* = 0.7$ using an extension of the method developed by Labik et al. The grid spacing was 0.025$\sigma$ with 1024 grid points. For further details on the numerical solution of the SSOZ-PY equation, see Appendix C.

In Figure 5-2, I plot the solvent-solvent, solvent-head, and solvent-tail pair correlation functions of this system. The results are as expected. Specifically, the solvent-solvent correlation function is the same as that for a pure Lennard-Jones fluid. The first peak of the solvent-tail correlation function is lower than that of either the solvent-solvent or solvent-head correlation functions. This is due to the fact that the interaction potential between solvent and tail particles is purely repulsive, while that between two solvent particles or a head and a solvent particle has also an attractive well. The first peak in the solvent-head correlation function is lower than that of the solvent-solvent correlation function because the head particle is attached to a tail particle.

In Figure 5-3, I plot the head-head, tail-tail, and head-tail pair correlation functions. Here, the results are somewhat more interesting. The large first peak in $g_{tt}(r)$ (dashed line) indicates that the surfactant molecules have a tendency to cluster together with the tail groups in close proximity. The fact that the three surfactant-surfactant pair correlation functions are greater than unity beyond the first peak corroborates the clustering hypothesis. I have also found that as the surfactant concentration increases, the magnitude of the peaks of the surfactant-surfactant pair correlation functions increase.

Once the various pair correlation functions have been computed, one can calculate the thermodynamic properties of the system. A key property of interest for systems which form aggregates is the osmotic compressibility, which is given by

$$
\frac{1}{\rho_o} \left( \frac{\partial \beta \pi}{\partial x_u} \right)_{T,p} = \frac{1}{x_u} \left[ 1 - \frac{x_u \rho_o (\hat{h}_{vv}(0) + \hat{h}_{uu}(0) - 2\hat{h}_{uv}(0))}{1 + x_u \rho_o (\hat{h}_{uu}(0) + \hat{h}_{uv}(0) - 2\hat{h}_{vv}(0))} \right]
$$

where $\hat{h}_{ij}(0)$ is the Fourier transform of the total correlation function between $i$ and
Figure 5-2: Predicted pair correlation functions for a HT surfactant at infinite dilution in a Lennard-Jones solvent at $T^* = 1.0$ and $\rho_v^* = 0.7$: (i) solvent-solvent (solid line), (ii) solvent-head (dashed line), and (iii) solvent-tail (dotted line).

Figure 5-3: Predicted pair correlation functions for a HT surfactant at infinite dilution in a Lennard-Jones solvent at $T^* = 1.0$ and $\rho_v^* = 0.7$: (i) head-head (solid line), (ii) tail-tail (dashed line), and (iii) head-tail (dotted line).
\( j \) at \( k = 0 \), \( \rho_v \) is the number density of the solvent, \( x_v \) is the mole fraction of the solvent, and \( x_u \) is the mole fraction of the solute.

For comparison, the osmotic compressibility of an ideal solution is given by\(^{24}\)

\[
\frac{1}{\rho_v} \left( \frac{\partial \beta \pi}{\partial x_u} \right)_{T,p} = \frac{1}{1 - x_u} \tag{5.4}
\]

and the osmotic compressibility of a regular solution, is given by\(^{24}\)

\[
\frac{1}{\rho_v} \left( \frac{\partial \beta \pi}{\partial x_u} \right)_{T,p} = \frac{1}{1 - x_u} - 2\beta C x_u \tag{5.5}
\]

where \( C \), which is only a function of temperature and pressure, provides a measure of the interactions (attractive or repulsive) between the solute molecules. The larger the value of \( C \), the larger these interactions. For \( C = 0 \), the regular solution reduces to an ideal solution.

A successful phenomenological model of surfactant-water micellar solutions has been developed by Blankschtein et al.\(^{122}\) Within this formalism, the osmotic compressibility is given by

\[
\frac{1}{\rho_v} \left( \frac{\partial \beta \pi}{\partial x_u} \right)_{T,p} = \frac{x_u}{1 - x_u} + \frac{1}{M_2} - \frac{\beta C x_u}{[1 + (\gamma - 1)x_u]^3} \tag{5.6}
\]

where \( M_2 \) is the second moment of the size distribution of the aggregates, \( C \) is a mean-field interaction parameter between aggregates, and \( \gamma \) is the ratio of the volume of a surfactant molecule to the volume of a solvent molecule.

The typical behavior of the osmotic compressibility as a function of solute concentration for (i) an ideal solution, (ii) a regular solution, and (iii) a micellar solution is plotted in Figure 5-4. For an ideal solution, the osmotic compressibility is relatively constant, increasing slowly with solute concentration. For a regular solution, characterized by a net attraction between solute molecules, the osmotic compressibility decreases with solute concentration. The greater the attractive interaction between the solute molecules, the faster the decrease of the osmotic compressibility. The concentration at which the osmotic compressibility curve crosses zero corresponds to the spinodal of the mixture. The formation of micellar aggregates should be accompanied
Figure 5-4: Schematic behavior of the osmotic compressibility as a function of solute concentration for different types of solutions: (i) ideal solution (solid line), (ii) regular solution (dotted lines), and (iii) micellar solution (dashed line)

by a sharp decrease of the solution osmotic compressibility. The larger the aggregates which form, the sharper the break. The concentration at which this break occurs is known as the critical micellar concentration (cmc), see Figure 5-4.

The variation of the osmotic compressibility with the concentration of HT molecules in solution, as predicted by the SSOZ-PY equation, is shown in Figure 5-5. As can be seen, the osmotic compressibility gradually decreases with surfactant concentration, reflecting the effect of the attractive forces acting between surfactant molecules. However, there is no indication of a break which would signal the formation of stable aggregates. This is expected, and consistent with the fact that no aggregates were found in the molecular dynamics simulations of this system.¹¹⁶

5.4.2 The H₂T₅-Solvent System

After analyzing the HT-solvent system, I then proceeded to study the H₂T₅-solvent system. The H₂T₅ surfactant molecule is flexible, and therefore the average confor-
Figure 5-5: Dependence of the osmotic compressibility on the HT surfactant concentration.

mation of the molecule is not known a priori. I studied two models of flexible chains to describe the conformations of the surfactant molecule. The first is the Gaussian chain, where

\[ \hat{w}_{\alpha \gamma}(k) = \left( e^{-k^2 \rho / \sigma} \right)^{\alpha - \gamma} \]  

and the second is the freely-jointed chain, where

\[ \hat{w}_{\alpha \gamma}(k) = \left( \frac{\sin kl}{kl} \right)^{\alpha - \gamma} \]  

In both models, \( l \) refers to a characteristic segment length scale of the chain, which is equal to \( \sigma \) for this system. I found that the predictions of the SSOZ-PY equation do not depend significantly on the chain model used, which is probably a consequence of the fact that the chain is short. I will therefore present results which utilize the freely-jointed chain model.

In order to keep the computations tractable, the equivalent-site approximation was invoked. Consequently, all the segments in the head group and the tail group were
treated as equivalent within each group. Therefore, in this approximation, there are only three distinct interaction sites to be considered: (i) the solvent, (ii) a head-group segment, and (iii) a tail-group segment.

The predictions of the SSOZ-PY equation for the \( \text{H}_2\text{T}_5 \)-solvent system are somewhat confusing. While the solvent-solvent and surfactant-solvent pair correlation functions are typical (see Figure 5-6), the predictions of the surfactant-surfactant pair correlation functions (see Figure 5-i) display some unphysical features. Specifically, there is a large negative region in all the surfactant-surfactant pair correlation functions. The PY closure is known to give a small negative region immediately before the first peak of \( g(r) \) for a system with strong attractive forces. However, the predicted behavior for the \( \text{H}_2\text{T}_5 \) case has not been observed before.

As the temperature increases, the negative regions become gradually larger until suddenly, at \( T^* = 1.25 \), they transform into very large positive peaks. It is interesting to note that the SSOZ-PY equation for the surfactant-surfactant pair correlation functions are linear at zero surfactant concentration. At \( T^* = 1.25 \), these linear
Figure 5-7: Predicted pair correlation functions for a H$_2$T$_5$ surfactant at infinite dilution in a Lennard-Jones solvent at $T^* = 1.0$ and $\rho^*_s = 0.7$: (i) head-head (solid line), (ii) tail-tail (dashed line), and (iii) head-tail (dotted line).

Figure 5-8: Predicted pair correlation functions for a H$_2$T$_5$ surfactant at infinite dilution in a Lennard-Jones solvent at $T^* = 1.26$ and $\rho^*_s = 0.7$: (i) head-head (solid line), (ii) tail-tail (dashed line), and (iii) head-tail (dotted line).
Figure 5-9: Regions of solution of the SSOZ-PY equation in the temperature-surfactant concentration plane for the $\text{H}_2\text{T}_5$ surfactant system. The SSOZ-PY equation predicts physically reasonable surfactant-surfactant pair correlation functions in Region 1, and unphysical surfactant-surfactant pair correlation functions in Region 2. No solutions are found between these two regions.

equations lose solutions.

Regions of solutions of the SSOZ-PY equation in the temperature-surfactant concentration plane for the $\text{H}_2\text{T}_5$ surfactant system are plotted in Figure 5-9. As can be seen, there are three distinct regions. The first region corresponds to physically reasonable pair correlation functions, such as those shown in Figure 5-8. The second region corresponds to pair correlation functions displaying large unphysical negative regions, such as those shown in Figure 5-7. In the third region, I was unable to find solutions to the SSOZ-PY equation. It is very interesting to note that the simulations performed by Smit et al. lie within the region in which I do not find solutions to the SSOZ-PY equation.

To determine the dependence of the unphysical behavior found for the SSOZ-PY equation on the closure relation, I also solved the SSOZ equation with the HNC closure for the $\text{H}_2\text{T}_5$-solvent system. One favorable feature of the HNC closure is that, unlike
the PY closure, it enforces the nonnegativity of the pair correlation functions. As a consequence, the SSOZ-HNC equation will never predict unphysical pair correlation functions such as those shown in Figure 5-7.

For surfactant densities in the range, $0 \leq \rho_u^* \leq 0.005$, I was unable to find solutions to the SSOZ-HNC equation for temperatures below about $T^* \approx 9 \sim 10$. This behavior is unphysical because at these temperatures, which are much higher than the critical temperature, $T_c^* = 1.085$, of the pure solvent, a solution to the SSOZ equation should exist, at least at zero surfactant density. In contrast, recall that at these conditions, I found solutions to the SSOZ-PY equation which gave physically reasonable pair correlation functions. Interestingly, above $T^* = 10$, where solutions to the SSOZ-HNC equation were found, the pair correlation functions predicted by the SSOZ-HNC and SSOZ-PY equations were found to be quite similar.

This large difference in the behavior of the SSOZ-PY and the SSOZ-HNC equations, combined with the fact that both equations yield unphysical predictions, calls into question their predictive capabilities for the types of systems considered here.

The SSOZ equation is known not to perform well at low densities, and therefore, the strange behavior at low surfactant concentrations is not entirely surprising. However, the results described above seem to indicate that the SSOZ equation, when combined with a simple fluid closure, is not sufficiently accurate to model systems which may contain micellar aggregates. In order to properly model these systems, one must either construct new approximate closure relations for the SSOZ equation, or develop a new integral equation for interaction site fluids altogether.

5.5 Concluding Remarks

The SSOZ-PY equation was applied to study a surfactant-water model system in order to probe whether it could predict micellization. For the HT-solvent system, the results are as expected. There is no indication of the formation of aggregates, which is consistent with the results of computer simulations.

Some of the predictions of the SSOZ-PY equation for the $H_2T_e$-solvent system
were found to be unphysical. While the predictions for the solvent-solvent and solvent-surfactant pair correlation functions are physically reasonable, the predicted surfactant-surfactant pair correlation functions have a large negative region for $\sigma < r < 3\sigma$. In addition, for a large region in the temperature-surfactant concentration plane, I was unable to find solutions to the SSOZ-PY equation. At higher temperatures, the SSOZ-PY predictions become physically reasonable. When the HNC closure was employed, no solutions were found for $T^* < 9 \sim 10$ at low surfactant densities, which is also unphysical. The disparate and unphysical behavior of the predictions of the SSOZ-HNC and SSOZ-PY equations suggests that the SSOZ equation with a simple fluid closure is not sufficiently accurate to adequately model self-assembling systems.

The breakdown of the SSOZ equation can be understood in terms of the fact that this equation does not perform well at low densities. The severe shortcomings of the SSOZ equation become clear for the model system examined in this chapter, and illustrates the need for the development of a new set of integral equations. Work toward this goal will be discussed in the following chapters.
Chapter 6

The Chandler-Silbey-Ladanyi Equations

6.1 The Need for a New Integral Equation

As we have seen in the previous chapters, by combining the SSOZ equation with a simple fluid closure, it is possible to obtain reasonable predictions of the structure and thermodynamics of interaction site fluids. Indeed, in Chapters 3 and 4, I showed that the SSOZ equation can provide meaningful predictions of structural and bulk thermodynamic properties of pure water as well as of hydrocarbon-water systems. However, as clearly illustrated in Chapter 5, the SSOZ equation has limitations as well, being incapable of providing physically reasonable predictions in the case of a model surfactant-water self-assembling system.

Almost all the applications of the SSOZ equation have utilized a simple fluid closure. It is noteworthy, however, that in the case of polyatomic molecules, using a simple fluid closure is in itself an approximation. Specifically, this will generate an infinite number of diagrams which are unallowed in the exact theory of interaction site fluids at every level of the density. Accordingly, the SSOZ equation sums over a subset of the diagrams for the total correlation function, a situation which is similar to that encountered in the case of approximate closures for the OZ equation. In contrast to the OZ equation, however, the SSOZ equation also sums over diagrams which are
not present in the exact expansion of the total correlation function. Indeed, using a simple fluid closure in conjunction with the SSOZ equation leads to a theory with well-known and well-documented deficiencies. For example, (i) the predicted dielectric constant is always equal to that of an ideal gas,\textsuperscript{123,124} (ii) the total correlation function depends on the presence of auxiliary sites,\textsuperscript{49,125} (iii) the theory does not reduce to the proper limit when all the sites in a molecule are collapsed to a single point,\textsuperscript{126} and (iv) it leads to the wrong scaling behavior of the critical temperature with polymer molecular weight.\textsuperscript{75}

Naturally, a key question then arises as to what is the correct form of the closure relation. Cummings and Stell have determined\textsuperscript{127,128} the exact $r \to \infty$ asymptotic behavior of the direct correlation function, $c_{\alpha\gamma}(r)$, for the SSOZ equation. For diatomic molecules, they found that\textsuperscript{127,128}

$$c_{\alpha\gamma}(r) \longrightarrow \frac{A_{\alpha\gamma}}{r}, \quad \text{as } r \to \infty \quad (6.1)$$

where

$$A_{\alpha\gamma} = \begin{cases} -\beta q_0 q_1^{1+\epsilon(3\nu-1)} & \text{for polar diatomic molecules} \\ (-1)^{\alpha+\gamma} \frac{3}{4\pi \rho \mu^2} g_1 & \text{for nonpolar diatomic molecules} \end{cases} \quad (6.2)$$

where $y = \frac{4\pi}{9} \rho \beta \mu^2$, $\mu$ is the dipole moment of the molecule, $g_1$ is an orientational parameter,\textsuperscript{128} $l$ is the bond length, and $\epsilon$ is the dielectric constant of the fluid. Equation (6.1) indicates that the direct correlation function can be long-ranged even in the absence of long-ranged interactions, as is the case for nonpolar diatomic molecules (see Eq. (6.2)).

For triatomic fluids, they found that\textsuperscript{128}

$$c_{\alpha\gamma}(r) \longrightarrow \begin{cases} \frac{D_{\alpha\gamma}}{r} & \text{for nonlinear triatomic molecules} \\ F_{\alpha\gamma} r & \text{for linear triatomic molecules} \end{cases}, \quad \text{as } r \to \infty \quad (6.3)$$

where $D_{\alpha\gamma}$ and $F_{\alpha\gamma}$ depend on temperature, density, and molecular geometry. Note that the functional forms of both $D_{\alpha\gamma}$ and $F_{\alpha\gamma}$ are unknown.\textsuperscript{20} As illustrated in Eq.
(6.3), for certain geometries, the direct correlation function, $c_{\alpha\gamma}$, can even increase with increasing $r$. This long-range behavior is clearly not compatible with the behavior enforced by a simple fluid closure, namely,

$$c_{\alpha\gamma}(r) \rightarrow -\beta u_{\alpha\gamma}(r), \quad \text{as } r \rightarrow \infty$$  

(6.4)

since the site-site intermolecular potential, $u_{\alpha\gamma}(r)$, always decreases with increasing $r$.

Improving upon the existing closure relations for the SSOZ equation is not a straightforward task. Cummings and Stell concluded\textsuperscript{128} that it is unlikely that a simple closure relation for the SSOZ equation exists. Some attempts have been made by Yethiraj and Curro\textsuperscript{129,130} to develop new closures for polymeric fluids. However, the theoretical basis as well as the extent of applicability of these closures to different systems is uncertain. What is needed is a theory for interaction site fluids which has the same graphical basis as that of the OZ equation for simple fluids. This situation clearly highlights the need to develop a new set of integral equations for interaction site fluids. One such set of equations, which is based on the application of graph theory to interaction site fluids, has been developed by Chandler et al.\textsuperscript{131} and will be described in the next section.

### 6.2 Description of the New Formalism

The total correlation function, $h_{\alpha\gamma}(r)$, between two sites $\alpha$ and $\gamma$ can be written\textsuperscript{27,132} as a sum of contributions from interaction site diagrams. Specifically,
\[ h_{\alpha\gamma}(r) = \text{Sum of all connected interaction site diagrams with two white circles, any number of black circles, one or more f-bonds, and zero or more s-bonds, such that: (1) any two circles are connected directly two each other by at most one bond, (2) the white circles may be connected directly by an f-bond, (3) all black circles must be intersected by an f-bond, (4) any circle can be intersected by at most one s-bond, and (5) there are no articulation circles or articulation s-bonds.} \]

An example of some of the diagrams generated in the case of a diatomic fluid are shown and explained in Figure 6-1. Note that an articulation circle is a circle whose removal will separate a diagram into at least two separate parts, where at least one part does not contain a white circle. For the diagram in Figure 6-2, the black circle intersected by the s-bond is an articulation circle. An articulation s-bond is an s-bond whose removal has the same effect as the removal of an articulation circle. The s-bond in Figure 6-2 is an articulation s-bond. For a description of the application of graph theory to interaction site fluids, see Ref. 27.

In order to construct a graphically proper set of integral equations, Chandler et al. divided\textsuperscript{31} the interaction site diagrams into four groups: (1) no s-bonds intersecting either root circle, denoted by "o", (2) an s-bond intersecting the left-root circle and no s-bonds intersecting the right-root circle, denoted by "l", (3) an s-bond intersecting the right-root circle and no s-bonds intersecting the left-root circle, denoted by "r", and (4) an s-bond intersecting both the left- and right-root circles, denoted by "b". The total correlation function between sites \( \alpha \) and \( \gamma \), \( h_{\alpha\gamma} \), can therefore be written as the sum of four contributions, that is,

\[ h_{\alpha\gamma}(r) = h^o_{\alpha\gamma}(r) + h^l_{\alpha\gamma}(r) + h^r_{\alpha\gamma}(r) + h^b_{\alpha\gamma}(r) \] (6.5)

where \( h^i_{\alpha\gamma} \) (i=o, l, r, or b) is the contribution to the site-site total correlation function associated with the \( i \)th group of diagrams. From a graphical analysis of the diagrams generated in the interaction site formalism, Chandler et al. developed\textsuperscript{31} a set of
Figure 6-1: The interaction site diagrams contributing at zeroth-order in the density to \( h \) for a diatomic fluid. The straight lines represent Mayer \( f \)-bonds, and the wavy lines represent \( s \)-bonds. The white circles are root sites, and the black circles are field sites. The diagram on the first line contributes to \( h^0 \). The two diagrams on the second line contribute to \( h^1 \), the two diagrams on the third line contribute to \( h^r \), and the remaining ten diagrams contribute to \( h^b \).

Figure 6-2: Example of an unallowed diagram. The notation is the same as that in Figure 6-1.
integral equations for the correlation functions of the interaction site fluid, referred to as the Chandler-Silbey-Ladanyi (CSL) equations. For a detailed description of the CSL equations, the interested reader is referred to Ref. 131. In matrix form and in momentum \((k)\) space, the CSL equations can be expressed as follows\(^\text{131}\)

\[
\begin{align*}
\hat{h}^o(k) &= \hat{c}^o(k) + \hat{c}^o(k)\rho \hat{h}^o(k) + \hat{c}^o(k)\rho \hat{h}^l(k) + \hat{c}^o(k)\rho \hat{h}^r(k) \\
\hat{h}^l(k) &= \hat{c}^l(k) + \hat{c}^l(k)\rho \hat{h}^o(k) + \hat{c}^l(k)\rho \hat{h}^l(k) + \hat{c}^l(k)\rho \hat{h}^l(k) \\
\hat{h}^r(k) &= \hat{c}^r(k) + \hat{c}^r(k)\rho \hat{h}^o(k) + \hat{c}^r(k)\rho \hat{h}^r(k) + \hat{c}^r(k)\rho \hat{h}^r(k) \\
\hat{h}^b(k) &= \hat{c}^b(k) + \hat{c}^b(k)\rho \hat{h}^b(k) + \hat{c}^b(k)\rho \hat{h}^b(k) + \hat{c}^b(k)\rho \hat{h}^b(k)
\end{align*}
\]  

(6.6) \quad (6.7) \quad (6.8) \quad (6.9)

where \(c^i_{\alpha}(r)\) (\(i=0, 1, r, \text{ or } b\)) is the contribution to the site-site direct correlation function associated with the \(i\)th group of diagrams. The symbol \(^\wedge\) denotes the Fourier transform of a function. Each of the functions appearing in Eqs. (6.6)–(6.9) is a \(n \times n\) matrix, where \(n\) is the number of interaction sites on the molecule. The matrix, \(\rho\), is diagonal, and its elements are equal to the number density of each of the sites in the system. The matrix, \(s\), describes the geometrical arrangement of the interaction sites of the molecules comprising the system, and is given by

\[
\hat{s}_{\alpha\gamma}(k) = (1 - \delta_{\alpha\gamma})\frac{\sin(kl_{\alpha\gamma})}{kl_{\alpha\gamma}}
\]

(6.10)

where \(l_{\alpha\gamma}\) is the distance between sites \(\alpha\) and \(\gamma\) in a given molecule, and \(\delta_{\alpha\gamma}\) is the Kronecker delta function. In what follows, I will refer to Eqs. (6.6)–(6.9) as the Chandler-Silbey-Ladanyi (CSL) equations.

The CSL equations can be rearranged such that the \(h\)-component bonds are written in terms of only the site-site direct correlation functions. In this form, the CSL
equations are given by\textsuperscript{131}

\begin{align*}
\hat{h}^\circ(k) &= [1 + \hat{\Omega}^\circ(k)] \hat{H}^\circ(k)[1 + \hat{\Omega}^\circ(k)] \quad (6.11) \\
\hat{h}^l(k) &= \rho^{-1} \hat{\Omega}^l(k) + [\hat{\Omega}^l(k) + \hat{\Omega}^b(k)] \hat{H}^\circ(k)[1 + \hat{\Omega}^l(k)] \quad (6.12) \\
\hat{h}^r(k) &= \rho^{-1} \hat{\Omega}^r(k) + [1 + \hat{\Omega}^r(k)] \hat{H}^\circ(k)[\hat{\Omega}^r(k) + \hat{\Omega}^b(k)] \quad (6.13) \\
\hat{h}^b(k) &= \rho^{-1} [\hat{\Omega}^b(k) - \hat{\delta}(k)] + [\hat{\Omega}^l(k) + \hat{\Omega}^b(k)] \hat{H}^\circ(k)[\hat{\Omega}^r(k) + \hat{\Omega}^b(k)] \quad (6.14)
\end{align*}

where

\begin{align*}
\hat{\Omega}(k) &= [1 - \rho \hat{c}_l(k)]^{-1} [1 + \hat{\delta}(k) + \rho \hat{c}_b(k)[1 - \rho \hat{c}_r(k)]^{-1} \quad (6.15) \\
\hat{\Omega}^l(k) &= \rho \hat{c}_l(k)[1 - \rho \hat{c}_l(k)]^{-1} \quad (6.16) \\
\hat{\Omega}^r(k) &= \rho \hat{c}_r(k)[1 - \rho \hat{c}_r(k)]^{-1} \quad (6.17) \\
\hat{\Omega}^b(k) &= \hat{\Omega}(k) - \hat{\Omega}^l(k) - \hat{\Omega}^r(k) - 1 \quad (6.18) \\
\hat{H}^\circ(k) &= \hat{c}_\circ(k)[1 - \hat{\Omega}(k) \rho \hat{c}_\circ(k)]^{-1} \quad (6.19)
\end{align*}

Rossky and Chiles showed\textsuperscript{133} that the CSL equations can be rewritten in a more compact form which resembles the Ornstein-Zernike (OZ) equation. Specifically,

\begin{equation}
\hat{H}(k) = \hat{C}(k) + [\hat{C}(k) + \hat{S}(k)] \rho_0 [\hat{H}(k) + \hat{S}(k)] \quad (6.20)
\end{equation}
where
\[
\bar{\rho} = \begin{pmatrix} \rho & \rho \\ \rho & 0 \end{pmatrix}
\]  

(6.21)

\[
\hat{H}(k) = \begin{pmatrix} \hat{h}^o(k) & \hat{h}^e(k) \\ \hat{h}^i(k) & \hat{h}^b(k) \end{pmatrix}
\]  

(6.22)

\[
\hat{C}(k) = \begin{pmatrix} \hat{c}^o(k) & \hat{c}^e(k) \\ \hat{c}^i(k) & \hat{c}^b(k) \end{pmatrix}
\]  

(6.23)

and
\[
\hat{S}(k) = \begin{pmatrix} 0 & 0 \\ 0 & \rho^{-1}\hat{s}(k) \end{pmatrix}
\]  

(6.24)

Note that each of the functions appearing in Eq. (6.20) is a \(2n \times 2n\) symmetric matrix.

The CSL equations provide a relation between the site-site total and direct correlation functions, \(\hat{H}\) and \(\hat{C}\), neither of which is known a priori. Therefore, in order to solve for \(\hat{H}\) and \(\hat{C}\), another set of equations between these correlation functions, known as the closure relations, is needed to complement Eq. (6.20). The required closure relations were obtained by Rossky and Chiles\(^{133}\) utilizing the technique of topological reduction,\(^{19, 33, 16}\) and are given by

\[
1 + h^o_{\alpha\gamma}(r) = [1 + f_{\alpha\gamma}(r)]e^{w^o_{\alpha\gamma}(r)}
\]  

(6.25)

\[
h^i_{\alpha\gamma}(r) = [1 + f_{\alpha\gamma}(r)]e^{w^i_{\alpha\gamma}(r)}w^i_{\alpha\gamma}(r)
\]  

(6.26)

\[
h^e_{\alpha\gamma}(r) = [1 + f_{\alpha\gamma}(r)]e^{w^e_{\alpha\gamma}(r)}w^e_{\alpha\gamma}(r)
\]  

(6.27)

\[
h^b_{\alpha\gamma}(r) = [1 + f_{\alpha\gamma}(r)]e^{w^b_{\alpha\gamma}(r)}[w^i_{\alpha\gamma}(r)w^e_{\alpha\gamma}(r) + w^b_{\alpha\gamma}(r)]
\]  

(6.28)
where the site-site thermal correlation functions, \( w_{\alpha\gamma}^i(r) \) (i=0, 1, r, or b), are given by

\[
\begin{align*}
  w_{\alpha\gamma}^0(r) &= t_{\alpha\gamma}^0(r) + b_{\alpha\gamma}^0(r) \\
  w_{\alpha\gamma}^1(r) &= t_{\alpha\gamma}^1(r) + b_{\alpha\gamma}^1(r) \\
  w_{\alpha\gamma}^r(r) &= t_{\alpha\gamma}^r(r) + b_{\alpha\gamma}^r(r) \\
  w_{\alpha\gamma}^b(r) &= t_{\alpha\gamma}^b(r) + b_{\alpha\gamma}^b(r)
\end{align*}
\]  

where \( t_{\alpha\gamma}^i(r) = h_{\alpha\gamma}^i(r) - e_{\alpha\gamma}^i(r) \) (i=0, 1, r, or b) are the chain functions. The CSL equations, Eqs. (6.6)-(6.9), and their complementary closure relations, Eqs. (6.25)-(6.28), form a complete set of equations which can be solved to obtain the correlation functions of an interaction site fluid. The function, \( f \), in Eqs. (6.25)-(6.28) is known as the Mayer f-function, and is given by

\[
  f_{\alpha\gamma}(r) = \exp[-u_{\alpha\gamma}(r)] - 1,
\]

where \( u_{\alpha\gamma}(r) = 1/k_BT \), where \( k_B \) is the Boltzmann constant, and \( T \) is the absolute temperature. The functions \( b_{\alpha\gamma}^0, b_{\alpha\gamma}^1, b_{\alpha\gamma}^r, \) and \( b_{\alpha\gamma}^b \) are the bridge functions, which are complicated functionals of the correlation functions. As in the case of the simple fluids, the precise dependence of the bridge functions on the Mayer f-function is formally known. However, these functions are too complex to be evaluated exactly, and therefore, approximations must be made to actually compute the site-site total correlation functions. One such approximation involves the use of the hypernetted-chain (HNC) closure, in which the bridge functions are set equal to zero. The HNC closure takes on the following form

\[
\begin{align*}
  1 + h_{\alpha\gamma}^0(r) &= [1 + f_{\alpha\gamma}(r)] e^{t_{\alpha\gamma}^0(r)} \\
  h_{\alpha\gamma}^1(r) &= [1 + f_{\alpha\gamma}(r)] e^{t_{\alpha\gamma}^0(r)} t_{\alpha\gamma}^1(r)
\end{align*}
\]
Another approximation involves the use of the Percus-Yevick (PY) closure, \(^{133}\) where the total correlation functions are linear in the chain functions, that is

\[
1 + h^{o}_{\alpha \gamma}(r) = [1 + f_{\alpha \gamma}(r)][1 + t^{o}_{\alpha \gamma}(r)]
\]  

(6.37)

\[
h^{l}_{\alpha \gamma}(r) = [1 + f_{\alpha \gamma}(r)]t^{l}_{\alpha \gamma}(r)
\]  

(6.38)

\[
h^{r}_{\alpha \gamma}(r) = [1 + f_{\alpha \gamma}(r)]t^{r}_{\alpha \gamma}(r)
\]  

(6.39)

\[
h^{b}_{\alpha \gamma}(r) = [1 + f_{\alpha \gamma}(r)]t^{b}_{\alpha \gamma}(r)
\]  

(6.40)

A connection between the CSL equations, which apply to interaction site fluids, and the OZ equation, which applies to simple fluids, can be seen in the extended-atom (ea) limit. In the ea limit, all the bond lengths, \(l_{\alpha \gamma}\), for every molecule in the system become infinitely long, which, according to Eq. (6.10), implies that \(\hat{s}_{\alpha \gamma}(k) = 0\) for all \(\alpha\) and \(\gamma\). The resulting system is mathematically equivalent to a multicomponent mixture of atoms. Accordingly, in this limit, the CSL equations should reduce to the OZ equation, and indeed they do. The manner in which the CSL equations collapse to the OZ equation can be seen as follows. Since \(\hat{s}_{\alpha \gamma}(k) = 0\), all diagrams having an \(s\)-bond have a value equal to zero. The "l", "r", and "b" site-site total correlation functions are therefore equal to zero in this case because every diagram contributing to these correlation functions contains an \(s\)-bond. The only nonzero site-site total correlation functions are the "o" functions. In other words, in the ea limit, the site-site total correlation functions of a simple fluid in the OZ formalism are equal to the "o" contributions to the site-site total correlation functions of an interaction site fluid.
in the CSL formalism. This, in turn, implies that the CSL equations reduce to the OZ equation, and that the CSL closures reduce to the OZ closure. In addition, in the ea limit, the CSL-HNC equations reduce to the OZ-HNC equation, and the CSL-PY equations reduce to the OZ-PY equation.

In the next section, I will derive expressions to compute the residual Helmholtz free energy and the residual chemical potential in terms of the correlation functions and bridge functions in the context of the CSL formalism.

6.3 Formulae for Thermodynamic Properties

As mentioned earlier, the thermodynamic properties of a system can be computed from knowledge of the various site-site correlation functions. Formulae for various thermodynamic properties of a fluid written in terms of the site-site correlation functions for the SSOZ equation have been given in Section 2.2. With the exception of the Helmholtz free energy and the chemical potential, all the formulae for the thermodynamic properties for the CSL equations are identical to those for the SSOZ equation.

In the spirit of the derivation of Morita and Hiroike\textsuperscript{33, 32} for the OZ equation and that of Singer and Chandler\textsuperscript{34} for the SSOZ equation, I have developed\textsuperscript{34} expressions for (i) the residual Helmholtz free energy, and (ii) the residual chemical potential for the CSL equations in terms of the correlation and bridge functions. I have also found that under certain restrictions on the bridge functions, the Helmholtz free energy is stationary with respect to variations in the correlation functions. These findings are described next.

6.3.1 Residual Helmholtz Free Energy

In the canonical ensemble, where temperature, volume, and number of particles in a system are held constant, the Helmholtz free energy is minimized at equilibrium. The residual Helmholtz free energy, $A^{\text{res}}$, can be obtained\textsuperscript{36} from the site-site pair
correlation function as follows

\[
\frac{A_{\text{res}}}{V} = \frac{\rho^2}{2} \sum_{\alpha \gamma} \int_0^1 d\zeta \int d^3r g_{\alpha \gamma}(r; \zeta) \frac{\partial u_{\alpha \gamma}(r; \zeta)}{\partial \zeta}
\]  

(6.41)

where \(g_{\alpha \gamma}(r) = 1 + h_{\alpha \gamma}(r)\) is the site-site pair correlation function, \(u_{\alpha \gamma}(r; \zeta)\) is the interaction potential between sites \(\alpha\) and \(\gamma\), \(V\) is the volume of the system, and the coupling constant, \(\zeta\), is a measure of the strength of the interactions between the molecules in the system. Specifically, when \(\zeta = 1\), the molecules interact fully with each other, and \(u_{\alpha \gamma}(r; \zeta = 1) = u_{\alpha \gamma}(r)\). On the other hand, when \(\zeta = 0\), the molecules do not interact with each other, which implies that \(u_{\alpha \gamma}(r; \zeta = 0) = 0\).

Performing the coupling constant integration (see Appendix B for details), one obtains

\[
\frac{\beta A_{\text{res}}}{V} = -\frac{\rho^2}{2} \sum_{\alpha \gamma} \int d^3r \left\{ h_{\alpha \gamma}^o(r) + h_{\alpha \gamma}^i(r) + h_{\alpha \gamma}^\tau(r) + h_{\alpha \gamma}^b(r) 
- w_{\alpha \gamma}^o(r) - w_{\alpha \gamma}^i(r) - w_{\alpha \gamma}^\tau(r) - w_{\alpha \gamma}^b(r) \right\} 
+ \frac{1}{2} \int d^3r \left\{ Tr[W(r)\bar{p}H(r)\bar{p}] - \frac{1}{2} Tr[H(r)\bar{p}]^2 + Tr[C(r)\bar{p}H(r)\bar{p}] \right\} 
+ \frac{1}{2} \int \frac{d^3k}{(2\pi)^3} \left\{ Tr[(\bar{p} + \bar{p}\hat{S}(k)\bar{p})\hat{C}(k)] + \ln \det[1 - (\bar{p} + \bar{p}\hat{S}(k)\bar{p})\hat{C}(k)] \right\} 
+ \frac{\beta A'}{V}
\]  

(6.42)

where

\[
\frac{\beta A'}{V} = -\frac{1}{2} \int_0^1 d\zeta \int d^3r Tr[B(r; \zeta)\bar{p} \frac{\partial H(r; \zeta)}{\partial \zeta})] \bar{p}
\]  

(6.43)

\[
\tilde{W}(k) = \left( \begin{array}{cc}
\tilde{w}^o(k) & \tilde{w}^\tau(k) \\
\tilde{w}^i(k) & \tilde{w}^b(k)
\end{array} \right)
\]  

(6.44)

and

\[
\tilde{B}(k) = \left( \begin{array}{cc}
\tilde{b}^o(k) & \tilde{b}^\tau(k) \\
\tilde{b}^i(k) & \tilde{b}^b(k)
\end{array} \right)
\]  

(6.45)

Note that the last term in Eq. (6.42), \(\beta A'/V\), involves an integration over the coupling constant, \(\zeta\), (see Eq. (6.43)). This implies that in order to evaluate this term, it is
necessary to solve the CSL equations at every value of \( \zeta \) from zero to one. In the case of the HNC approximation, where the bridge functions are equal to zero (that is, \( B=0 \) in Eq. (6.43)), this term vanishes. In that case, the value of \( A^{\text{res}} \) in Eq. (6.42) depends solely on the correlation functions of the system at full coupling \( (\zeta = 1) \). Accordingly, the computation of the residual Helmholtz free energy becomes much simpler by eliminating the need to both solve the CSL equations at all values of \( \zeta \), as well as perform a numerical integration over \( \zeta \).

The expression for the residual Helmholtz free energy of a molecular fluid, given in Eq. (6.42), is similar in form to that for a simple fluid mixture, which is given by\(^{32,33}\)

\[
\frac{\beta A^{\text{res}}}{V} = -\frac{1}{2} \sum_{\alpha \gamma} \rho_{\alpha} \rho_{\gamma} \int d^3 r \{ h_{\alpha \gamma}(r) - w_{\alpha \gamma}(r) \} \\
+ \frac{1}{2} \int d^3 r \left\{ Tr[w(r)\rho h(r)\rho] - \frac{1}{2} Tr[h(r)\rho]^2 + Tr[c(r)\rho h(r)\rho]\right\} \\
+ \frac{1}{2} \int \frac{d^3 k}{(2\pi)^3} \left\{ Tr[\rho \hat{c}(k)] + \ln \det[1 - \rho \hat{c}(k)]\right\} + \frac{\beta A'}{V} \tag{6.46}
\]

In the \( \rho \alpha \) limit, where all diagrams with an \( s \)-bond go to zero, only the "\( o \)" functions are nonzero. In that limit, the expression for \( A^{\text{res}} \) for an interaction site fluid, given in Eq. (6.42), reduces to that for a simple fluid, given in Eq. (6.46).

### 6.3.2 The Variational Principle

In this section, I show that a variational principle exists for the residual Helmholtz free energy. To this end, I first examine the term, \( \beta A'/V \), in the expression for \( A^{\text{res}} \) given in Eq. (6.42) (see also Eq. (6.43)). Recall that the bridge functions in Eq. (6.43) are functions of the site-site separation, \( r \), and functionals of the various site-site total correlation function components. If the integral with respect to \( \zeta \) in Eq. (6.43) is path independent, then \( \beta A'/V \) is an exact functional of the various \( h \)-component bonds. This implies that the variation of \( A' \) is given by

\[
\frac{\beta \delta A'}{V} = -\frac{1}{2} \int d^3 r Tr\{ B(r, [H(r)])\bar{\rho}\delta H(r)\bar{\rho}\} \tag{6.47}
\]
Equation (6.47) indicates that $A'$ is a functional of only the $h$-component bonds. This, in turn, implies that any variation of the system which holds the $h$-component bonds fixed will not affect the value of $A'$. Equation (6.47) also indicates that the functional derivatives of $\beta A'/V$ with respect to the various $h$-component bonds are related to the bridge functions as follows

$$\frac{\delta}{\delta h_{\alpha\gamma}^a(r)} \left( \frac{\beta A'}{V} \right) = -\frac{\rho^2}{2} [b_{\alpha\gamma}^o(r) + b_{\alpha\gamma}^l(r) + b_{\alpha\gamma}^r(r) + b_{\alpha\gamma}^b(r)] \quad (6.48)$$

$$\frac{\delta}{\delta h_{\alpha\gamma}^l(r)} \left( \frac{\beta A'}{V} \right) = -\frac{\rho^2}{2} [b_{\alpha\gamma}^o(r) + b_{\alpha\gamma}^l(r)] \quad (6.49)$$

$$\frac{\delta}{\delta h_{\alpha\gamma}^r(r)} \left( \frac{\beta A'}{V} \right) = -\frac{\rho^2}{2} [b_{\alpha\gamma}^o(r) + b_{\alpha\gamma}^r(r)] \quad (6.50)$$

$$\frac{\delta}{\delta h_{\alpha\gamma}^b(r)} \left( \frac{\beta A'}{V} \right) = -\frac{\rho^2}{2} b_{\alpha\gamma}^o(r) \quad (6.51)$$

The expressions in Eqs. (6.48)-(6.51) should be compared with the equivalent expression for the simple fluid mixture case, which is given by\textsuperscript{32,33}

$$\frac{\delta}{\delta h_{\alpha\gamma}(r)} \left( \frac{\beta A'}{V} \right) = -\frac{\rho}{2} b_{\alpha\gamma}(r) \quad (6.52)$$

Having derived Eqs. (6.48)-(6.51), I proceed next to show that $A^{\text{res}}$ is stationary when the correlation functions of a fluid satisfy both the CSL equations and the closure relations. To this end, it is convenient to consider the residual Helmholtz free energy, $A^{\text{res}}$, as a functional of the site-site correlation functions $h$, $c$, and $w$. To make the computations more transparent, let us rewrite Eq. (6.42) using the CSL equations and closure relations. This yields

$$\frac{\beta A^{\text{res}}}{V} = -\frac{\rho^2}{2} \sum_{\alpha\gamma} \int d^3r \left\{ [1 + f_{\alpha\gamma}(r)]e^{w_{\alpha\gamma}(r)}[(1 + w_{\alpha\gamma}^l(r))(1 + w_{\alpha\gamma}^r(r)) + w_{\alpha\gamma}^b(r)] 
- 1 - w_{\alpha\gamma}^o(r) - w_{\alpha\gamma}^l(r) - w_{\alpha\gamma}^r(r) - w_{\alpha\gamma}^b(r) \right\} + \frac{1}{2} \int \frac{d^3k}{(2\pi)^3} \left\{ T_r[\hat{W}(k)\hat{p}\hat{H}(k)\hat{p}] - \frac{1}{2} T_r[\hat{H}(k)\hat{p}\hat{H}(k)\hat{p}] + T_r[\hat{C}(k)\hat{p}\hat{H}(k)\hat{p}] \right\}$$
+Tr(\bar{\rho} + \bar{\rho} \hat{S}(k) \bar{\rho}) \hat{C}(k) + \ln \det[1 - (\bar{\rho} + \bar{\rho} \hat{S}(k) \bar{\rho}) \hat{C}(k)] + \frac{\beta A'}{V} \quad (6.53)

Taking the variations of the residual Helmholtz free-energy expression given in Eq. (6.53) with respect to the site-site total, \( h \), direct, \( c \), and thermal, \( w \), correlation functions at constant temperature, volume, and density, one obtains

\[
\frac{\beta \delta A^{\text{res}}}{V} = \frac{\rho^2}{2} \sum_{\alpha\gamma} \int d^3 r \left\{ [1 + f_{\alpha\gamma}(r)] e^{w^o_{\alpha\gamma}(r)} \left\{ [1 + w^l_{\alpha\gamma}(r)][1 + u^*_{\alpha\gamma}(r)] + w^b_{\alpha\gamma}(r) \right\} \right.
\]

- \left\{ 1 - h^o_{\alpha\gamma}(r) - h^l_{\alpha\gamma}(r) - h^r_{\alpha\gamma}(r) - h^b_{\alpha\gamma}(r) \right\} \delta w^o_{\alpha\gamma}(r)

+ \frac{\rho^2}{2} \sum_{\alpha\gamma} \int d^3 r \left\{ [1 + f_{\alpha\gamma}(r)] e^{w^o_{\alpha\gamma}(r)} [1 + u^l_{\alpha\gamma}(r)] - 1 - h^o_{\alpha\gamma}(r) - h^r_{\alpha\gamma}(r) \right\} \delta w^l_{\alpha\gamma}(r)

+ \frac{\rho^2}{2} \sum_{\alpha\gamma} \int d^3 r \left\{ [1 + f_{\alpha\gamma}(r)] e^{w^o_{\alpha\gamma}(r)} [1 + u^l_{\alpha\gamma}(r)] - 1 - h^o_{\alpha\gamma}(r) - h^l_{\alpha\gamma}(r) \right\} \delta w^l_{\alpha\gamma}(r)

+ \frac{\rho^2}{2} \sum_{\alpha\gamma} \int d^3 r \left\{ [1 + f_{\alpha\gamma}(r)] e^{w^o_{\alpha\gamma}(r)} - 1 - h^o_{\alpha\gamma}(r) \right\} \delta w^b_{\alpha\gamma}(r)

- \frac{\rho^2}{2} \sum_{\alpha\gamma} \int d^3 r \left\{ h^o_{\alpha\gamma}(r) + h^l_{\alpha\gamma}(r) + h^r_{\alpha\gamma}(r) + h^b_{\alpha\gamma}(r) \right.

- \left\{ w^o_{\alpha\gamma}(r) - w^l_{\alpha\gamma}(r) - w^r_{\alpha\gamma}(r) - w^b_{\alpha\gamma}(r) \right\}

- \left\{ c^o_{\alpha\gamma}(r) - c^l_{\alpha\gamma}(r) - c^r_{\alpha\gamma}(r) - c^b_{\alpha\gamma}(r) \right\}

+ b^o_{\alpha\gamma}(r) + b^l_{\alpha\gamma}(r) + b^r_{\alpha\gamma}(r) + b^b_{\alpha\gamma}(r) \right\} \delta h^o_{\alpha\gamma}(r)

- \frac{\rho^2}{2} \sum_{\alpha\gamma} \int d^3 r \left\{ h^o_{\alpha\gamma}(r) + h^l_{\alpha\gamma}(r) - w^l_{\alpha\gamma}(r) \right.

- c^o_{\alpha\gamma}(r) - c^l_{\alpha\gamma}(r) + b^o_{\alpha\gamma}(r) + b^l_{\alpha\gamma}(r) \right\} \delta h^l_{\alpha\gamma}(r)

- \frac{\rho^2}{2} \sum_{\alpha\gamma} \int d^3 r \left\{ h^o_{\alpha\gamma}(r) + h^r_{\alpha\gamma}(r) - w^r_{\alpha\gamma}(r) \right.

- c^o_{\alpha\gamma}(r) - c^r_{\alpha\gamma}(r) + b^o_{\alpha\gamma}(r) + b^r_{\alpha\gamma}(r) \right\} \delta h^r_{\alpha\gamma}(r)

- \frac{\rho^2}{2} \sum_{\alpha\gamma} \int d^3 r \left\{ h^o_{\alpha\gamma}(r) - w^o_{\alpha\gamma}(r) - c^o_{\alpha\gamma}(r) + b^o_{\alpha\gamma}(r) \right\} \delta h^b_{\alpha\gamma}(r)

- \frac{\rho^2}{2} \sum_{\alpha\gamma} \int \frac{d^3 k}{(2\pi)^3} \left\{ -\hat{h}^o_{\alpha\gamma}(k) - \hat{h}^l_{\alpha\gamma}(k) - \hat{h}^r_{\alpha\gamma}(k) - \hat{h}^b_{\alpha\gamma}(k) \right.

\]

\[
+ \rho^{-1} \{ [1 - \hat{\Omega}(k) \rho \hat{c}_{\alpha\gamma}(k)]^{-1} \hat{\Omega}(k) - \hat{w}(k) \} \delta \hat{c}^o_{\alpha\gamma}(k) \quad (6.54)
\]
\[-\frac{\rho^2}{2} \sum_{\alpha\gamma} \int \frac{d^3k}{(2\pi)^3} \left\{ -\hat{h}^o_{\alpha\gamma}(k) - \hat{h}^l_{\alpha\gamma}(k) + \{\rho^{-1}\hat{1}^l(k) + \hat{\Omega}(k)\hat{H}_a(k)[1 + \hat{\Omega}(k)]\}_{\alpha\gamma}\right\} \delta \xi^o_{\alpha\gamma}(k) \]

\[-\frac{\rho^2}{2} \sum_{\alpha\gamma} \int \frac{d^3k}{(2\pi)^3} \left\{ -\hat{h}^o_{\alpha\gamma}(k) + \hat{h}^r_{\alpha\gamma}(k) + \{\rho^{-1}\hat{1}^r(k) + [1 + \hat{\Omega}(k)]\hat{H}_a(k)\hat{\Omega}(k)\}_{\alpha\gamma}\right\} \delta \xi^r_{\alpha\gamma}(k) \]

\[-\frac{\rho^2}{2} \sum_{\alpha\gamma} \int \frac{d^3k}{(2\pi)^3} \left\{ -\hat{h}^o_{\alpha\gamma}(k) + \{1 + \hat{\Omega}(k)\hat{H}_a(k)[1 + \hat{\Omega}(k)]\}_{\alpha\gamma}\right\} \delta \xi^b_{\alpha\gamma}(k) \]  \hspace{1cm} (6.54)

The resulting expression in Eq. (6.54) should be compared to the corresponding expression for the simple fluid mixture given in Eq. (5.4) of Ref. 33.

If the CSL equations, Eqs. (6.11)-(6.14), the closure relations, Eqs. (6.25)-(6.28), and the definitions of the site-site thermal correlation functions, Eqs. (6.29)-(6.32), are satisfied, then each of the expressions inside the large curly braces of Eq. (6.54) is equal to zero. In that case, the residual Helmholtz free-energy function is stationary with respect to variations in \( h, c, \) and \( w. \)

Note that the derivation presented above leading to Eq. (6.54) is applicable only if Eqs. (6.48)-(6.51) are valid. In other words, the variational principle is applicable only for closures which make the integral in Eq. (6.43) path independent. The exact closure for the CSL equations, as well as the HNC closure, both satisfy this requirement.

To summarize, I have shown that if the integral in Eq. (6.43) is path independent such that Eqs. (6.48)-(6.51) are valid, then the CSL equations with their corresponding closure relations make the residual Helmholtz free energy stationary with respect to the correlation functions at constant temperature, \( T, \) density, \( \rho, \) and total volume, \( V. \)

### 6.3.3 Residual Chemical Potential

The residual chemical potential, \( \mu^{\text{res}} \), can be obtained\(^{36}\) from the site-site pair correlation function through the following relation

\[
\mu^{\text{res}} = \rho \sum_{\alpha\gamma} \int_0^1 d\zeta' \int d^3r g_{\alpha\gamma}(r; \zeta'; \zeta) \frac{\partial u_{\alpha\gamma}(r; \zeta')}{\partial \zeta'}
\]  \hspace{1cm} (6.55)

107
where the coupling constant, $\zeta'$, couples the interactions of a single molecule, referred to as the solute, to the rest of the molecules in the fluid, referred to as the solvent, $\rho$ is the density of the solvent, and the indices $\alpha$ and $\gamma$ run over all the sites in the molecule. When $\zeta' = 1$, the solute molecule interacts fully with the solvent, and $u_{\alpha\gamma}(r; \zeta' = 1) = u_{\alpha\gamma}(r)$. On the other hand, when $\zeta' = 0$, the solute molecule does not interact with the solvent at all, and $u_{\alpha\gamma}(r; \zeta' = 0) = 0$.

Performing the integration over the coupling constant, $\zeta'$, (see Appendix B for details) yields

\[
\beta \mu^{\text{res}} = -\sum_{\alpha\gamma} \rho \int d^3 r \left\{ h_{\alpha\gamma}(r) + h_{\alpha\gamma}^*(r) + h_{\alpha\gamma}^{\text{b}}(r) + h_{\alpha\gamma}^{\text{b}}(r) \right\}
\]

\[
-w_{\alpha\gamma}(r) - w_{\alpha\gamma}^*(r) - w_{\alpha\gamma}^{\text{b}}(r) - w_{\alpha\gamma}^{\text{b}}(r)
\]

\[
+ \frac{1}{\rho} \int \frac{d^3 k}{(2\pi)^3} \left\{ Tr[\mathcal{W}(k)\rho \mathcal{H}(k)\rho] - \frac{1}{2} Tr[\mathcal{H}(k)\rho]^2 + \frac{1}{2} Tr[\mathcal{H}(k)\rho \hat{C}(k)\rho] \right\}
\]

\[
+ \beta \mu'
\]

where

\[
\beta \mu' = -\frac{1}{\rho} \int_0^1 d\zeta' \int d^3 r Tr[B(r; \zeta') \partial \mathcal{H}(r; \zeta') \partial \rho]
\]

Note that the last term, $\beta \mu'$, in Eq. (6.56) still requires performing an integration over $\zeta'$ (see Eq. (6.57)). In the HNC approximation, where the bridge functions, $B$, vanish, this term is equal to zero.

The expression for $\mu^{\text{res}}$ given in Eq. (6.56) should be compared to the corresponding expression for the simple fluid mixture, which is given by\textsuperscript{33}

\[
\beta \mu^{\text{res}} = -\rho \int d^3 r \left\{ h(r) - w(r) \right\}
\]

\[
+ \frac{1}{\rho} \int \frac{d^3 k}{(2\pi)^3} \left\{ \rho \hat{w}(k)\rho \hat{h}(k) - \frac{1}{2}[\rho \hat{h}(k)]^2 + \frac{1}{2} \rho \hat{h}(k)\rho \hat{c}(k) \right\} + \beta \mu'
\]

6.4 Previous Applications of the CSL Equations

The first application of the CSL equations was to homonuclear diatomic Lennard-Jones molecules.\textsuperscript{133} Rossky and Chiles applied\textsuperscript{133} the CSL-HNC and the CSL-PY
equations to predict the structure of these systems and compared the results with the predictions of the SSOZ-PY equation and of computer simulations. Disappointingly, for the situations studied, they found that the CSL equations did not perform as well as the SSOZ-PY equation.

Monson and coworkers later developed a cluster perturbation theory based on the CSL equations. This theory was applied to homonuclear diatomic Lennard-Jones molecules and dipolar hard dumbbells to predict their structure, thermodynamics, and phase behavior. The results were found to be in good agreement with those of computer simulations, and represented an improvement over the SSOZ equation results. The SSOZ-PY equation provided the structural properties of the reference system, and the hard dumbbell equation of state developed by Tildesley and Streett was used to provide the thermodynamic properties.

Despite the success of Monson and coworkers, a need still exists for developing new approximate integral equations, because there are many inherent problems with utilizing perturbation theories for molecular fluids. First, the properties of the reference system are not known accurately. For simple fluids, the reference system is typically the hard-sphere fluid, for which the structure and thermodynamics have been studied extensively. The OZ-PY equation provides fairly accurate values for the pair correlation function, and in cases where more accuracy is required, the pair correlation function computed from computer simulations has been parameterized. In terms of thermodynamics, the Carnahan-Starling equation of state is extremely accurate over a wide range of densities.

On the other hand, for molecular fluids, the analogous reference system, consisting of molecules having hard-sphere interaction sites, has not been studied as thoroughly. The SSOZ-PY equation can be used to provide approximate structural information for the reference fluid, while for the thermodynamic properties, there exist equations of state given the volume and surface area of the reference molecule. These equations, however, are not as accurate for molecular fluids as the equations available for simple fluids. Another major downfall of the application of perturbative methods to molecular fluids is that the structure of the reference system may not be close to
that of the system of interest. For example, in the case of water, the structure of the reference fluid is hexagonally-close packed while that of water is actually tetrahedral.

6.5 Analysis of the CSL Equations

In Section 6.2 and 6.3, I presented a diagrammatically rigorous formalism for computing the correlation functions of interaction site fluids. In this section, I will analyze several aspects of the CSL equations with the exact closure as well as with the HNC closure.

For the CSL equations with the exact closure, I will first examine the constraints imposed by the connectivity of sites within molecules on the form of the correlation functions. I will then discuss the relation between these connectivity constraints and the local neutrality conditions, which must be satisfied\textsuperscript{124} by any theory in order to properly predict the dielectric constant of the fluid. In addition, the asymptotic behavior of the $h$-component bonds, as well as of the bridge functions, for the exact closure will be determined.

For the CSL equations with the HNC closure, I will show that the resulting correlation functions do not fulfill either the connectivity constraints or the local neutrality conditions. As a result, the $h$-component bonds are short-ranged. In contrast, when the exact closure is used, the $h$-component bonds are long-ranged. Finally, I will show that the CSL equations with the HNC closure satisfy the Stillinger-Lovett conditions\textsuperscript{145} for ionic fluids, and as a result, predict a dielectric constant which is infinite.

The final issue which I will examine involves the effect of auxiliary sites, which are sites that do not contribute to the intermolecular interaction potential. Accordingly, the addition of auxiliary sites to a system should not alter the pair correlation functions between the other sites in the system. For an approximate integral equation, however, this may not be the case. In fact, it is known that the SSOZ equation exhibits a dependence on auxiliary sites. For a certain class of systems, I will demonstrate that the SSOZ equation does not exhibit this unphysical dependence. In addition, I
will show that the CSL equations, for a general approximate closure, do not exhibit such a dependence.

### 6.5.1 The Exact Closure Relations

In this section, I examine the CSL equations with the exact closure relations. First, I present some key relations which I will utilize later. The only assumption made is that the functions \( c^o - \phi, \ c^l, \ c^r, \) and \( c^b \) are short-ranged,\(^{124}\) where

\[
\phi_{\alpha \gamma}(r) = -\frac{\beta q_{\alpha} q_{\gamma}}{r} \quad (6.59)
\]

Although this assumption has never been proven, it is physically reasonable and is satisfied by all known approximate closures. Note that \( c^o \) is associated with the direct interactions between two disconnected interaction sites, and, therefore, is expected to behave as \( \phi \) for large \( r \), where \( \phi \) is long-ranged. In mathematical terms, the fact the \( c \) functions are short-ranged implies that their small-\( k \) expansions can be written as

\[
\begin{align*}
\hat{c}^o(k) &= \frac{\Phi}{k^2} + \hat{c}^{o(0)} + \hat{c}^{o(2)}k^2 + ... \\
\hat{c}^l(k) &= \hat{c}^{l(0)} + \hat{c}^{l(2)}k^2 + ... \\
\hat{c}^r(k) &= \hat{c}^{r(0)} + \hat{c}^{r(2)}k^2 + ... \\
\hat{c}^b(k) &= \hat{c}^{b(0)} + \hat{c}^{b(2)}k^2 + ...
\end{align*}
\] (6.60-6.63)

where \( \hat{c}^{i(j)} \) (i=0, l, r, b) denotes the coefficient of the \( k^j \) term in the small-\( k \) expansion of \( \hat{c}^i(k) \), and

\[
\Phi_{\alpha \gamma} = -4\pi\beta q_{\alpha} q_{\gamma} \quad (6.64)
\]

Note that I will only be concerned with systems composed of neutral molecules for which \( \sum_{\alpha} q_{\alpha} = 0 \). For these systems, the following relations follow from Eq. (6.64)

\[
\sum_{\alpha} \Phi_{\alpha \gamma} = \sum_{\gamma} \Phi_{\alpha \gamma} = 0 \quad (6.65)
\]

The fact that the direct correlation functions, \( c^i \) (i=0, l, r, and b), are short-
ranged has consequences for the functions $\Omega$, $\Omega'$, $\Omega^r$, and $\Omega^b$ defined earlier in Eqs. (6.15)–(6.18). Inserting Eqs. (6.60)-(6.63) into Eqs. (6.15)-(6.18), one finds that these functions are also short-ranged.

Next, let us analyze the consequence of requiring that the sites within a molecule are connected. Kirkwood and Buff showed that the fluctuation in the number of molecules in an open system is related to the total correlation function by the following relation

$$
\rho_\alpha + \rho_\alpha \hat{h}_{\alpha\gamma}(0) \rho_\gamma = V \frac{\langle N_\alpha N_\gamma \rangle - \langle N_\alpha \rangle \langle N_\gamma \rangle}{\langle N_\alpha \rangle \langle N_\gamma \rangle}
$$

(6.66)

where $V$ is the volume of the system, $N_\alpha$ is the number of sites of type $\alpha$ in the system, and the angular brackets represent ensemble averages. Note that only entire molecules can enter or leave an open system. In other words, all the sites within a molecule must enter or leave the system together. As a result, the number of sites of type $\alpha$ ($\gamma$) in the system at a particular moment, $N_\alpha$ ($N_\gamma$), is always equal to the total number of molecules in the system, $N$, regardless of the type of site $\alpha$ ($\gamma$). This implies that the right-hand side of Eq. (6.66) is independent of $\alpha$ and $\gamma$, and that

$$
\hat{h}_{\alpha\gamma}(0) \text{ is independent of } \alpha \text{ and } \gamma
$$

I refer to this restriction on the total correlation function, $h$, as the connectivity constraints. Note that, in the extended atom (ea) limit, where all the intramolecular bonds are broken, the connectivity constraints no longer apply because the interaction sites are no longer connected. In the united atom limit, where all the bond lengths are equal to zero, all the site-site total correlation functions should be identical for all $r$ (and, therefore, also $k$). The connectivity constraints then apply not only for $k = 0$ but also for all $k > 0$.

The connectivity constraints also impose restrictions on the forms of $\hat{\Omega}(0)$, $\hat{\Omega}'(0)$, $\hat{\Omega}^r(0)$, $\hat{\varphi}(0)$, $\hat{\varphi}^r(0)$, and $\hat{\varphi}^b(0)$. This can be shown as follows. Adding Eqs. (6.11)-(6.14), one finds that

$$
\hat{\omega}(k) + \rho \hat{\Omega}(k) = [1 - \rho \hat{\Omega}(k) \hat{\varphi}^r(k)]^{-1} \hat{\Omega}(k)
$$

(6.67)
Expanding each of the functions in Eq. (6.67) in powers of \( k \), and collecting terms of order \( k^0 \), one finds that

\[
\hat{\psi}(0) + \rho \hat{h}(0) = \hat{\Omega}(0) + \rho \hat{\Omega}(0) \tilde{\Phi}[\hat{\psi}(2) + \rho \hat{h}(2)] + \rho \hat{\Omega}(0) e^{\alpha(0)}[\hat{\psi}(0) + \rho \hat{h}(0)] + \rho \hat{\Omega}(2) \tilde{\Phi}[\hat{\psi}(0) + \rho \hat{h}(0)]
\]

\[
= \hat{\Omega}(0) + \rho \hat{\Omega}(0) \tilde{\Phi}[\hat{\psi}(2) + \rho \hat{h}(2)] + \rho \hat{\Omega}(0) e^{\alpha(0)}[\hat{\psi}(0) + \rho \hat{h}(0)]
\]

(6.68)

Multiplying the right-hand side of Eq. (6.68) by the matrix \( \Phi \) yields

\[
0 = \hat{\Omega}(0) \tilde{\Phi}\left\{ 1 + Tr[\hat{\psi}(2) + \rho \hat{h}(2)] \right\}
\]

\[
0 = \hat{\Omega}(0) \tilde{\Phi} \frac{1}{\epsilon}
\]

(6.69)

(6.70)

where \( \epsilon \) is the static dielectric constant, which is given by

\[
\frac{1}{\epsilon} = 1 + \rho Tr(\hat{\psi}(2) + \rho \hat{h}(2))
\]

(6.71)

\[
\epsilon = 1 - \rho Tr(\hat{\Omega}(2))
\]

(6.72)

Note that in deriving Eq. (6.70), I have used the fact that \([\hat{\psi}(0) + \rho \hat{h}(0)] \tilde{\Phi} = 0\), since \( \hat{\psi}_\alpha(0) + \rho \hat{h}_\alpha(0) \) is independent of \( \alpha \) and \( \gamma \).

Recall that in a system composed of neutral molecules, the dielectric constant is finite, which, when used with Eq. (6.70), implies that \( \hat{\Omega}(0) \tilde{\Phi} = 0 \). With this in mind, Eq. (6.68) can be rewritten as

\[
\hat{\psi}(0) + \rho \hat{h}(0) = \hat{\Omega}(0) + \rho \hat{\Omega}(0) \tilde{\Phi}[\hat{\psi}(0) + \rho \hat{h}(0)]
\]

(6.73)

The fact that \( \hat{\psi}_\alpha(0) + \rho \hat{h}_\alpha(0) \) is independent of \( \alpha \) and \( \gamma \), combined with Eq. (6.73), implies that \( \hat{\Omega}_\alpha(0) \) is independent of \( \alpha \) and \( \gamma \).

To determine the consequence of the connectivity constraints on the forms of \( \tilde{c}^b(0) \),
\( \hat{\Omega}(0) \), and \( \hat{\Omega}(0) \), I rewrite Eq. (6.15) as

\[
\hat{\Omega}(0) = (1 + \hat{\Omega}(0))[\hat{\omega}(0) + \rho\hat{c}(0)][1 + \hat{\Omega}(0)]
\]

\[
= (1 + \hat{\Omega}(0))[\hat{\omega}(0) + \rho\hat{c}(0)][1 + \hat{\Omega}(0)]^T \tag{6.74}
\]

The form of \( \hat{\Omega}(0) \) and Eq. (6.74) implies that (i) all the elements of \( \hat{c}(0) \) are equal to each other, (ii) \( \sum_\alpha \hat{\Omega}_{\alpha\gamma}(0) \) is independent of \( \gamma \), and (iii) \( \sum_\gamma \hat{\Omega}_{\alpha\gamma}(0) \) is independent of \( \gamma \).

To summarize the results for the omega matrices, one finds that

\( \hat{\Omega}_{\alpha\gamma}(0) \) is independent of \( \alpha \) and \( \gamma \)
\( \sum_\gamma \hat{\Omega}_{\alpha\gamma}(0) \) is independent of \( \alpha \)
\( \sum_\alpha \hat{\Omega}_{\alpha\gamma}(0) \) is independent of \( \gamma \)

This symmetry of \( \Omega, \Omega_l, \) and \( \Omega_r \), combined with their definitions (see Eqs. (6.15)–(6.17)), imposes constraints on the c-component bonds. These are given by

\( \hat{c}(0) \) is independent of \( \alpha \) and \( \gamma \)
\( \sum_\gamma \hat{c}_{\alpha\gamma}(0) \) is independent of \( \alpha \)
\( \sum_\alpha \hat{c}_{\alpha\gamma}(0) \) is independent of \( \gamma \)

Note that the connectivity constraints do not impose any restrictions on \( c^\circ \).

Next, let us examine the relation between the connectivity constraints introduced above and the local neutrality conditions which are given by

\[
\Phi \hat{\Omega}(0) = \hat{\Omega}(0)\Phi = 0 \tag{6.75}
\]

\[
\Phi \hat{\Omega}(0) = 0 \tag{6.76}
\]

\[
\hat{\Omega}(0)\Phi = 0 \tag{6.77}
\]

Chandler et al. have shown that in order for the CSL equations to properly predict the dielectric constant of a fluid, the local neutrality conditions, Eqs. (6.75)–(6.77), must be satisfied. Equation (6.75) is indeed satisfied by the connectivity constraints. (This can be seen by using the fact that \( \hat{\Omega}_{\alpha\gamma}(0) \) is independent of \( \alpha \) and \( \gamma \), combined with Eq. (6.65).) However, Eqs. (6.76) and (6.77) are not necessarily satisfied by the
connectivity constraints. Therefore, satisfying the connectivity constraints solely is not sufficient to construct a proper theory for the dielectric constant.

Next, let us examine the long-range behavior of the $h$-component bonds, which is important from a practical viewpoint if one wants to obtain numerical solutions to the CSL equations. Substituting the small-$k$ expansions of the various functions appearing in Eqs. (6.11)–(6.14), and applying the local neutrality conditions, Eqs. (6.75)–(6.77), as well as Eq. (6.72), one finds that

\[
\begin{align*}
    h^c_{\alpha\gamma}(r) & \longrightarrow -\frac{\beta q_\alpha q_\gamma}{e r}, \quad \text{as } r \to \infty \quad (6.78) \\
    h^l_{\alpha\gamma}(r) & \longrightarrow \frac{\beta q_\alpha q_\gamma}{e r}, \quad \text{as } r \to \infty \quad (6.79) \\
    h^r_{\alpha\gamma}(r) & \longrightarrow \frac{\beta q_\alpha q_\gamma}{e r}, \quad \text{as } r \to \infty \quad (6.80) \\
    h^b_{\alpha\gamma}(r) & \longrightarrow -\frac{\beta q_\alpha q_\gamma}{e r}, \quad \text{as } r \to \infty \quad (6.81)
\end{align*}
\]

Equation (6.78) has already been obtained by Chandler et al.,\textsuperscript{124} and implies that the potential of mean force between two ions, which is equal to $k_B T \ln[1 + h^c_{\alpha\gamma}(r)]$, is screened by the dielectric medium. Chandler et al. showed that a set of local neutrality conditions actually forces\textsuperscript{124} the long-range behavior of the various $h$-component bonds to decay as $1/r$.

Finally, let us examine the bridge functions. As noted earlier, the functions $c^\phi$, $c^l$, $c^r$, and $c^b$ are short-ranged. However, as shown in Eqs. (6.78)–(6.81), the $h$-component bonds are long-ranged. In view of this, the closure relations, Eqs. (6.25)–(6.28), impose the following long-range behavior on the bridge functions

\[
\begin{align*}
    b^c_{\alpha\gamma}(r) & = -\frac{1}{2} \left( \frac{\beta q_\alpha q_\gamma}{e r} \right)^2 - \frac{1}{3} \left( \frac{\beta q_\alpha q_\gamma}{e r} \right)^3 + \ldots \quad (6.82) \\
    b^l_{\alpha\gamma}(r) & = \left( \frac{\beta q_\alpha q_\gamma}{e r} \right)^2 + \left( \frac{\beta q_\alpha q_\gamma}{e r} \right)^3 + \ldots \quad (6.83) \\
    b^r_{\alpha\gamma}(r) & = \left( \frac{\beta q_\alpha q_\gamma}{e r} \right)^2 + \left( \frac{\beta q_\alpha q_\gamma}{e r} \right)^3 + \ldots \quad (6.84) \\
    b^b_{\alpha\gamma}(r) & = -2 \left( \frac{\beta q_\alpha q_\gamma}{e r} \right)^2 - 3 \left( \frac{\beta q_\alpha q_\gamma}{e r} \right)^3 + \ldots \quad (6.85)
\end{align*}
\]
Consequently, the bridge functions are long-ranged (diverging as $k^{-1}$ when $k \to 0$), although their range is shorter than that of the $h$-component bonds. Interestingly, the bridge functions diverge in a similar fashion for simple fluids near the critical point,\textsuperscript{146} where the total correlation function also decays asymptotically as $1/r$.

### 6.5.2 The Hypernetted-Chain Closure

In this section, I analyze the CSL equations with the HNC closure. First, I will show that the connectivity constraints are not necessarily satisfied by an approximate closure. Then, I will examine the impact of this result on the calculation of the dielectric constant. Finally, I will examine the long-range behavior of the $h$-component bonds when the HNC closure is used.

As an illustration, let us consider diatomic molecules at zero density, with the interaction sites labeled $A$ and $B$. The diagrams which contribute to $h$ at zero density are shown in Figure 6-1. Figures 6-3, 6-4, and 6-5 show the diagrams which contribute to $h_{AA}(0)$, $h_{AB}(0)$, and $h_{BB}(0)$, respectively. Because $h(0)$ is the Fourier transform of $h(r)$ at $k = 0$, which involves the integration of $h$ over all $r$, the root sites (white circles) are integrated over all possible positions, and, therefore, become field sites (black circles). Recall that the connectivity constraints require that the various $h_{ij}(0)$'s be identical (that is, $h_{AB}(0) = h_{AB}(0) = h_{BB}(0)$), and that this is indeed the case because the exact expressions are utilized.

Unlike the case of the exact closure relation, not all the diagrams shown in Figures 6-1–6-5 are included when an approximate closure is used. Specifically, the HNC closure does not include the last two diagrams in each of the figures, while the PY closure does not include the last two diagrams in the fourth row in addition to the last two diagrams in each of the figures. When the above mentioned diagrams are excluded from the site-site total correlation function, the connectivity constraints are no longer satisfied, unless both sites $A$ and $B$ are identical (that is, $f_{AA}(r) = f_{AB}(r) = f_{BB}(r)$). Accordingly, the CSL equations with an arbitrary closure relation do not always satisfy the connectivity constraints. In a similar manner, it can be shown that the local neutrality conditions (see Eqs. (6.75)–(6.77)) are also not necessarily satisfied.
Figure 6-3: Diagrams contributing to $\hat{h}_{AA}(0)$ at zero density for a diatomic fluid.
Figure 6-4: Diagrams contributing to $\hat{h}_{AB}(0)$ at zero density for a diatomic fluid.
Figure 6-5: Diagrams contributing to $\hat{h}_{BB}(0)$ at zero density for a diatomic fluid.
when a general approximate closure relation is used.

Given the exact closure, the CSL equations will, in fact, satisfy both the connectivity constraints and the local neutrality conditions. On the other hand, the CSL equations with an arbitrary approximate closure, such as the HNC or PY closures, will not, in general, satisfy either of them.

The fact that the local neutrality conditions are violated has a profound influence on the long-range behavior of the $h$-component bonds. To determine the precise long-range decay of the $h$-component bonds, I expand Eqs. (6.11)-(6.14) in powers of $k$, collect terms of lowest order in $k$, and inverse Fourier transform the result. This procedure yields

\[
\begin{align*}
    h_{\alpha \gamma}^o(r) &\rightarrow A_{\alpha \gamma}^o \frac{\exp[-ar]}{\epsilon' r}, \quad \text{as } r \rightarrow \infty \quad (6.86) \\
    h_{\alpha \gamma}^i(r) &\rightarrow A_{\alpha \gamma}^i \frac{\exp[-ar]}{\epsilon' r}, \quad \text{as } r \rightarrow \infty \quad (6.87) \\
    h_{\alpha \gamma}^r(r) &\rightarrow A_{\alpha \gamma}^r \frac{\exp[-ar]}{\epsilon' r}, \quad \text{as } r \rightarrow \infty \quad (6.88) \\
    h_{\alpha \gamma}^b(r) &\rightarrow A_{\alpha \gamma}^b \frac{\exp[-ar]}{\epsilon' r}, \quad \text{as } r \rightarrow \infty \quad (6.89)
\end{align*}
\]

where

\[
\begin{align*}
    A^o &= \frac{1}{4\pi} [1 + \hat{\Omega}^r(0)] \Phi [1 - \rho \hat{\Omega}(0)\hat{\sigma}^o(0)]^{-1} [1 + \hat{\Omega}^i(0)] \quad (6.90) \\
    A^i &= \frac{1}{4\pi} [\hat{\Omega}^i(0) + \hat{\Omega}^b(0)] \Phi [1 - \rho \hat{\Omega}(0)\hat{\sigma}^o(0)]^{-1} [1 + \hat{\Omega}^i(0)] \quad (6.91) \\
    A^r &= \frac{1}{4\pi} [1 + \hat{\Omega}^r(0)] \Phi [1 - \rho \hat{\Omega}(0)\hat{\sigma}^o(0)]^{-1} [\hat{\Omega}^r(0) + \hat{\Omega}^b(0)] \quad (6.92) \\
    A^b &= \frac{1}{4\pi} [\hat{\Omega}^i(0) + \hat{\Omega}^b(0)] \Phi [1 - \rho \hat{\Omega}(0)\hat{\sigma}^o(0)]^{-1} [\hat{\Omega}^r(0) + \hat{\Omega}^b(0)] \quad (6.93) \\
    \epsilon' &= 1 - \rho Tr [1 - \rho \hat{\Omega}(0)\hat{\sigma}^o(0)]^{-1} \hat{\Omega}^{(2)} \Phi \quad (6.94) \\
    a^2 &= -\rho Tr [1 - \rho \hat{\Omega}(0)\hat{\sigma}^o(0)]^{-1} \hat{\Omega}(0) \Phi / \epsilon' \quad (6.95)
\end{align*}
\]

Each of the $h$-component bonds decays exponentially for the HNC closure, and is therefore short-ranged. Recall that with the exact closure, the CSL equations yield $h$-component bonds which are long-ranged (see Eqs. (6.78)-(6.81)).
If the connectivity constraints were satisfied, then \( \hat{\Omega}_{\alpha\gamma}(0) \) would be independent of the indices \( \alpha \) and \( \gamma \), and as a result \( \hat{\Omega}(0)\Phi = 0 \). It would then follow from Eq. (6.95) that \( a = 0 \), in which case the \( h \)-component bonds would be long-ranged, decaying as \( 1/r \). However, the coefficients associated with the decay, \( A^i/\epsilon' \) \( (i=0, 1, r, b) \), would not be the same as those corresponding to the exact closure. If the local neutrality conditions were satisfied, then \( A^o = A^b = \Phi/4\pi \) and \( A^l = A^r = -\Phi/4\pi \), and the \( h \)-component bonds would decay asymptotically as \( 1/r \) with the same coefficients as those corresponding to the exact closure.

As I have shown, if the connectivity constraints are not satisfied, the \( h \)-component bonds are short-ranged, in which case their small-\( k \) expansion can be written as

\[
\begin{align*}
\hat{h}^o(k) &= \hat{h}^o(0) + \hat{h}^{o(2)}k^2 + \ldots \\
\hat{h}^l(k) &= \hat{h}^l(0) + \hat{h}^{l(2)}k^2 + \ldots \\
\hat{h}^r(k) &= \hat{h}^r(0) + \hat{h}^{r(2)}k^2 + \ldots \\
\hat{h}^b(k) &= \hat{h}^b(0) + \hat{h}^{b(2)}k^2 + \ldots 
\end{align*}
\]

(6.96) (6.97) (6.98) (6.99)

Expanding the functions appearing in the CSL equations (see Eqs. (6.6)–(6.9)) in a power series in \( k \), collecting terms of order \( k^{-2} \), and multiplying both sides of the equation from the left by \( \Phi \), one finds that

\[
\begin{align*}
\Phi + \Phi\rho[\hat{h}^o(0) + \hat{h}^l(0)] &= 0 \\
-\Phi + \Phi\rho[\hat{h}^r(0) + \hat{h}^b(0)] &= 0
\end{align*}
\]

(6.100) (6.101)

Adding Eqs. (6.100) and (6.101) yields

\[
\Phi\rho\hat{h}(0) = 0
\]

(6.102)

Collecting terms of order \( k^0 \) in the CSL equations (see Eqs. (6.6)–(6.9)), one finds that

\[
1 + \rho Tr\Phi[\hat{\omega}^{(2)} + \rho\hat{h}^{(2)}] = 0
\]

(6.103)
In view of Eq. (6.71), Eq. (6.103) implies that the dielectric constant, \( \epsilon \), is infinite. It is interesting to note that Eqs. (6.102) and (6.103) also occur in the theory of simple fluids which are ionic, where they are referred\(^{145}\) to as the Stillinger-Lovett conditions. Equation (6.102) is\(^{145, 147}\) a statement of bulk electroneutrality of a thermodynamic system consisting of charged particles. Equation (6.103) describes\(^{145, 147}\) the effect of dielectric screening on the long-ranged correlations between charged particles.

One should stress that although the CSL equations themselves enforce the electroneutrality conditions, regardless of the form of the closure relation, they do not enforce the connectivity constraints. Due to the violation of the connectivity constraints, the dielectric constant becomes infinite. This can be rationalized as follows. The failure of the approximate equations to obey the connectivity constraints causes free ions to exist in the solution. These ions are then able to screen any externally applied electric fields in the system, similar to what takes place in an ionic solution. As a result, the dielectric constant is infinite.

### 6.5.3 Auxiliary Sites

Auxiliary sites are interaction sites on a molecule, which merely label positions, but do not contribute to the intermolecular interaction potential. These sites are useful in that one can determine the correlation functions between different sites in the molecules which are not necessarily located on the interaction sites. Physically, the presence of auxiliary sites should not affect the correlations between sites on different molecules.

The SSOZ equation, when combined with a general closure, has been shown\(^{49, 125}\) to yield correlations which are affected by the inclusion of auxiliary sites. However, I will show that the SSOZ-PY equation is independent of the presence of certain types of auxiliary sites when applied to molecules composed of hard-sphere interaction sites. In addition, I will show that the predictions of the CSL equations, under a certain restriction on the closure relations, is unaffected by the presence of certain types of auxiliary sites.
Auxiliary Sites in the Context of the SSOZ Equation

The SSOZ equation has been shown\textsuperscript{49,125} to exhibit a dependence on auxiliary sites. In this section, I prove that under certain restrictions, this dependence is no longer present. Let us consider a system with hard-sphere interaction sites described by the SSOZ-PY equation. In the following derivation, I label all real sites with a Greek index and all auxiliary sites with a Latin index.

The PY closure (see Eq. (2.4)) for a system of hard-sphere interaction sites can be written as

\begin{align}
    h_{\alpha\gamma}(r) &= -1, \quad \text{for } r < \sigma_{\alpha\gamma} \\
    c_{\alpha\gamma}(r) &= 0, \quad \text{for } r < \sigma_{\alpha\gamma}
\end{align}

(6.104) (6.105)

where \( \sigma_{\alpha\gamma} \) is the hard-sphere diameter between interaction sites \( \alpha \) and \( \gamma \).

The type of auxiliary sites under consideration do not interact with any other sites in the system. In other words, \( f_{\alpha i} = f_{ij} = 0 \) (or \( \sigma_{\alpha i} = \sigma_{ij} = 0 \) for hard-sphere interaction sites) for all real sites \( \alpha \) and auxiliary sites \( i \) and \( j \). The PY closure then reduces to

\[ c_{\alpha i}(r) = c_{ij}(r) = 0 \quad (6.106) \]

Note that because, \( \sigma_{\alpha i} = \sigma_{ij} = 0 \), the PY closure does not impose any restrictions on the total correlation functions, \( h_{\alpha i} \) and \( h_{ij} \).

If one writes explicitly the SSOZ equation (see Eq. (2.13)) for the site-site total correlation function between real sites, one finds that

\[ \hat{h}_{\alpha\gamma}(k) = [\hat{w}_{\alpha\sigma}(k)\hat{c}_{\sigma\tau}(k)\hat{w}_{\tau\gamma}(k) + \hat{w}_{\alpha\tau}(k)\hat{c}_{\tau\sigma}(k)\hat{w}_{\sigma\gamma}(k) + \hat{w}_{\alpha\sigma}(k)\hat{c}_{\sigma\delta}(k)\hat{w}_{\delta\gamma}(k)] + [\hat{w}_{\alpha\sigma}(k)\hat{c}_{\sigma\tau}(k)\rho_{\tau\gamma}(k) + \hat{w}_{\alpha\tau}(k)\hat{c}_{\tau\sigma}(k)\rho_{\sigma\gamma}(k) + \hat{w}_{\alpha\sigma}(k)\hat{c}_{\sigma\delta}(k)\rho_{\delta\gamma}(k)] + \hat{w}_{\alpha\sigma}(k)\hat{c}_{\sigma\tau}(k)\rho_{\tau\gamma}(k) + \hat{w}_{\alpha\tau}(k)\hat{c}_{\tau\sigma}(k)\rho_{\sigma\gamma}(k) + \hat{w}_{\alpha\sigma}(k)\hat{c}_{\sigma\delta}(k)\rho_{\delta\gamma}(k) \]

\[ = \hat{w}_{\alpha\sigma}(k)\hat{c}_{\sigma\tau}(k)\hat{w}_{\tau\gamma}(k) + \hat{w}_{\alpha\tau}(k)\hat{c}_{\tau\sigma}(k)\rho_{\sigma\gamma}(k) + \hat{w}_{\alpha\sigma}(k)\hat{c}_{\sigma\delta}(k)\rho_{\delta\gamma}(k) \quad (6.107) \]
Note that all the correlation functions appearing in Eq. (6.107) are between real interaction sites, since none of the indices refers to auxiliary sites. In addition, the closure relation depends solely on the correlations between real interaction sites. Accordingly, the correlations between real sites are independent of the presence of auxiliary sites.

Next, one should verify that there exists a consistent solution for the other correlation functions. For this purpose, let us examine the real site-auxiliary site total correlations functions, that is,

\[
\hat{h}_{i}(k) = \hat{w}_{a\sigma}(k)\hat{c}_{\sigma}(k)\hat{w}_{\tau i}(k) + \hat{w}_{a\tau}(k)\hat{c}_{\tau}(k)\hat{w}_{\sigma i}(k)
\]

\[
+ \hat{w}_{a\sigma}(k)\hat{c}_{\sigma}(k)\hat{w}_{\tau i}(k) + \hat{w}_{a\tau}(k)\hat{c}_{\tau}(k)\hat{w}_{\sigma i}(k)
\]

\[
+ \hat{w}_{a\sigma}(k)\hat{c}_{\sigma}(k)\rho_{\tau i}\hat{h}_{i}(k) + \hat{w}_{a\tau}(k)\hat{c}_{\tau}(k)\rho_{\sigma i}\hat{h}_{i}(k)
\]

\[
= \hat{w}_{a\sigma}(k)\hat{c}_{\sigma}(k)\hat{w}_{\tau i}(k) + \hat{w}_{a\tau}(k)\hat{c}_{\tau}(k)\rho_{\sigma i}\hat{h}_{i}(k) 
\]

\[
= [1 - \hat{w}(k)\hat{c}(k)\rho_{a\sigma}]^{2}\hat{w}_{\sigma}(k)\hat{c}_{\tau}(k)\hat{w}_{\mu i}(k) 
\]

(6.109)

As can be seen from Eq. (6.109), the total correlation functions between real sites and auxiliary sites are fixed by the direct correlation functions between real sites. This is compatible with the closure relation, since it does not pose any constraints on the \( h_{\alpha i} \)'s.

Next, let us examine the total correlation functions between auxiliary sites. The SSOZ equation yields

\[
\hat{h}_{ij}(k) = \hat{w}_{i\sigma}(k)\hat{c}_{\sigma}(k)\hat{w}_{\tau j}(k) + \hat{w}_{a\tau}(k)\hat{c}_{\tau}(k)\hat{w}_{\sigma j}(k)
\]

\[
+ \hat{w}_{i\sigma}(k)\hat{c}_{\sigma}(k)\hat{w}_{\tau j}(k) + \hat{w}_{a\tau}(k)\hat{c}_{\tau}(k)\hat{w}_{\sigma j}(k)
\]

\[
+ \hat{w}_{i\sigma}(k)\hat{c}_{\sigma}(k)\rho_{\tau j}\hat{h}_{ij}(k) + \hat{w}_{a\tau}(k)\hat{c}_{\tau}(k)\rho_{\sigma j}\hat{h}_{ij}(k)
\]

\[
= \hat{w}_{i\sigma}(k)\hat{c}_{\sigma}(k)\hat{w}_{\tau j}(k) + \hat{w}_{i\sigma}(k)\hat{c}_{\sigma}(k)\rho_{\tau j}\hat{h}_{ij}(k) 
\]

(6.110)

Equation (6.110) indicates that the total correlation functions between auxiliary sites
are uniquely specified from knowledge of the direct correlation functions between real sites and the total correlation functions between real and auxiliary sites. It is important to note that the closure relation does not make any statements about $h_{ij}(r)$. If it did, then the results for $h_{ij}$ given in Eq. (6.110) might be incompatible with the constraints imposed by the closure relation.

This completes the proof that the predictions of the SSOZ-PY equation for molecules with hard-sphere interaction sites are not affected by the presence of auxiliary sites.

**Auxiliary Sites in the Context of the CSL Equations**

In this section, I will analyze the influence of auxiliary sites on the CSL equations. As in the previous section, the auxiliary sites under consideration do not interact with any other sites in the system, all real sites are labeled with a Greek index, and all auxiliary sites are labelled with a Latin index.

To begin, let us consider, from a physical stand point, how the $h$-component bonds should behave. For this purpose, let us recall the physical interpretation of the $h$-component bonds. Specifically,

\[ h^\circ_{\alpha\gamma} = \text{total correlation function between a disconnected site of type } \alpha \text{ and a disconnected site of type } \gamma \text{ both at infinite dilution in the bulk fluid.} \]

\[ h^\circ_{\alpha\gamma} + h^l_{\alpha\gamma} = \text{total correlation function between a site of type } \alpha \text{ located within a molecule and a disconnected site of type } \gamma \text{ at infinite dilution in the bulk fluid.} \]

\[ h^\circ_{\alpha\gamma} + h^r_{\alpha\gamma} = \text{total correlation function between a disconnected site of type } \alpha \text{ at infinite dilution and a site of type } \gamma \text{ located within a molecule in the bulk fluid.} \]

\[ h_{\alpha\gamma} = \text{total correlation function between a site of type } \alpha \text{ located within a molecule and a site of type } \gamma \text{ located within a molecule in bulk fluid.} \]

Because an auxiliary site does not interact with any other sites in the system, one
expects that a disconnected auxiliary site should have no correlations with any other site in the system. From the physical interpretation of the \( h \)-component bonds given above, this implies that any correlation function involving a disconnected auxiliary site should be equal to zero. In other words,

\[ h_{ai}(r) = h_{ia}(r) = h_{ij}(r) = 0 \quad (6.111) \]
\[ h_{ai}^l(r) = h_{ij}^l(r) = 0 \quad (6.112) \]
\[ h_{ia}^e(r) = h_{ij}^e(r) = 0 \quad (6.113) \]

and

\[ c_{ai}^e(r) = c_{ia}^e(r) = c_{ij}^e(r) = 0 \quad (6.114) \]
\[ c_{ai}^l(r) = c_{ij}^l(r) = 0 \quad (6.115) \]
\[ c_{ia}^e(r) = c_{ij}^e(r) = 0 \quad (6.116) \]

The \( f \)-bond between an auxiliary site and any other site is equal to zero. For any physically reasonable approximation for the bridge functions, it follows that \( b_{ai}^e, b_{ai}^l, b_{ai}^e, b_{ij}^e, b_{ij}^l, \) and \( b_{ij}^e \) are equal to zero when \( f_{ai} = f_{ij} = 0 \). This can be seen using the same arguments that were used above for the total and direct correlation functions. Using these facts, we see that Eqs. (6.111)–(6.116) satisfy the closure relations for the CSL equations (see Eqs. (6.25)–(6.28)).

I will now proceed to show that Eqs. (6.111)–(6.116) satisfy the CSL equations, as well as make the equations for the interaction site-interaction site correlation functions independent of the auxiliary sites.

By substituting Eqs. (6.111)–(6.116) into the CSL equations (see Eqs. (6.6)–(6.9)), I will show that Eqs. (6.111)–(6.116) do, in fact, satisfy the CSL equations and the corresponding closure relations. Note that in the following derivation, summations over repeated indices are implied. The CSL equations (see Eqs. (6.6)–(6.9)) for the
correlations between interaction sites can be written as

\[
\hat{h}_{\alpha\gamma}(k) = \hat{c}_{\alpha\gamma}(k) + [\hat{c}_{\alpha\sigma}(k)\rho\hat{h}_{\sigma\gamma}(k) + \hat{c}_{\alpha\sigma}(k)\rho\hat{h}_{\sigma\gamma}(k)]
\]

\[
+ [\hat{c}_{\alpha\sigma}(k)\rho\hat{h}_{\sigma\gamma}(k) + \hat{c}_{\alpha\sigma}(k)\rho\hat{h}_{\sigma\gamma}(k)]
\]

\[
+ [\hat{c}_{\alpha\sigma}(k)\rho\hat{h}_{\sigma\gamma}(k) + \hat{c}_{\alpha\sigma}(k)\rho\hat{h}_{\sigma\gamma}(k)]
\]

\[
= \hat{c}_{\alpha\gamma}(k) + \hat{c}_{\alpha\sigma}(k)\rho\hat{h}_{\sigma\gamma}(k) + \hat{c}_{\alpha\sigma}(k)\rho\hat{h}_{\sigma\gamma}(k) + \hat{c}_{\alpha\sigma}(k)\rho\hat{h}_{\sigma\gamma}(k) (6.117)
\]

\[
\hat{h}_{\alpha\gamma}(k) = \hat{c}_{\alpha\gamma}(k) + [\hat{\delta}_{\alpha\sigma}(k)\hat{h}_{\sigma\gamma}(k) + \hat{\delta}_{\alpha\sigma}(k)\hat{h}_{\sigma\gamma}(k)]
\]

\[
+ [\hat{\delta}_{\alpha\sigma}(k)\hat{h}_{\sigma\gamma}(k) + \hat{\delta}_{\alpha\sigma}(k)\hat{h}_{\sigma\gamma}(k)]
\]

\[
+ [\hat{\delta}_{\alpha\sigma}(k)\hat{h}_{\sigma\gamma}(k) + \hat{\delta}_{\alpha\sigma}(k)\hat{h}_{\sigma\gamma}(k)]
\]

\[
= \hat{c}_{\alpha\gamma}(k) + \hat{\delta}_{\alpha\sigma}(k)\hat{h}_{\sigma\gamma}(k) + \hat{\delta}_{\alpha\sigma}(k)\hat{h}_{\sigma\gamma}(k) + \hat{\delta}_{\alpha\sigma}(k)\hat{h}_{\sigma\gamma}(k) (6.118)
\]

\[
\hat{h}_{\alpha\gamma}(k) = \hat{c}_{\alpha\gamma}(k) + [\hat{c}_{\alpha\sigma}(k)\hat{\delta}_{\sigma\gamma}(k) + \hat{c}_{\alpha\sigma}(k)\hat{\delta}_{\sigma\gamma}(k)]
\]

\[
+ [\hat{c}_{\alpha\sigma}(k)\hat{\delta}_{\sigma\gamma}(k) + \hat{c}_{\alpha\sigma}(k)\hat{\delta}_{\sigma\gamma}(k)]
\]

\[
+ [\hat{c}_{\alpha\sigma}(k)\hat{\delta}_{\sigma\gamma}(k) + \hat{c}_{\alpha\sigma}(k)\hat{\delta}_{\sigma\gamma}(k)]
\]

\[
= \hat{c}_{\alpha\gamma}(k) + \hat{c}_{\alpha\sigma}(k)\hat{\delta}_{\sigma\gamma}(k) + \hat{c}_{\alpha\sigma}(k)\hat{\delta}_{\sigma\gamma}(k) + \hat{c}_{\alpha\sigma}(k)\hat{\delta}_{\sigma\gamma}(k) (6.119)
\]

\[
\hat{h}_{\alpha\gamma}(k) = \hat{c}_{\alpha\gamma}(k) + [\hat{c}_{\alpha\sigma}(k)\hat{\delta}_{\sigma\gamma}(k) + \hat{c}_{\alpha\sigma}(k)\hat{\delta}_{\sigma\gamma}(k)]
\]

\[
+ [\hat{\delta}_{\alpha\sigma}(k)\hat{h}_{\sigma\gamma}(k) + \hat{\delta}_{\alpha\sigma}(k)\hat{h}_{\sigma\gamma}(k)]
\]

\[
+ [\hat{c}_{\alpha\sigma}(k)\hat{\delta}_{\sigma\gamma}(k) + \hat{c}_{\alpha\sigma}(k)\hat{\delta}_{\sigma\gamma}(k)]
\]

\[
= \hat{c}_{\alpha\gamma}(k) + \hat{c}_{\alpha\sigma}(k)\hat{\delta}_{\sigma\gamma}(k) + \hat{\delta}_{\alpha\sigma}(k)\hat{h}_{\sigma\gamma}(k) + \hat{\delta}_{\alpha\sigma}(k)\hat{h}_{\sigma\gamma}(k) + \hat{\delta}_{\alpha\sigma}(k)\hat{h}_{\sigma\gamma}(k) (6.120)
\]
An examination of Eqs. (6.117)–(6.120) indicates that they are independent of correlations involving auxiliary sites (no Latin indices are present).

What remains to be shown is that Eqs. (6.111)–(6.116) satisfy the CSL equations for the interaction site-auxiliary site correlations and the auxiliary site-auxiliary site correlations. The CSL equations for the correlations between real and auxiliary sites are given below

\[
\hat{h}_{\alpha j}(k) = \hat{\epsilon}_{\alpha j}(k) + [\epsilon_{\alpha\sigma}(k)\hat{h}_{\sigma j}(k) + \hat{\epsilon}_{\alpha s}(k)\hat{h}_{s j}(k)] + [\epsilon_{\alpha\sigma}(k)\hat{h}_{\sigma j}(k) + \hat{\epsilon}_{\alpha s}(k)\hat{h}_{s j}(k)] + [\epsilon_{\alpha\sigma}(k)\hat{h}_{\sigma j}(k) + \hat{\epsilon}_{\alpha s}(k)\hat{h}_{s j}(k)] = 0 \quad (6.121)
\]

\[
\hat{h}_{\alpha j}(k) = \hat{\epsilon}_{\alpha j}(k) + [\delta_{\alpha\sigma}(k)\hat{h}_{\sigma j}(k) + \delta_{\alpha s}(k)\hat{h}_{s j}(k)] + [\epsilon_{\alpha\sigma}(k)\hat{h}_{\sigma j}(k) + \hat{\epsilon}_{\alpha s}(k)\hat{h}_{s j}(k)] + [\epsilon_{\alpha\sigma}(k)\hat{h}_{\sigma j}(k) + \hat{\epsilon}_{\alpha s}(k)\hat{h}_{s j}(k)] + [\epsilon_{\alpha\sigma}(k)\hat{h}_{\sigma j}(k) + \hat{\epsilon}_{\alpha s}(k)\hat{h}_{s j}(k)] = 0 \quad (6.122)
\]

\[
\hat{h}_{\alpha j}(k) = \hat{\epsilon}_{\alpha j}(k) + [\epsilon_{\alpha\sigma}(k)\hat{h}_{\sigma j}(k) + \hat{\epsilon}_{\alpha s}(k)\hat{h}_{s j}(k)] + [\epsilon_{\alpha\sigma}(k)\hat{h}_{\sigma j}(k) + \hat{\epsilon}_{\alpha s}(k)\hat{h}_{s j}(k)] + [\epsilon_{\alpha\sigma}(k)\hat{h}_{\sigma j}(k) + \hat{\epsilon}_{\alpha s}(k)\hat{h}_{s j}(k)] + [\epsilon_{\alpha\sigma}(k)\hat{h}_{\sigma j}(k) + \hat{\epsilon}_{\alpha s}(k)\hat{h}_{s j}(k)] = 0 \quad (6.123)
\]

\[
\hat{h}_{\alpha j}(k) = \hat{\epsilon}_{\alpha j}(k) + [\epsilon_{\alpha\sigma}(k)\hat{h}_{\sigma j}(k) + \hat{\epsilon}_{\alpha s}(k)\hat{h}_{s j}(k)] + [\epsilon_{\alpha\sigma}(k)\hat{h}_{\sigma j}(k) + \hat{\epsilon}_{\alpha s}(k)\hat{h}_{s j}(k)] + [\epsilon_{\alpha\sigma}(k)\hat{h}_{\sigma j}(k) + \hat{\epsilon}_{\alpha s}(k)\hat{h}_{s j}(k)] + [\epsilon_{\alpha\sigma}(k)\hat{h}_{\sigma j}(k) + \hat{\epsilon}_{\alpha s}(k)\hat{h}_{s j}(k)] = 0 \quad (6.124)
\]
\[ \begin{align*}
+ [\hat{c}^b_{a\sigma}(k)\rho\hat{h}^{s_{a\sigma}}_{b}(k)]
& + \hat{c}^b_{a\sigma}(k)\rho\hat{h}^{s_{a\sigma}}_{b}(k) + \hat{c}^i_{a\sigma}(k)\rho\hat{h}^{b}_{a\sigma}(k) \\
& = \hat{c}^b_{a\sigma}(k) + \hat{c}^i_{a\sigma}(k)\hat{\sigma}_{a\sigma}(k) \\
& + \hat{\sigma}_{a\sigma}(k)\hat{h}^{s_{a\sigma}}_{b}(k) + \hat{c}^i_{a\sigma}(k)\rho\hat{h}^{s_{a\sigma}}_{b}(k) \\
& + \hat{c}^b_{a\sigma}(k)\rho\hat{h}^{s_{a\sigma}}_{b}(k) + \hat{c}^i_{a\sigma}(k)\rho\hat{h}^{s_{a\sigma}}_{b}(k) \\
&= \hat{c}^b_{a\sigma}(k) + \hat{c}^i_{a\sigma}(k)\hat{\sigma}_{a\sigma}(k) \\
& + \hat{\sigma}_{a\sigma}(k)\hat{h}^{s_{a\sigma}}_{b}(k) + \hat{c}^i_{a\sigma}(k)\rho\hat{h}^{s_{a\sigma}}_{b}(k) \\
& + \hat{c}^b_{a\sigma}(k)\rho\hat{h}^{s_{a\sigma}}_{b}(k) + \hat{c}^i_{a\sigma}(k)\rho\hat{h}^{s_{a\sigma}}_{b}(k) \\
&= 0 \\
&= 0 \\
&= 0 \\
&= 0 \\
&= 0 \\
&= 0 \\
&= 0 \\
&= \hat{c}^b_{i\sigma}(k) + \hat{c}^i_{i\sigma}(k)\hat{\sigma}_{i\sigma}(k) + \hat{\sigma}_{i\sigma}(k)\hat{h}^{s_{i\sigma}}_{b}(k) \\
& + \hat{c}^b_{i\sigma}(k)\rho\hat{h}^{s_{i\sigma}}_{b}(k) + \hat{c}^i_{i\sigma}(k)\rho\hat{h}^{s_{i\sigma}}_{b}(k) \\
& + \hat{\sigma}_{i\sigma}(k)\hat{h}^{s_{i\sigma}}_{b}(k) + \hat{c}^i_{i\sigma}(k)\rho\hat{h}^{s_{i\sigma}}_{b}(k) \\
& + \hat{c}^b_{i\sigma}(k)\rho\hat{h}^{s_{i\sigma}}_{b}(k) + \hat{c}^i_{i\sigma}(k)\rho\hat{h}^{s_{i\sigma}}_{b}(k) \\
&= 0 \\
&= \hat{c}^b_{i\sigma}(k) + \hat{c}^i_{i\sigma}(k)\hat{\sigma}_{i\sigma}(k) + \hat{\sigma}_{i\sigma}(k)\hat{h}^{s_{i\sigma}}_{b}(k) \\
& + \hat{c}^b_{i\sigma}(k)\rho\hat{h}^{s_{i\sigma}}_{b}(k) + \hat{c}^i_{i\sigma}(k)\rho\hat{h}^{s_{i\sigma}}_{b}(k) \\
& + \hat{\sigma}_{i\sigma}(k)\hat{h}^{s_{i\sigma}}_{b}(k) + \hat{c}^i_{i\sigma}(k)\rho\hat{h}^{s_{i\sigma}}_{b}(k) \\
& + \hat{c}^b_{i\sigma}(k)\rho\hat{h}^{s_{i\sigma}}_{b}(k) + \hat{c}^i_{i\sigma}(k)\rho\hat{h}^{s_{i\sigma}}_{b}(k) \\
&= 0 \\
&= \hat{c}^b_{i\sigma}(k) + \hat{c}^i_{i\sigma}(k)\hat{\sigma}_{i\sigma}(k) + \hat{\sigma}_{i\sigma}(k)\hat{h}^{s_{i\sigma}}_{b}(k) \\
& + \hat{c}^b_{i\sigma}(k)\rho\hat{h}^{s_{i\sigma}}_{b}(k) + \hat{c}^i_{i\sigma}(k)\rho\hat{h}^{s_{i\sigma}}_{b}(k) \\
& + \hat{\sigma}_{i\sigma}(k)\hat{h}^{s_{i\sigma}}_{b}(k) + \hat{c}^i_{i\sigma}(k)\rho\hat{h}^{s_{i\sigma}}_{b}(k) \\
& + \hat{c}^b_{i\sigma}(k)\rho\hat{h}^{s_{i\sigma}}_{b}(k) + \hat{c}^i_{i\sigma}(k)\rho\hat{h}^{s_{i\sigma}}_{b}(k) \\
&= 0
\end{align*} \]

Note that these equations are consistent with Eqs. (6.111)-(6.116).

For the auxiliary site-auxiliary site correlations, one finds that the CSL equations can be written as

\[ \hat{h}^o_{ij}(k) = \hat{c}^o_{ij}(k) + \hat{c}^o_{i\sigma}(k)\hat{\sigma}_{ij}(k) + \hat{\sigma}_{ij}(k)\hat{h}^{o}_{i\sigma}(k) \]
\[ + [\hat{c}^o_{i\sigma}(k)\rho\hat{h}^{o}_{i\sigma}(k) + \hat{c}^o_{i\sigma}(k)\rho\hat{h}^{o}_{i\sigma}(k)] \]
\[ + [\hat{c}^o_{i\sigma}(k)\rho\hat{h}^{o}_{i\sigma}(k) + \hat{c}^o_{i\sigma}(k)\rho\hat{h}^{o}_{i\sigma}(k)] \]
\[ = 0 \quad (6.125) \]

\[ \hat{h}^l_{ij}(k) = \hat{c}^l_{ij}(k) + [\hat{c}^l_{i\sigma}(k)\hat{h}^{l}_{i\sigma}(k) + \hat{h}^{l}_{i\sigma}(k)\hat{c}^l_{i\sigma}(k)] \]
\[ + [\hat{c}^l_{i\sigma}(k)\rho\hat{h}^{l}_{i\sigma}(k) + \hat{c}^l_{i\sigma}(k)\rho\hat{h}^{l}_{i\sigma}(k)] \]
\[ + [\hat{c}^l_{i\sigma}(k)\rho\hat{h}^{l}_{i\sigma}(k) + \hat{c}^l_{i\sigma}(k)\rho\hat{h}^{l}_{i\sigma}(k)] \]
\[ = 0 \quad (6.126) \]

\[ \hat{h}^t_{ij}(k) = \hat{c}^t_{ij}(k) + [\hat{c}^t_{i\sigma}(k)\hat{h}^{t}_{i\sigma}(k) + \hat{h}^{t}_{i\sigma}(k)\hat{c}^t_{i\sigma}(k)] \]
\[ + [\hat{c}^t_{i\sigma}(k)\rho\hat{h}^{t}_{i\sigma}(k) + \hat{c}^t_{i\sigma}(k)\rho\hat{h}^{t}_{i\sigma}(k)] \]
\[ + [\hat{c}^t_{i\sigma}(k)\rho\hat{h}^{t}_{i\sigma}(k) + \hat{c}^t_{i\sigma}(k)\rho\hat{h}^{t}_{i\sigma}(k)] \]
\[ = 0 \quad (6.127) \]

\[ \hat{h}^b_{ij}(k) = \hat{c}^b_{ij}(k) + [\hat{c}^b_{i\sigma}(k)\hat{h}^{b}_{i\sigma}(k) + \hat{h}^{b}_{i\sigma}(k)\hat{c}^b_{i\sigma}(k)] \]
These equations are also consistent with Eqs. (6.111)-(6.116).

Accordingly, the CSL equations with a general approximate closure will yield a theory which is unaffected by the presence of auxiliary sites. The flow of the proof presented above seems to indicate that it is the presence of illegal diagrams which causes the SSOZ equation to have an unphysical dependence on this type of auxiliary sites.

### 6.6 Concluding Remarks

In this chapter, I have reviewed a rigorous formalism for predicting the structural and thermodynamic properties of interaction site fluids, known as the Chandler-Silbey-Ladanyi equations. Along with these equations, I have also presented the form of the exact closure relation as well as two approximate closure relations (HNC and PY).

In addition, I have developed analytical expressions for computing the residual Helmholtz free energy and the residual chemical potential from the correlation functions. When the correlation functions are given by the CSL equations, the residual Helmholtz free energy was found to be stationary with respect to variations in the site-site total, direct, and thermal correlation functions.

Several aspects of the CSL equations were also analyzed. The constraints of maintaining the connectivity between sites within a molecule were found to pose restrictions on the form of the correlation functions. While these connectivity constraints and the local neutrality conditions are satisfied by correlation functions computed from the CSL equations with the exact closure, they are not necessarily satisfied by
the correlation functions when an approximate closure is used. Instead, it is found that the Stillinger-Lovett conditions for ionic fluids are satisfied. The violation of the connectivity constraints forces the $h$-component bonds to become short-ranged. Furthermore, it causes the predicted dielectric constant to become infinite.

Finally, I analyzed the effect of auxiliary sites on the predictions of the SSOZ and CSL equations. In general, the presence of auxiliary sites will affect the predictions of the SSOZ equation. However, when the SSOZ equation is combined with the PY closure and applied to molecules with hard-sphere interaction sites, auxiliary site have no influence. Moreover, auxiliary sites were found to have no effect on the CSL equations with a general approximate closure when applied to any system.

The remaining chapters of this thesis deal with the development of better approximate closure relations for the CSL equations. The predictions from the resulting integral equations will be compared with the predictions of the SSOZ equation, as well as with the results of computer simulations.
Chapter 7

The Chandler-Silbey-Ladanyi Equations: Application to Diatomic Molecules

7.1 Introduction and Overview

The SSOZ equation has been fairly successful in predicting the structural and thermodynamic properties of interaction site fluids such as water (see Chapter 3) and hydrocarbons in water (see Chapter 4). The major problem with this formalism, however, is that when the known approximate equations fail to provide physically reasonable results, such as in the case of the Lennard-Jones surfactant model system discussed in Chapter 5, there exists no straightforward method to improve their accuracy.

This difficulty led to the development and application of a new set of integral equations for interaction site fluids known as the Chandler-Silbey-Chandler (CSL) equations$^{131}$ (see Chapter 6). However, initial studies$^{133}$ indicated that the CSL equations were less accurate than the SSOZ equation. As a result, these equations have not received sufficient attention in the past. In this chapter, I will analyze in detail the range of applicability of the CSL equations and compare it to that of the SSOZ equation. In addition, I will present a new method to compute better
approximations for the bridge functions, as well as examine the influence of these functions on the predictions of the CSL equations.

This chapter is structured as follows. In Section 7.2, I present a discussion of the bridge functions, as well as of a method for computing approximations to the bridge functions. In Section 7.3, I compare the predictions of the pair correlation functions corresponding to various homonuclear diatomic Lennard-Jones fluids for various integral equations. In Section 7.4, I apply the CSL and SSOZ equations to polar and nonpolar heteronuclear diatomic molecules and compare their predictive capabilities. Finally, in Section 7.5, I present a summary of the key findings of this chapter.

7.2 The Bridge Functions

The bridge functions are complicated functionals of the Mayer f-functions. The precise dependence of the bridge functions on the Mayer f-functions and the density is known in diagrammatic terms. Specifically,

\[ b^i(r) = \text{subset of all diagrams in } h^i(r) \text{ which contain no } f\text{-bonds between root circles, no articulation root pairs, and no nodal circles,} \]

where \( h^i(r) \) and \( b^i(r) \) (i=\( o, 1, r, \text{ or } b \)) are the total correlation functions and the bridge functions, respectively (see Chapter 6). An articulation root pair is a pair of root circles that, when removed from a diagram, breaks the diagram into, at least, two disconnected parts where, at least, one of them does not contain a root circle. For example, the pair of root circles in the third diagram on the fourth row of Figure 6-1 is an articulation root pair. A nodal circle is a circle through which all paths between a pair of root circles pass. For example, the black circle in the first diagram on the second row of Figure 6-1 is a nodal circle. For an explanation of the application of graph theory to both simple fluids and interaction site fluids, see Refs. 19 and 27, respectively.
In principle, the integrals corresponding to each of the diagrams contributing to \( b'(r) \) can be evaluated and summed up in order to obtain the bridge functions. In practice, however, two main problems prevent the actual implementation of this procedure. The first problem involves the enumeration of the diagrams which contribute to \( b' \), since the number of diagrams is, in fact, infinite. In addition, the number of diagrams present at each order of the density increases rapidly as the order of the density increases. The second problem involves the actual computation of the various integrals corresponding to each of the diagrams. Indeed, as the order of the diagrams increases, the dimension of the corresponding integrals increases by at least three (or even by more for multisite molecules) for each order of the density. For these reasons, the bridge functions cannot be evaluated exactly, and approximations must be made.

One of the simplest approximations is to neglect the bridge functions altogether, which leads to the well-known HNC closure (see Chapter 6). This approximation is fairly successful in the case of simple fluids. On the other hand, the HNC approximation for interaction site fluids is not as good. This reflects the fact that while the OZ-HNC equation is exact to first order in the density, the CSL-HNC equations are not exact even at zero density because the bridge functions \( b' \), \( b^r \), and \( b^b \) include diagrams which are zeroth-order in the density and higher. Note that for molecules having less than three interaction sites, the bridge functions \( b' \) and \( b^r \) do not contain any diagrams which are zeroth order in the density, while the function \( b^o \) contains diagrams which are first order and higher in the density. On the other hand, the bridge functions corresponding to simple fluids contain diagrams which are second order and higher in the density. Since an integral equation becomes more accurate at higher orders in the density, its predictive capabilities improve as higher-order terms are included. This is similar to what happens in the case of the virial expansion for the equation of state, which becomes more accurate as higher order virial coefficients are included. For this reason, the predictions of the CSL-HNC equations for interaction site fluids are not expected to be as accurate as those of the OZ-HNC equation for simple fluids.
The diagrams contributing to the bridge functions can be expressed as a power series in density. Therefore, the next level of approximation to the CSL- HNC equations is to expand the bridge functions in powers of the density and compute the low-order terms. Mathematically, this involves writing the bridge functions as follows

\[ b^0_{\alpha\gamma}(r) = b^{0(0)}_{\alpha\gamma}(r) + \rho b^{0(1)}_{\alpha\gamma}(r) + \ldots \]  
\[ b^i_{\alpha\gamma}(r) = b^{i(0)}_{\alpha\gamma}(r) + \rho b^{i(1)}_{\alpha\gamma}(r) + \ldots \]  
\[ b^b_{\alpha\gamma}(r) = b^{b(0)}_{\alpha\gamma}(r) + \rho b^{b(1)}_{\alpha\gamma}(r) + \ldots \]

and computing the functions \( b^{i(0)}_{\alpha\gamma}, b^{i(1)}_{\alpha\gamma}, \) etc., for \( i = 0, 1, r, \) or \( b. \) Note that the superscript in parentheses denotes the order of the density. Note also that \( b^r_{\alpha\gamma} = b^i_{\alpha\gamma}, \) and, therefore, in the remainder of this chapter, I will not present any equations referring to \( b^r. \) To compute the bridge functions, the various bridge diagrams need to be enumerated. In the case of interaction site fluids, the number of bridge diagrams increases rapidly with the number of interaction sites present on the molecules.

In order to calculate the low-order contributions to the bridge functions (\( b^{0(0)}_{\alpha\gamma}, b^{i(1)}_{\alpha\gamma}, \) etc.), I will develop a method to rewrite the diagrams in such a way that their number does not increase with the number of interaction sites, although the complexity (dimensionality) of each diagram may increase. This method is based on the observation that the interaction site diagrams arise from molecular diagrams. Note that interaction site diagrams deal explicitly with the actual sites that make up the molecules, and account for the individual interactions between sites on different molecules. On the other hand, molecular diagrams treat each molecule as a single entity and account for interactions between entire molecules.

I begin by writing the bridge functions in terms of the thermal, \( w^i, \) and chain, \( t^i, \) correlation functions as defined in Chapter 6. At zeroth-order in the density, the bridge functions are given by (see Eqs. (6.29)-(6.32))

\[ b^{0(0)}_{\alpha\gamma}(r) = 0 \]  
\[ b^{i(0)}_{\alpha\gamma}(r) = w^{i(0)}_{\alpha\gamma}(r) - t^{i(0)}_{\alpha\gamma}(r) \]
The first-order bridge functions are given by

\[ b^{\beta(0)}(r) = w^{\beta(0)}_{a\gamma}(r) - t^{\beta(0)}_{a\gamma}(r) \]  
\[ (7.6) \]

\[ b^{\beta(1)}(r) = w^{\beta(1)}_{a\gamma}(r) - t^{\beta(1)}_{a\gamma}(r) \]  
\[ (7.7) \]

\[ b^{\beta(1)}(r) = w^{\beta(1)}_{a\gamma}(r) - t^{\beta(1)}_{a\gamma}(r) \]  
\[ (7.8) \]

\[ b^{\beta(1)}(r) = w^{\beta(1)}_{a\gamma}(r) - t^{\beta(1)}_{a\gamma}(r) \]  
\[ (7.9) \]

In order to simplify the computation of the thermal correlation functions, \( w^i_{a\gamma}(r) \) (i=o, l, r, b), I rewrite these functions in terms of the indirect correlation functions, \( y^i_{a\gamma}(r) \) (i=o, l, r, b), using the following definitions

\[ y^o_{a\gamma}(r) = e^{w^o_{a\gamma}(r)} \]  
\[ (7.10) \]

\[ y^o_{a\gamma}(r) + y^l_{a\gamma}(r) = e^{w^o_{a\gamma}(r)}[1 + w^l_{a\gamma}(r)] \]  
\[ (7.11) \]

\[ y^{b}_{a\gamma}(r) = e^{w^b_{a\gamma}(r)} \{ [1 + w^{i}_{a\gamma}(r)][1 + w^{r}_{a\gamma}(r)] + w^{b}_{a\gamma}(r) \} \]  
\[ (7.12) \]

where \( y_{a\gamma}(r) = y^o_{a\gamma}(r) + y^l_{a\gamma}(r) + y^r_{a\gamma}(r) + y^b_{a\gamma}(r) \).

Expanding the indirect and thermal correlation functions in Eqs. (7.10)–(7.12) in powers of the density, and equating terms of the same order in density, one finds that the zeroth-order thermal correlation functions are given by

\[ w^{o(0)}_{a\gamma}(r) = 0 \]  
\[ (7.13) \]

\[ w^{l(0)}_{a\gamma}(r) = y^{l(0)}_{a\gamma}(r) \]  
\[ (7.14) \]

\[ w^{b(0)}_{a\gamma}(r) = y^{(0)}_{a\gamma}(r) - [1 + y^{(0)}_{a\gamma}(r)][1 + y^{r(0)}_{a\gamma}(r)] \]  
\[ (7.15) \]

and that the first-order thermal correlation functions are given by

\[ w^{o(1)}_{a\gamma}(r) = y^{o(1)}_{a\gamma}(r) \]  
\[ (7.16) \]

\[ w^{l(1)}_{a\gamma}(r) = y^{o(1)}_{a\gamma}(r) + y^{l(1)}_{a\gamma}(r) - w^{o(1)}_{a\gamma}(r)[1 + w^{l(0)}_{a\gamma}(r)] \]  
\[ (7.17) \]

\[ w^{b(1)}_{a\gamma}(r) = y^{l(1)}_{a\gamma}(r) - w^{b(1)}_{a\gamma}(r)[1 + w^{r(0)}_{a\gamma}(r)] \]
\[-[1 + w_{\alpha \gamma}^{i(0)}(r)]w_{\alpha \gamma}^{r(1)}(r)\]  

(7.18)

The indirect correlation functions at each order in the density can be written as a sum of integrals, each of which can be represented by a diagram. To obtain these diagrams, I first examine those which contribute to the molecular total correlation function. These diagrams are typically written in terms of molecular \( f \)-bonds, where \( f(r) = e(r) - 1 \), but it is more convenient in this case to use molecular \( e \)-bonds. The molecular \( e \)-bond, \( e(R_1, R_2) = \exp[-\beta u(R_1, R_2)] \), can then be written as a product of site-site \( e \)-bonds, \( e_{\alpha \gamma}(r) = \exp[-\beta u_{\alpha \gamma}(r)] \), as follows

\[ e(R_1, R_2) = \prod_{\alpha \gamma} e_{\alpha \gamma}(r_1^\alpha, r_2^\gamma) \]  

(7.19)

where \( R_1 \) (\( R_2 \)) denotes the position and orientation of molecule 1 (2), and \( r_1^\alpha \) (\( r_2^\gamma \)) denotes the position of site \( \alpha \) (\( \gamma \)) on molecule 1 (2). This is depicted diagrammatically in Figure 7-1 for a system of diatomic molecules. Note that Eq. (7.19) is a direct manifestation of the fact that for an interaction site fluid, the interaction potential between two molecules, \( u(R_1, R_2) \), can be written as

\[ u(R_1, R_2) = \sum_{\alpha \gamma} u_{\alpha \gamma}(r_1^\alpha, r_2^\gamma) \]  

(7.20)

where \( u_{\alpha \gamma}(r_1^\alpha, r_2^\gamma) \) is the interaction potential between sites \( \alpha \) and \( \gamma \).

To obtain the interaction site diagram which contributes to the site-site correlation function from the corresponding molecular diagram, one just integrates over all sites which are not chosen to be root sites. Note that root sites are those sites between which one wants to know the correlations. An illustration of this procedure is presented in Figure 7-2. Beginning with the molecular diagram on the left-hand side of Figure 7-2, one expands the molecular circles to \( s \)-component bonds, and the molecular \( e \)-bonds to site-site \( e \)-bonds. In order to obtain the site-site correlation function between two sites, the bottom two white circles of the second diagram are chosen to be root circles, and the remaining white circles are darkened.
Figure 7-1: The dependence of the molecular \( e \)-bond on the site-site \( e \)-bonds for a system of diatomic molecules. The thick dashed line represents the molecular \( e \)-bond, the thin dashed lines represent the site-site \( e \)-bonds, and the wavy lines represent \( s \)-bonds (see Eq. 6.10). The large white circles represent molecular root sites, and the small white circles represent interaction site root sites.

Figure 7-2: Illustration of the procedure involved in obtaining an interaction site diagram from a molecular diagram. The notation is the same as that in Figure 7-1.
Figure 7-3: Diagrams contributing to the zeroth-order molecular pair correlation function, \( g^{(0)}(R_1, R_2) \), and the zeroth-order indirect correlation functions. The thick dashed line represents a molecular e-bond, the thin dashed lines represent site-site e-bonds, and the wavy lines represent s-bonds. The white circles represent root sites, and the black circles represent field sites.

Using this procedure, one can obtain the diagrams which contribute to the site-site total correlation function from the diagrams which contribute to the total correlation function. Finally, to obtain the diagrams which contribute to the site-site indirect correlation function, one employs the following definition

\[
y^i(r) = \delta_{i,o} + \text{subset of all diagrams in } h^i(r) \text{ which contain no } f \text{-bonds between root circles},
\]

where \( i = o, l, r, \) or b. The diagrams contributing to the zeroth-order indirect correlation functions are shown in Figure 7-3, and those contributing to the first-order indirect correlation functions are shown in Figure 7-4.

The chain functions can also be written as a sum of diagrams. To determine the relevant diagrams, I first rewrite the CSL equations (see Eqs. (6.6)–(6.9)) as

\[
\begin{align*}
\hat{\delta}^o(k) &= \hat{c}^o(k)\rho \hat{h}^o(k) + \hat{c}^o(k)\rho \hat{h}^l(k) + \hat{c}^r(k)\rho \hat{h}^o(k) \\
\hat{c}^l(k) &= \hat{s}(k)\hat{h}^o(k) + \hat{c}^b(k)\hat{h}^o(k) + \hat{c}^l(k)\rho \hat{h}^o(k) + \hat{c}^l(k)\rho \hat{h}^l(k) \\
\hat{c}^b(k) &= \hat{c}^l(k)\hat{s}(k) + \hat{s}(k)\hat{h}^o(k) + \hat{c}^l(k)\rho \hat{h}^o(k) + \hat{c}^l(k)\rho \hat{h}^l(k) + \hat{c}^b(k)\rho \hat{h}^r(k)
\end{align*}
\]
Expanding Eqs. (7.21)–(7.23) in powers of the density, and collecting terms of zeroth-order in the density yields

\[ \dot{\hat{\alpha}}^{(0)}(k) = 0 \quad (7.24) \]

\[ \dot{\hat{\iota}}^{(0)}(k) = \dot{s}(k)\hat{h}_{\alpha}(0)(k) \quad (7.25) \]

\[ \dot{\hat{b}}^{(0)}(k) = \dot{\bar{\iota}}^{(0)}(k)\hat{s}(k) + \dot{s}(k)\hat{h}_{\bar{\iota}}(0)(k) \quad (7.26) \]

Collecting terms of first-order in the density yields

\[ \dot{\hat{\alpha}}^{(1)}(k) = \dot{\bar{\iota}}^{(0)}(k)\hat{h}_{\alpha}(0)(k) + \dot{\iota}^{(0)}(k)\hat{h}_{\iota}(0)(k) + \dot{\bar{\iota}}^{(0)}(k)\hat{h}_{\bar{\iota}}(0)(k) + \dot{\bar{\iota}}^{(1)}(k)\hat{h}_{\bar{\iota}}(0)(k) \quad (7.27) \]

\[ \dot{\hat{\iota}}^{(1)}(k) = \dot{s}(k)\hat{h}_{\alpha}(0)(k) + \dot{\iota}^{(0)}(k)\hat{h}_{\iota}(0)(k) + \dot{\bar{\iota}}^{(0)}(k)\hat{h}_{\bar{\iota}}(0)(k) + \dot{\bar{\iota}}^{(0)}(k)\hat{h}_{\bar{\iota}}(0)(k) \quad (7.28) \]

\[ \dot{\hat{b}}^{(1)}(k) = \dot{\bar{\iota}}^{(0)}(k)\hat{s}(k) + \dot{s}(k)\hat{h}_{\bar{\iota}}(0)(k) + \dot{\bar{\iota}}^{(0)}(k)\hat{h}_{\bar{\iota}}(0)(k) + \dot{\bar{\iota}}^{(0)}(k)\hat{h}_{\bar{\iota}}(0)(k) + \dot{\bar{\iota}}^{(0)}(k)\hat{h}_{\bar{\iota}}(0)(k) \quad (7.29) \]
Substituting the diagrammatic expansions for the site-site total correlation functions (see Section 6.2) in Eqs. (7.24)-(7.29), one obtains the diagrams which contribute to the chain functions at zeroth- and first-order in the density. The resulting diagrams which contribute to the chain functions for diatomic molecules at zeroth-order in the density are shown in Figure 7-5, and those which contribute at first-order are shown in Figure 7-6. Note that for molecules having more than two interaction sites, the number of diagrams does not increase, although the complexity (dimensionality) of each diagram increases.

Finally, substituting the diagrams which contribute to the thermal correlation functions and the chain functions into Eqs. (7.4)-(7.9) yields the diagrams which contribute to the zeroth-order and first-order bridge functions (not shown due to space limitations).

So far, I have discussed a procedure for specifying the diagrams with contribute to the zeroth-order and first-order bridge functions. Next, these diagrams must be converted into integrals having the proper symmetry number, namely, the proper numerical prefactor multiplying each diagram. For complete details on this procedure, the reader is referred to Ref. 27. The integrals which appear at zeroth-order are at
\[ t^{(0)}(r) = \]
\[ t^{(n)}(r) = \]

Figure 7-6: Diagrams contributing to the first-order chain functions for diatomic molecules. The notation is the same as that in Figure 7-5.
most three dimensional. At first-order, the integrals are six dimensional and lower. These integrals are performed using a Monte Carlo integration technique\textsuperscript{149} for each value of $r$. In principle, the higher-order contributions to the bridge functions can also be computed using the method which I have outlined, but the calculations become intractable fairly quickly.

Next, I will apply the formalism discussed above to three model systems: (i) homonuclear diatomic Lennard-Jones molecules, (ii) nonpolar heteronuclear diatomic Lennard-Jones molecules, and (iii) polar heteronuclear diatomic Lennard-Jones molecules.

### 7.3 Homonuclear Diatomic Lennard-Jones Molecules

One of the simplest systems to model consists of diatomic molecules having two identical Lennard-Jones atoms rigidly connected to each other. The Lennard-Jones interaction potential, $u(r)$, is given by

$$u(r) = 4\epsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^{6} \right]$$

(7.30)

where $\epsilon$ characterizes the depth of the attractive interaction, and $\sigma$ characterizes the width of the repulsive core. Three parameters are needed to uniquely specify the state of a system of homonuclear diatomic Lennard-Jones molecules: (i) the reduced temperature, $T^* = k_BT/\epsilon$, (ii) the reduced density, $\rho^* = \rho \sigma^3$, and (iii) the reduced bond length, $l^* = l/\sigma$. The structure and thermodynamics of these systems have been studied in the past using the SSOZ equation\textsuperscript{50, 51, 49, 135} as well as computer simulations.\textsuperscript{150, 151, 152, 153}

As shown in Chapter 6, in the extended-atom (ea) limit, the bond lengths become infinitely long, and therefore all the interaction sites are disconnected and the interaction site fluid reduces to a simple fluid. In this limit, the CSL-HNC equations reduce to the OZ-HNC equation, and the SSOZ-PY equation reduces to the OZ-PY
equation. Note that both the OZ-HNC and OZ-PY equations work fairly well for simple fluids. On the other hand, in the united-atom (ua) limit, where all the bond lengths are equal to zero and again the system reduces to a simple fluid, neither of these integral equations reduces to a simple fluid equation. In view of these arguments, both the CSL and the SSOZ equations are expected to perform better for systems having longer bond lengths, that is, as the ea limit is approached.

I first solved the CSL-HNC equations and the SSOZ-PY equation at various values of $T^*$, $\rho^*$, and $l^*$ to assess the range over which each of the integral equations yields accurate predictions of the fluid structure, as well as to identify which equation performs better. Both the CSL-HNC and the SSOZ-HNC equations were solved using an extension of the method developed by Labik et al. The grid spacing was 0.025$\sigma$ with 1024 grid points. The long-ranged interactions were handled using the method of Ng. For more details, see Appendix C.

To determine the accuracy of the predictions of the CSL-HNC and SSOZ-PY equations, I also performed computer simulations using the NVT Metropolis Monte Carlo method. The system consisted of 108 molecules with a potential cutoff of 3$\sigma$. Each simulation was started with an equilibration run of 1000 passes, and each pair correlation function was obtained using a run of 30000 steps.

In Figures 7-7-7-11, I show the predicted site-site pair correlation functions for homonuclear diatomic Lennard-Jones systems having a bond length, $l^* = 0.603$, for reduced densities ranging from $\rho^* = 0.1$ to $\rho^* = 0.5$ at $T^* = 3.0$. The solid lines are the predictions of the CSL-HNC equations, the dashed lines are the predictions of the SSOZ-PY equation, and the circles represent the results of Monte Carlo simulations. At the higher densities (above the critical density, $\rho^*_c \approx 0.18$ for this particular system), the SSOZ-PY predictions tend to be in better agreement with the simulation results than those of the CSL-HNC equations. However, as the density decreases, the SSOZ-PY equation tends to overpredict the pair correlation function, while the CSL-HNC equations tend to yield more accurate estimates. Examining reduced temperatures other than $T^* = 3.0$ and bond lengths other than $l^* = 0.603$ leads to a similar conclusion regarding the dependence on $\rho^*$. To summarize, for homonuclear
Figure 7-7: Predicted site-site pair correlation function for homonuclear diatomic Lennard-Jones molecules at $T^* = 3.0$, $\rho^* = 0.1$, and $l^* = 0.603$: (i) predicted using the CSL-HNC equations (solid line), (ii) predicted using the SSOZ-PY equation (dashed line), and (iii) predicted from Monte Carlo simulations (circles).

diatomic fluids, the CSL-HNC equations will yield better predictions for the site-site pair correlation function than the SSOZ-PY equation when $\rho^* < \rho_c^*$, and the converse is true when $\rho^* > \rho_c^*$.

Next, I examined the effect of bond length on the predictive capabilities of the CSL and SSOZ equations. In Figures 7-11–7-13, I show the predicted site-site pair correlation functions of homonuclear diatomic Lennard-Jones molecules having bond lengths, $l^* = 0.603$, 0.329, and 0.793, respectively. Note that varying $l^*$ actually changes the phase behavior of the system, including its critical density and critical temperature. For each of the systems considered, $\rho^*$ and $T^*$ were chosen such that each system was in the liquid regime with a density well above the critical density. Accordingly, the SSOZ-PY equation is expected to perform better than the CSL-HNC equations, which is indeed the case. However, it is interesting to note that the predictions of the CSL-HNC equations improve significantly as $l^*$ increases. On the other hand, the predictive capabilities of the SSOZ-PY equation seem to improve as
Figure 7-8: Predicted site-site pair correlation function for homonuclear diatomic Lennard-Jones molecules at $T^* = 3.0$, $\rho^* = 0.2$, and $l^* = 0.603$. The notation is the same as that in Figure 7-7.

Figure 7-9: Predicted site-site pair correlation function for homonuclear diatomic Lennard-Jones molecules at $T^* = 3.0$, $\rho^* = 0.3$, and $l^* = 0.603$. The notation is the same as that in Figure 7-7.
Figure 7-10: Predicted site-site pair correlation function for homonuclear diatomic Lennard-Jones molecules at $T^* = 3.0$, $\rho^* = 0.4$, and $l^* = 0.603$. The notation is the same as that in Figure 7-7.

Figure 7-11: Predicted site-site pair correlation function for homonuclear diatomic Lennard-Jones molecules at $T^* = 3.0$, $\rho^* = 0.5$, and $l^* = 0.603$. The notation is the same as that in Figure 7-7.
Figure 7-12: Predicted site-site pair correlation function for homonuclear diatomic Lennard-Jones molecules at $T^* = 3.0$, $\rho^* = 0.55$, and $l^* = 0.329$. The notation is the same as that in Figure 7-7.

$I^*$ decreases. Once again, this trend for the dependence on $l^*$ remains valid for other values of $\rho^*$ and $T^*$.

Finally, I examined the effect of reduced temperature, $T^*$, on the predictions of the CSL-HNC and SSOZ-PY equations. Note that as the reduced temperature increases, the attractive interaction becomes less important, and the system behaves more like a fluid of symmetric hard dumbbells. In Figures 7-11, 7-14, and 7-15, I show the predicted site-site pair correlation functions for a homonuclear diatomic Lennard-Jones fluid with $\rho^* = 0.5$ and $l^* = 0.603$ for $T^* = 3.0$, 4.0, and 5.0, respectively. It is seen that temperature does not significantly influence the accuracy of the CSL-HNC equations. On the other hand, the predictions of the SSOZ-PY equation improve slightly with increasing temperature.

As mentioned in Sections 6.2 and 7.2, approximations enter the CSL-HNC equations through the neglect of the bridge functions. For simple fluids, the first bridge diagrams enter at second order in the density. However, for molecular fluids, the first bridge diagrams enter already at zeroth order in the density. Accordingly, the
Figure 7-13: Predicted site-site pair correlation function for homonuclear diatomic Lennard-Jones molecules at $T^* = 2.0$, $\rho^* = 0.5$, and $l^* = 0.793$. The notation is the same as that in Figure 7-7.

Figure 7-14: Predicted site-site pair correlation function for homonuclear diatomic Lennard-Jones molecules at $T^* = 4.0$, $\rho^* = 0.5$, and $l^* = 0.603$. The notation is the same as that in Figure 7-7.
Figure 7-15: Predicted site-site pair correlation function for homonuclear diatomic Lennard-Jones molecules at $T^* = 5.0$, $\rho^* = 0.5$, and $l^* = 0.603$. The notation is the same as that in Figure 7-7.

The first correction to the CSL-HNC equations involves adding the zeroth-order bridge diagrams. The resulting integral equation for interaction site fluids is exact at zero density, which is not the case for either the CSL-HNC or SSOZ-PY equations. The low-order density terms of the bridge functions for a homonuclear diatomic Lennard-Jones fluid at $T^* = 3.0$, $\rho^* = 0.5$, and $l^* = 0.603$ are plotted in Figure 7-16. The solid line is the function $b^{b(0)}$, the dashed line is the function $\rho b^{\rho(1)}$, the dotted line is the function $\rho b^{l(1)}$, and the dash-dotted line is the function $\rho b^{l(1)}$. Recall that $b^{\rho(0)}$ and $b^{l(0)}$ are equal to zero for diatomic fluids and therefore are not plotted. Note that all the bridge functions are essentially zero for $r \geq 2\sigma$, which is consistent with the fact that they are short-ranged.

In Figure 7-17, I plot the predicted site-site pair correlation function for a system of homonuclear diatomic Lennard-Jones molecules at $T^* = 3.0$, $\rho^* = 0.5$, and $l^* = 0.603$. The solid line is the prediction of the CSL-HNC equations, presented earlier in Figure 7-11, the dashed line is the prediction of the CSL-HNC+B(0) equations, which includes the zeroth-order bridge diagrams, the dotted line is the prediction of
the CSL-HNC+B(1) equations, which includes both the zeroth-order and first-order bridge diagrams, the dash-dotted line is the prediction of the SSOZ-PY equation, and the circles represent the results of Monte Carlo simulations. As can be seen, the addition of the zeroth-order bridge functions does not greatly alter the predictions of the CSL equations. The addition of the first-order bridge diagrams, however, significantly improves the accuracy of the CSL equations. It is noteworthy, that the predictions of the CSL-HNC+B(1) equations are in better agreement with the simulation data than the predictions of the SSOZ-PY equation.

In Figure 7.18, I plot the predicted site-site pair correlation function for a system of homonuclear diatomic Lennard-Jones molecules at $T^* = 3.0$, $\rho^* = 0.55$, and $l^* = 0.329$. The predictions of the CSL-HNC and CSL-HNC+B(0) equations are very similar. The predictions of the CSL-HNC+B(1) equations again represent an improvement over those of the CSL-HNC and CSL-HNC+B(0) equations. However, in the present case, they are inferior to those of the SSOZ-PY equation, which is consistent with my earlier observation that the accuracy of the CSL equations worsens as $l^*$ de-
Figure 7-17: Predicted site-site pair correlation function for homonuclear diatomic Lennard-Jones molecules at $T^* = 3.0$, $\rho^* = 0.5$, and $l^* = 0.603$: predictions of the (i) CSL-HNC (solid line), (ii) CSL-HNC+B(0) (dashed line), (iii) CSL-HNC+B(1) (dotted line), (iv) SSOZ-PY (dash-dotted line) equations, and (v) Monte Carlo simulation (circles). Note that the predictions of the CSL-HNC and CSL-HNC+B(0) equations are almost identical.
Figure 7-18: Predicted site-site pair correlation function for homonuclear diatomic Lennard-Jones molecules at $T^* = 3.0$, $\rho^* = 0.55$, and $l^* = 0.329$. The notation is the same as that in Figure 7-17.

Increases. This, in turn, indicates that the higher-order bridge functions become more important for molecules having shorter bond lengths.

In summary, the same trends which were observed for the CSL-HNC equations are also followed when the bridge functions are added. Specifically, the predictions of the CSL equations become better for longer bond lengths and lower densities. In addition, the predictions of the CSL equations improve when higher-order bridge functions are included.

### 7.4 Heteronuclear Diatomic Lennard-Jones Molecules

In this section, I will evaluate the formalism presented in Section 7.2 for the case of heteronuclear diatomic Lennard-Jones molecules. Specifically, I will consider a model for hydrogen chloride (HCl) which consists of two Lennard-Jones atoms having
Figure 7-19: Schematic drawing of the model HCl molecule.

different sizes, which are rigidly connected to each other. The interaction potential between sites \( \alpha \) and \( \gamma \), \( u_{\alpha \gamma}(r) \), is given by

\[
u_{\alpha \gamma}(r) = 4\varepsilon_{\alpha \gamma} \left[ \left( \frac{\sigma_{\alpha \gamma}}{r} \right)^{12} \left( \frac{\sigma_{\alpha \gamma}}{r} \right)^{6} \right] + \frac{q_{\alpha} q_{\gamma}}{r} \quad (7.31)\]

The parameters which describe this potential model are: \( \sigma_{HH} = 0.4 \, \text{Å} \), \( \epsilon_{HH}/k_B = 20 \, \text{K} \), \( q_H = 0.2e \), \( \sigma_{CI} = 3.353 \, \text{Å} \), \( \epsilon_{CI}/k_B = 259 \, \text{K} \), \( q = -0.2e \), and \( l = 1.3 \, \text{Å} \). The cross interaction terms are given by

\[
\begin{align*}
\sigma_{\alpha \gamma} &= \frac{1}{2} (\sigma_{\alpha \alpha} + \sigma_{\gamma \gamma}) \\
\varepsilon_{\alpha \gamma} &= \sqrt{\varepsilon_{\alpha \alpha} \varepsilon_{\gamma \gamma}}
\end{align*} \quad (7.32)\]

An interesting feature of this molecule is that the smaller interaction site (H) is fully enclosed by the larger interaction site (Cl). A schematic drawing of this molecule is shown in Figure 7-19.
7.4.1 Nonpolar Molecules

Initially, I examined this model without the charges, namely, I set $q_H = q_C = 0$ in Eq. (7.31). The CSL equations with the HNC, HNC+$B^{(0)}$, and HNC+$B^{(1)}$ closures, and the SSOZ equation with the HNC closure were solved using an extension of the method of Labik. 121 This time, however, the grid consisted of 2048 points with $\Delta r = 0.036$ Å. For details, see Appendix C. The predicted site-site pair correlation functions of this system, $g_{HH}$, $g_{HCl}$, and $g_{CICI}$, at $T = 210$ K and $\rho = 0.018$ Å$^{-3}$ are plotted in Figures 7-20 to 7-22, respectively. The solid lines are the predictions of the CSL-HNC equations, the dashed lines are the predictions of the CSL-HNC+$B^{(0)}$ equations, the dotted lines are the predictions of the CSL-HNC+$B^{(1)}$ equations, the dash-dotted lines are the predictions of the SSOZ-PY equation, and the circles represent the simulation data of Hirata et al. 50
Figure 7-21: Predicted hydrogen-chlorine pair correlation function for uncharged HCl at $T = 210$ K and $\rho = 0.018$ Å$^{-3}$. The notation is the same as that in Figure 7-20.

Figure 7-22: Predicted chlorine-chlorine pair correlation function for uncharged HCl at $T = 210$ K and $\rho = 0.018$ Å$^{-3}$. The notation is the same as that in Figure 7-20.
The CSL equations are in closest agreement with the simulation data for the Cl-Cl pair correlation function (see Figure 7-22), although the SSOZ-PY predictions are fairly similar. With the exception of the observed small negative region, the predictions of the CSL equations and the SSOZ-PY equation are in close agreement with the computer simulation data for $g_{HCl}(r)$ (see Figure 7-21). The negative region predicted by the SSOZ-PY equation is much less pronounced than that predicted by the CSL equations. Note also, that the addition of the bridge functions tends to decrease the magnitude of the negative region.

For $g_{HH}(r)$ (see Figure 7-20), the predictions of the four integral equations are all in close agreement with the computer simulation results for $r \geq 2$ Å. However, for both $g_{HH}(r)$ and $g_{HCl}(r)$ (see Figures 7-20 and 7-21, respectively) there are a few unphysical features predicted by the CSL-HNC equations. First, there is a negative region present immediately before the first peak in the H-H and H-Cl pair correlation functions. This feature is also predicted by the SSOZ-PY equation. Another unphysical prediction of the CSL-HNC equations is the presence of a sharp peak at about 0.4 Å in the H-H pair correlation function.

It is interesting to discuss possible sources of these unphysical predictions. To gain a better understanding of this problem, let us examine the predictions of the CSL-HNC equations for the individual $h$-component bonds (see Figures 7-23 to 7-25). Note that the function $h_{\alpha \gamma}$ is associated with the correlations between a site $\alpha$ located within a molecule and a disconnected site $\gamma$ at infinite dilution in the bulk liquid. Therefore, $h^l$ not a symmetric matrix, namely, $h^l_{\alpha \gamma} \neq h^l_{\gamma \alpha}$. The same applies to $c^l$ and $b^l$ as well.

The first peak in the $h^a_{HH}$ (see Figure 7-23) and the $h^b_{HH}$ (see Figure 7-25) functions is located at the minimum of the H-H interaction potential. These peaks should be canceled out by the negative peaks in the $h^l_{HH}$ and the $h^r_{HH}$ (=$h^l_{HH}$) functions (see Figure 7-24). However, slight errors in the positions and heights of these peaks result in the creation of the anomalous peak and the negative region in the H-H pair correlation function. The addition of the low-order bridge functions overcompensates for the anomalous peak at 0.4 Å. The peak is eliminated, but it becomes a negative
Figure 7-23: Predictions of the CSL-HNC equations for uncharged HCl for $h^0$: (i) $h_{HH}^0(r)$ (solid line), (ii) $h_{HCl}^0(r)$ (dashed line), and (iii) $h_{ClCl}^0(r)$ (dotted line).

Figure 7-24: Predictions of the CSL-HNC equations for uncharged HCl for $h^I$: (i) $h_{HH}^I(r)$ (solid line), (ii) $h_{HCl}^I(r)$ (dashed line), (iii) $h_{ClCl}^I(r)$ (dotted line), and (iv) $h_{CIH}^I(r)$ (dash-dotted line). Note that $h_{CIH}^I(r)$ is nearly equal to zero.
Figure 7-25: Predictions of the CSL-HNC equations for uncharged HCl for $h^b$: (i) $h^b_{HH}(r)$ (solid line), (ii) $h^b_{HCl}(r)$ (dashed line), and (iii) $h^b_{ClCl}(r)$ (dotted line). Note that $h^b_{HCl}(r)$ and $h^b_{ClCl}(r)$ are essentially equal to zero.

The predicted zeroth-order and first-order bridge functions are plotted in Figures 7-26 to 7-29. For the $b^b$ bridge functions (see Figures 7-26 and 7-29), only $b^b_{HH}$ is significantly different from zero. For the $b^e$ bridge functions, only $b^e_{ClCl}$ is different from zero. All the $b^l$ bridge functions seem to make a contribution, with the exception of $b^l_{ClH}$. Note that the bridge functions are all essentially equal to zero for $r > 6 \, \text{Å}$, reflecting their short-ranged character.

### 7.4.2 Polar Molecules

Next, I examined the same system with the addition of charge, $+0.2e$ to H and $-0.2e$ to Cl. The predicted pair correlation functions of this system are shown in Figures 7-30 to 7-32. For the H-H and Cl-Cl pair correlation functions, the SSOZ-HNC and the CSL-HNC equations are of comparable accuracy. The H-Cl potential no longer has an attractive region, and thus the peak in the corresponding correlation

159
Figure 7-26: Predicted zeroth-order bridge functions for uncharged HCl at $T = 210$ K and $\rho = 0.018 \text{ Å}^{-3}$: (i) $b_{HH}^{b(0)}(r)$ (solid line), (ii) $b_{HCl}^{b(0)}(r)$ (dashed line), and (iii) $b_{ClCl}^{b(0)}$ (dotted line). Note that $b_{HCl}^{b(0)}(r)$ and $b_{ClCl}^{b(0)}$ are essentially equal to zero.

Figure 7-27: Predicted first-order bridge functions for uncharged HCl at $T = 210$ K and $\rho = 0.018 \text{ Å}^{-3}$: (i) $\rho b_{HH}^{\alpha(1)}(r)$ (solid line), (ii) $\rho b_{HCl}^{\alpha(1)}(r)$ (dashed line), and (iii) $\rho b_{ClCl}^{\alpha(1)}$ (dotted line). Note that $\rho b_{HH}^{\alpha(1)}(r)$ and $\rho b_{HCl}^{\alpha(1)}(r)$ are essentially equal to zero.
Figure 7-28: Predicted first-order bridge functions for uncharged HCl at $T = 210$ K and $\rho = 0.018 \text{ Å}^{-3}$: (i) $\rho_{bH}^{l(1)}(r)$ (solid line), (ii) $\rho_{bHCl}^{l(1)}(r)$ (dashed line), (iii) $\rho_{bClCl}^{l(1)}(r)$ (dotted line), and (iv) $\rho_{bClH}^{l(1)}(r)$ (dash-dotted). Note that $\rho_{bH}^{l(1)}(r)$ and $\rho_{bHCl}^{l(1)}(r)$ are essentially equal to zero.

Figure 7-29: Predicted first-order bridge functions for uncharged HCl at $T = 210$ K and $\rho = 0.018 \text{ Å}^{-3}$: (i) $\rho_{bH}^{b(1)}(r)$ (solid line), (ii) $\rho_{bHCl}^{b(1)}(r)$ (dashed line), and (iii) $\rho_{bClCl}^{b(1)}(r)$ (dotted line).
Figure 7-30: Predicted hydrogen-hydrogen pair correlation function for charged HCl at \( T = 210 \) K and \( \rho = 0.018 \) Å\(^{-3}\). The notation is the same as that in Figure 7-20.

function disappears. However, for the H-Cl pair correlation functions, the CSL-HNC equations seem to offer an improvement over the SSOZ-HNC equation. We see that both integral equations predict an anomalous peak at about 2 Å, which is much less prominent for the CSL-HNC equations.

To examine why this peak is predicted by the CSL-HNC equations, one must examine the \( h \)-component bonds, which are shown in Figures 7-33 to 7-35. Recall that \( h_{\gamma}(r) = h_{\gamma}(r) + h_{\gamma}(r) + h_{\gamma}(r) + h_{\gamma}(r) \). For this system, the H-Cl site-site interaction potential has a minimum located at about 2 Å, which is where the anomalous peak is also located. At this position, we see a large peak in \( h_{HCl} \) which should be canceled out by the negative peaks in \( h_{HCl} \), \( h_{HCl} \) (\( = h_{HCl} \)), and \( h_{HCl} \). The small errors in each of these functions, due to the approximations involved in using the HNC closure, causes this cancellation to be incomplete and leads to the creation of this peak.

The addition of the zeroth-order bridge functions to the CSL-HNC equations does not significantly alter the predictions of the pair correlation functions. Adding
Figure 7-31: Predicted hydrogen-chlorine pair correlation function for charged HCl at $T = 210$ K and $\rho = 0.018 \text{ Å}^{-3}$. The notation is the same as that in Figure 7-20.

![Graph](image1)

Figure 7-32: Predicted chlorine-chlorine pair correlation function for charged HCl at $T = 210$ K and $\rho = 0.018 \text{ Å}^{-3}$; The notation is the same as that in Figure 7-20.

![Graph](image2)
Figure 7-33: Predictions of the CSL-HNC equations for charged HCl at \( T = 210 \text{ K} \) and \( \rho = 0.018 \, \text{Å}^{-3} \) for \( h^c \): (i) \( h^c_{HH}(r) \) (solid line), (ii) \( h^c_{HCl}(r) \) (dashed line), and (iii) \( h^c_{ClCl}(r) \) (dotted line).

Figure 7-34: Predictions of the CSL-HNC equations for charged HCl at \( T = 210 \text{ K} \) and \( \rho = 0.018 \, \text{Å}^{-3} \) for \( h^l \): (i) \( h^l_{HH}(r) \) (solid line), (ii) \( h^l_{HCl}(r) \) (dashed line), (iii) \( h^l_{ClCl}(r) \) (dotted line), and (iv) \( h^l_{ClH}(r) \) (dash-dotted line).
Figure 7-35: Predictions of the CSL-HNC equations for charged HCl at $T = 210$ K and $\rho = 0.018$ Å$^{-3}$ for $h^b$: (i) $h_{HH}^b(r)$ (solid line), (ii) $h_{HCl}^b(r)$ (dashed line), and (iii) $h_{ClCl}^b(r)$ (dotted line).

the first-order bridge functions causes the height of the anomalous peak in $g_{HCl}$ to increase, although, in general, it improves the agreement with the simulation data for all the pair correlation functions (see Figures 7-30-7-32).

In general, the CSL equations tend to yield more accurate predictions for correlations between larger interaction sites. This can be understood from the fact that the predictions of the CSL equations are independent of the presence of auxiliary sites. If the interactions between two molecules are governed primarily by one large interaction site, then the system can be approximated as a simple fluid. The correlations between these sites can be described quite accurately by the OZ equation, which is the limit approached by the CSL equations in this case. The other interaction sites, which are much smaller in comparison, can be viewed as being auxiliary sites. The correlations involving these interaction sites are also addressed by the CSL equations, although not as accurately.
7.5 Concluding Remarks

Comparisons have been made between the capabilities of the CSL-HNC and SSOZ-PY equations to predict pair correlation functions of homonuclear diatomic Lennard-Jones molecules at various temperatures, densities, and bond lengths. In general, the predictions of the CSL-HNC equations are in better agreement with the computer simulation data when the bond length increases or when the density decreases. Temperature does not have a significant influence on the structural predictive capabilities of these equations.

I have also presented a method for computing the low-order density bridge functions. For the homonuclear molecules, the zeroth-order bridge functions were found to have little effect on the predictions of the CSL equations. However, the addition of the first-order bridge functions resulted in a significant improvement in the predictive capabilities of the CSL equations. The accuracy of these equations was found to increase with decreasing density and increasing bond length, similar to the situation encountered with the CSL-HNC equations.

I have also investigated the predictive capabilities of the CSL-HNC and SSOZ-PY equations for pair correlation functions for heteronuclear diatomic Lennard-Jones molecules. For nonpolar molecules \( (q = 0) \), the CSL-HNC equations perform very well in predicting the correlation function between the larger interaction sites. For the other correlation functions, the predictions of the CSL-HNC equations were found to be good for medium to large values of \( r \). For separations around the atomic diameter, the CSL-HNC equations displayed anomalous behavior, including a negative region in \( g(r) \). This is a consequence of the delicate nature of the cancellations which must occur between the \( h \)-component bonds. For polar diatomic molecules \( (q \neq 0) \), the CSL-HNC equations seem to offer an improvement over the SSOZ-HNC equations. The CSL equations provide better predictions for correlation functions between the larger interaction sites.

The work in this chapter seems to offer hope for the CSL equations. In fact, there are systems for which the CSL equations offer an improvement over the SSOZ
equation. The success of the CSL-HNC equations for charged diatomic molecules offers hope that these equations may also work well for more complicated systems, such as water. The next chapter describes the application of the CSL equations to various potential models for water to predict structure, thermodynamics, and phase behavior of this complex fluid.
Chapter 8

The Chandler-Silbey-Ladanyi
Equations: Application to Water

8.1 Introduction and Overview

The structure of most liquids is governed primarily by the short-ranged repulsive interactions between the constituent molecules. In the case of water, however, the structure is also profoundly affected by the presence of highly anisotropic, strong, short-ranged attractive interactions between the molecules. This feature of water presents a difficult predictive challenge to integral equation theories.

In Chapter 3, the SSOZ-HNC equation was applied to the SPC, SPC/E, TIP3P, and MCY models of water and found to be moderately successful in describing the fluid structure. The short-ranged structure was captured quite well. However, correlations beyond the first coordination shell were predicted rather poorly. Unfortunately, as stressed in the preceding chapters, there is no straightforward method to improve the predictive accuracy of the SSOZ equation.

On the other hand, the CSL equations, which are diagrammatically rigorous, offer a method by which approximations can be successively improved upon (see Chapter 6). In Chapter 7, I applied the CSL equations to fluids composed of both homonuclear and heteronuclear diatomic Lennard-Jones molecules, and found them to work well for polar fluids. Therefore, it seems reasonable that the CSL equations may offer an
improved description of water.

In this chapter, I compare the accuracy of the CSL-HNC, CSL-HNC+B\(^{(0)}\), and SSOZ-HNC equations to predict the structural and bulk thermodynamic properties of water for the SPC, SPC/E, TIP3P, and MCY potential models of water. In addition, I predict the phase behavior of the SPC model of water using the CSL-HNC and SSOZ-HNC equations, and compare their predictions with results from computer simulations and experimental measurements.

This chapter is organized as follows. Section 8.2 discusses the bridge functions for water, and provides details on how I approximate them. In Section 8.3, I compute the pair correlation functions for several potential models of water using the CSL equations, and compare the predictions with those of the SSOZ-HNC equation and computer simulations. In Section 8.4, I compute the thermodynamic properties of several potential models of water, including a comparison with the predictions of the SSOZ-HNC equation and computer simulations. In Section 8.5, I predict the phase behavior of SPC water in the context of the CSL-HNC and SSOZ-HNC equations, including a comparison with experimental and computer simulation results. Finally, in Section 8.6, I summarize the key findings of this chapter.

### 8.2 The Bridge Functions for Water

In the work presented in this chapter, I make two different approximations for the bridge functions. The first one involves completely neglecting the bridge functions by setting them equal to zero, that is,

\[
\begin{align*}
    b_{\alpha\gamma}^c(r) &= 0 \\
    b_{\alpha\gamma}^l(r) &= 0 \\
    b_{\alpha\gamma}^b(r) &= 0
\end{align*}
\]  

This is known as the hypernetted-chain (HNC) approximation (see Chapter 6). The second one consists of approximating the bridge function by only including diagrams
at zeroth-order in the density. Specifically,

\[
b_{\alpha\gamma}^0(r) \approx b_{\alpha\gamma}^{(0)}(r) \tag{8.4}
\]
\[
b_{\alpha\gamma}'(r) \approx b_{\alpha\gamma}'^{(0)}(r) \tag{8.5}
\]
\[
b_{\alpha\gamma}(r) \approx b_{\alpha\gamma}^{(0)}(r) \tag{8.6}
\]

Recall that \(b_{\alpha\gamma}' = b_{\gamma\alpha}'\), and therefore, hereafter, I will not present any equations referring to \(b'\).

In Section 7.2, I have already discussed a general method for computing the zeroth-order bridge functions. Consequently, I will only describe briefly the key equations from Section 7.2 which will be used here as well as emphasize those features which are specific to water.

The first step in computing the zeroth-order bridge functions involves rewriting these functions in terms of the thermal and chain correlation functions (see Eqs. (7.4)-(7.6)), namely,

\[
b_{\alpha\gamma}^{(0)}(r) = 0 \tag{8.7}
\]
\[
b_{\alpha\gamma}'^{(0)}(r) = u_{\alpha\gamma}'^{(0)}(r) - t_{\alpha\gamma}'^{(0)}(r) \tag{8.8}
\]
\[
b_{\alpha\gamma}^{(0)}(r) = u_{\alpha\gamma}^{(0)}(r) - t_{\alpha\gamma}^{(0)}(r) \tag{8.9}
\]

where the notation is the same as that used in Chapter 7. The next step involves the separate computation of the zeroth-order thermal and chain correlation functions.

The zeroth-order thermal correlation functions are related to the zeroth-order indirect correlation functions by (see Eq. (7.13)–Eq. (7.15))

\[
u_{\alpha\gamma}^{(0)}(r) = 0 \tag{8.10}
\]
\[
u_{\alpha\gamma}'^{(0)}(r) = y_{\alpha\gamma}'^{(0)}(r) \tag{8.11}
\]
\[
u_{\alpha\gamma}^{(0)}(r) = y_{\alpha\gamma}^{(0)}(r) - [1 + y_{\alpha\gamma}'^{(0)}(r)] [1 + y_{\alpha\gamma}^{(0)}(r)] \tag{8.12}
\]

The diagrams contributing to \(y_{\alpha\gamma}'^{(0)}\), \(y_{\alpha\gamma}^{(0)}\), and \(y_{\alpha\gamma}^{(0)}\) can be generated from the graphical
Figure 8-1: Diagrams contributing to the indirect correlation functions for water at zeroth-order in the density. The white circles represent root sites, and the black circles represent field sites. A dashed line represents an e-bond (or a $g^o$-bond, where $g^o = 1 + h^o$). The shaded triangle represents a three-body intramolecular distribution function, which is analogous to an s-bond in the case of two-body intramolecular interactions.

representation of the indirect correlation functions (see Section 7.2). In the case of triatomic molecules such as water, the zeroth-order indirect correlation functions, written in diagrammatic terms, are shown in Figure 8-1. The thermal correlation functions can then be computed from the indirect correlation functions by using Eqs. (8.10)–(8.12).

After deriving expressions for the thermal correlation functions, the next step involves computing the zeroth-order chain functions. Expanding the CSL equations, Eqs. (7.21)–(7.23), in powers of the density, and collecting the zeroth-order terms yields (see Eqs. (7.24)–(7.26))

\[
\begin{align*}
\hat{c}^{(0)}(k) & = 0 \\
\hat{c}^{(0)}(k) & = \hat{s}(k)\hat{\Delta}^{(0)}(k) \\
\hat{s}^{(0)}(k) & = \hat{c}^{(0)}(k)\hat{s}(k) + \hat{s}(k)\hat{s}^{(0)}(k)
\end{align*}
\]
\[ t^{0,(0)}(r) = 0 \]
\[ t^{1,(0)}(r) = \]
\[ t^{b,(0)}(r) = \]

Figure 8-2: Diagrams contributing to the chain correlation functions for water at zeroth-order in the density. The white circles represent root sites, and the black circles represent field sites. A dashed line represents an e-bond (or a \( g^o \)-bond), a solid line represents an f-bond (or an \( h^o \)-bond), and a wavy line represents an s-bond. A shaded triangle represents a three-body intramolecular distribution function.

6.2) into Eqs. (8.13)-(8.15), one obtains the zeroth-order chain functions, which are shown in Figure 8-2.

The procedure outlined above specifies the diagrams which contribute to the zeroth-order bridge functions. As described in Chapter 7, each of these diagrams must then be converted into a corresponding integral, which needs to be computed. The translation of a diagram into its related integral is described in detail in Ref. 27. The calculation of the function, \( b^{0,(0)} \), involves the evaluation of two-dimensional integrals, while that of the function, \( b^{b,(0)} \), involves the evaluation of five-dimensional integrals. All these integrals are computed using a Monte Carlo integration technique.\(^{149}\)

Note that, in principle, the first-order bridge functions can be computed following a procedure similar to that described above. Unfortunately, due to the nature of the integration method which I currently employ, the calculation of the first-order bridge
Figure 8-3: Mayer $f$-function associated with the oxygen-hydrogen interaction for SPC water at 25°C. Note that $f_{OH}(r) < 0$ for $r < 1.5$ Å, and is therefore not plotted in this region because of the use of a log scale.

functions becomes intractable due to the high dimensionality of the integrals involved. Indeed, in order to compute the first-order bridge functions, five-dimensional integrals must be evaluated for $b^{(1)}$, eight-dimensional integrals must be evaluated for $b^{L(1)}$, and eleven-dimensional integrals must be evaluated for $b^{H(1)}$. Nevertheless, if a more sophisticated integration method could be identified, the computation of these integrals may become tractable. Work along these lines is in progress.

When trying to apply the method just described to evaluate the zeroth-order bridge functions of water, one runs into numerical difficulties associated with the ability of water molecules to form strong hydrogen bonds with other water molecules. This ability is reflected in a large attractive well in the oxygen-hydrogen interaction potential. As a result, the Mayer $f$-function, $f_{OH}$, has a very large peak. To illustrate this point, in Figure 8-3, I show $f_{OH}(r)$ for the SPC model of water at $T = 25°C$.

This large peak in $f_{OH}$, combined with the fact that it is long-ranged, makes the numerical evaluation of the integrals for the bridge functions extremely difficult. It would be much more convenient to work with a more well-behaved function. Richard-
son and Chandler have shown\textsuperscript{156} that in the diagrammatic representation of the total correlation function, the $f$-bond can be renormalized to a $h^0$-bond by excluding those diagrams possessing black articulation circles. The zeroth-order diagrams can then be rewritten using $h^0$-bonds instead of $f$-bonds. However, in this process, higher-order bridge diagrams are also generated. In the calculations of the bridge functions presented later, I have utilized these renormalized bridge diagrams.

### 8.3 The Structure of Water

I have solved the CSL-HNC, CSL-HNC+$B^{(0)}$, and SSOZ-HNC equations for the SPC, SPC/E, TIP3P, and MCY models of water at $T = 25^\circ$C and $\rho = 0.997$ g/cm$^3$. For a detailed description of these potential models for water, see Section 3.2. All these equations were solved numerically using an extension of the method of Labik et al.\textsuperscript{121} The mesh used consisted of $N = 2048$ points spaced $\Delta r = 0.036$ Å apart, and the long-ranged interactions were handled using the method of Ng.\textsuperscript{154} For details on the numerical solution of these equations, see Appendix C.

The predicted site-site pair correlation functions for SPC water are plotted in Figures 8-4–8-6, and compared with the corresponding pair correlation functions obtained from computer simulations. The solid lines are the predictions of the CSL-HNC equations, the dashed lines are the predictions of the CSL-HNC+$B^{(0)}$ equations, the dotted lines are the predictions of the SSOZ-HNC equation, and the circles denote results from Monte Carlo simulations.\textsuperscript{15}

The CSL-HNC, CSL-HNC+$B^{(0)}$, and the SSOZ-HNC equations predict a much broader first peak in $g_{oo}(r)$ as compared to the simulation results (see Figure 8-4). The predictions of the CSL-HNC+$B^{(0)}$ equations for the first peak are very similar to those of the CSL-HNC equations. All the three equations yield similar predictions for the location of the first peak, which occurs at a slightly higher value of $r$ than that predicted by the simulations. This may be due to the fact that, in these calculations, a small repulsive contribution was added to the oxygen-hydrogen interaction potential (see Section 3.2). The CSL-HNC and CSL-HNC+$B^{(0)}$ equations
Figure 8-4: Oxygen-oxygen pair correlation functions, $g_{oo}(r)$, as a function of the site-site separation, $r$, for SPC water at 25°C and 0.997 g/cm$^3$: (i) predicted using the CSL-HNC equations (solid line), (ii) predicted using the CSL-HNC+B(0) equations (dashed line), (iii) predicted using the SSOZ-HNC equation (dotted line), and (iv) predicted from the Monte Carlo simulations of Jorgensen et al.$^{15}$ (circles).
Figure 8-5: Oxygen-hydrogen pair correlation functions, $g_{OH}(r)$, as a function of the site-site separation, $r$, for SPC water at 25°C and 0.997 g/cm³. The notation is the same as that in Figure 8-4.

predict a small shoulder on the first peak (at $r \approx 3.5$ Å) as well as a deep minimum in $g_{OO}(r)$ (at $r = 4$ Å) which are not present in the simulation results. For values of $r$ beyond the first peak, the predictions of all the three equations differ significantly from each other. The second peak predicted by the SSOZ-HNC equation is located at about 5.8 Å, which is much further out than the simulation value of about 4.8 Å. On the other hand, the CSL-HNC and CSL-HNC+B(0) equations do correctly predict the location of this peak, perhaps indicating that these equations can capture the tetrahedral structure of water, while the SSOZ-HNC equation cannot.

For the oxygen-hydrogen pair correlation functions (see Figure 8-5), the CSL-HNC and CSL-HNC+B(0) equations seem to offer an improvement over the SSOZ-HNC equation. With the exception of the small negative region at 1.5 Å, the predictions of the CSL equations are almost identical with the simulation data for $r < 3$ Å. The addition of the zeroth-order bridge functions seems to decrease the magnitude of the negative peak. All the three equations predict a much broader second peak than that obtained from simulations. Again, beyond the first peak, the predictions
of the CSL-HNC, CSL-HNC+B(0), and SSOZ-HNC equations differ from each other and from the computer simulation data.

For the first peak in the hydrogen-hydrogen pair correlation function (see Figure 8-6), the CSL-HNC equations seem to be in better agreement with the simulation data than the SSOZ-HNC equation. However, the reverse is true for the second peak and beyond. The CSL-HNC equations underpredict the value of $g_{HH}(r)$ between the first and second peaks, while the SSOZ-HNC equation overpredicts this value. The addition of the zeroth-order bridge functions seems to worsen the accuracy of the CSL equations slightly in terms of the hydrogen-hydrogen correlations. Adding higher-order bridge functions should, however, correct this problem.

Overall, it is difficult to clearly assert which of the three integral equations provides predictions of the site-site pair correlation functions which are in the closest agreement with the computer simulation results. Nevertheless, it appears that both the CSL-HNC and CSL-HNC+B(0) equations are of comparable accuracy, while the SSOZ equation yields slightly less accurate predictions.
Figure 8-7: CSL-HNC predictions for the $h^0$-functions for SPC water at $T = 25^\circ C$ and $\rho = 0.997 \text{ g/cm}^3$: (i) $h_{\delta\delta}(r)$ (solid line), (ii) $h_{\delta H}(r)$ (dashed line), and (iii) $h_{HH}(r)$ (dotted line).

The various $h^0$-functions computed for SPC water using the CSL-HNC equations are shown in Figure 8-7. The function $h_{\alpha\gamma}$ is the total correlation function between a disconnected site of type $\alpha$ and a disconnected site of type $\gamma$ both at infinite dilution in the bulk fluid. As can be seen by comparing $h_{\delta H}(r)$ (dashed line in Figure 8-7) with $f_{OH}(r)$ (see Figure 8-3), $h_{\delta H}(r)$ is much easier to work with numerically than $f_{OH}(r)$. For this reason, these functions were used in place of the Mayer $f$-functions in the calculations of the bridge functions (see Section 8.2).

Since the results obtained for the TIP3P, SPC/E, and MCY models of water are similar to those shown for the SPC model of water, they are not reported here for the sake of brevity.

8.4 The Thermodynamics of Water

Once the pair correlation functions of the system have been computed, the thermodynamic properties can be calculated (see Sections 2.2 and 6.3). In Table 8.1, I present
Table 8.1: Predicted Values of the Residual Internal Energy, $U^{\text{res}}$, Residual Helmholtz Free Energy, $A^{\text{res}}$, Residual Chemical Potential, $\mu^{\text{res}}$, Isothermal Compressibility, $\kappa$, and Pressure, $p$, using the CSL-HNC and SSOZ-HNC Equations for SPC Water at 25°C and 0.997 g/cm$^3$, and Comparison with Computer Simulations and Experimental Values.

<table>
<thead>
<tr>
<th></th>
<th>CSL-HNC</th>
<th>SSOZ-HNC</th>
<th>Experimental</th>
<th>Simulations</th>
</tr>
</thead>
<tbody>
<tr>
<td>$-U^{\text{res}}$, kcal/mol</td>
<td>10.8</td>
<td>9.90</td>
<td>9.90$^a$</td>
<td>10.18$^d$, 9.01$^e$, 10.8$^e$, 9.82$^f$, 10.10$^g$</td>
</tr>
<tr>
<td>$-A^{\text{res}}$, kcal/mol</td>
<td>5.11</td>
<td>5.15</td>
<td>5.74$^a$</td>
<td>5.8$^h$, 6.45$^g$</td>
</tr>
<tr>
<td>$-\mu^{\text{res}}$, kcal/mol</td>
<td>4.34</td>
<td>2.50</td>
<td>6.324$^b$</td>
<td>—</td>
</tr>
<tr>
<td>$10^6 \kappa$, atm$^{-1}$</td>
<td>28.9</td>
<td>55.6</td>
<td>45.2472$^c$</td>
<td>27$^d$</td>
</tr>
<tr>
<td>$p$, atm</td>
<td>3110</td>
<td>7460</td>
<td>1.0$^c$</td>
<td>748.9$^g$</td>
</tr>
</tbody>
</table>

$^a$See Ref. 86. $^b$See Ref. 87. $^c$See Ref. 85. $^d$NPT Monte Carlo simulation with $p = 1$ atm and $T = 25°C$. See Ref. 15. $^e$See Ref. 92. $^f$See Ref. 93. $^g$See Ref. 157. $^h$NVT Monte Carlo simulation with $T = 25°C$ and $\rho = 1$ g/cm$^3$. See Ref. 88.

The predictions of the CSL-HNC and SSOZ-HNC equations for the SPC model of water at 25°C and 0.997 g/cm$^3$ for (i) the residual internal energy, $U^{\text{res}}$, (ii) the residual Helmholtz free energy, $A^{\text{res}}$, (iii) the residual chemical potential, $\mu^{\text{res}}$, (iv) the isothermal compressibility, $\kappa$, and (v) the pressure, $p$, and compare these with computer simulations and experimental results.

An examination of Table 8.1 indicates that the value of $U^{\text{res}}$ predicted by the CSL-HNC equations is about 1 kcal/mol lower than that predicted by the SSOZ-HNC equation. Recall that in order to prevent a "catastrophic overlap" of the oxygen and the hydrogen sites, a repulsive contribution was added to the SPC potential model of water, chosen such that the value of $U^{\text{res}}$ predicted by the SSOZ-HNC equation is equal to the experimental value (9.9 kcal/mol in Table 8.1, see also Section 3.2). Note that there is a wide spread in the $U^{\text{res}}$ value predicted by the computer simulations.
which reflects the different treatments of the long-range interactions between water molecules.

The predictions of both integral equations for $A^{e-e}$ are quite similar, in spite of the fact that the predictions for $U^{e-e}$ differ. These predictions are within 1 kcal/mol of the results of both computer simulations and experimental measurements.

The value for $\mu^{e-e}$ predicted by the CSL-HNC equations is much closer to the reported experimental value than that predicted by the SSOZ-HNC equation. Note, however, that the experimental $\mu^{e-e}$ value is about 2 kcal/mol lower.

The isothermal compressibility, $\kappa$, which is related to the long wavelength fluctuations in the density of a system, is predicted quite well by the CSL-HNC equations when compared with the simulation results. The value predicted by the SSOZ-HNC equation is nearly twice as large as that predicted by the CSL-HNC equations, although it is closer to the experimental value. Note, however, that the exact integral equation should predict the same value as that predicted by computer simulations which utilize the same potential model.

The CSL-HNC equations predict a much lower value for $p$ than that predicted by the SSOZ-HNC equation. However, this value is still about a factor of five higher than the simulation value. The simulation value is, in turn, about four orders of magnitude higher than the reported experimental value. This large discrepancy reflects the fact that the pressure is extremely sensitive to both the details of the intermolecular potentials as well as to the approximations made in the integral equation theory, much more so than the other properties listed.

The thermodynamic properties of the SPC/E, TIP3P, and MCY water models, as predicted by the CSL-HNC and SSOZ-HNC equations, are listed in Tables 8.2, 8.3, and 8.4, respectively, and compared with the results of computer simulations. In general, the same trends which are observed for the SPC model of water are also observed when these models are utilized.

From a diagrammatic viewpoint, the only difference between the SSOZ-HNC equation and the CSL-HNC equations is the presence of additional illegal diagrams which are included by the SSOZ-HNC equation. The fact that the SSOZ-HNC equation
Table 8.2: Predictions of the CSL-HNC and SSOZ-HNC Equations for SPC/E Water at 25°C and 0.997 g/cm³ and Comparison with Computer Simulations Values. The notation is the same as that in Figure 8.1.

<table>
<thead>
<tr>
<th></th>
<th>CSL-HNC</th>
<th>SSOZ-HNC</th>
<th>Simulations</th>
</tr>
</thead>
<tbody>
<tr>
<td>$-U^{\text{res}}$, kcal/mol</td>
<td>11.1 (12.2)</td>
<td>9.90 (11.1)</td>
<td>9.89 (11.1) a, 9.89 b</td>
</tr>
<tr>
<td>$-A^{\text{res}}$, kcal/mol</td>
<td>4.87 (6.12)</td>
<td>4.93 (6.18)</td>
<td>5.5 (6.4) c</td>
</tr>
<tr>
<td>$-\mu^{\text{res}}$, kcal/mol</td>
<td>4.26 (5.51)</td>
<td>2.52 (3.77)</td>
<td>—</td>
</tr>
<tr>
<td>$10^6 \kappa$, atm⁻¹</td>
<td>28.5</td>
<td>57.1</td>
<td>41.41 d</td>
</tr>
<tr>
<td>$p$, atm</td>
<td>2750</td>
<td>6860</td>
<td>6 a</td>
</tr>
</tbody>
</table>

a NVT molecular dynamics simulation with $T = 306$ K and $\rho = 0.998$ g/cm³. See Ref. 12. b NVT molecular dynamics simulation with $T = 25$°C. See Ref. 158. c NVT Monte Carlo simulation with $T = 25$°C and $\rho = 1$ g/cm³. See Ref. 88. d NPT molecular dynamics simulation with $p = 1$ atm and $T = 25$°C. See Ref. 94. For an explanation of the entries in parentheses for the SPC/E model, see Section 3.4.
Table 8.3: Predictions of the CSL-HNC and SSOZ-HNC Equations for TIP3P Water at 25°C and 0.997 g/cm³ and Comparison with Computer Simulations Values. The notation is the same as that in Figure 8.1.

<table>
<thead>
<tr>
<th></th>
<th>CSL-HNC</th>
<th>SSOZ-HNC</th>
<th>Simulations</th>
</tr>
</thead>
<tbody>
<tr>
<td>(-U^{res}), kcal/mol</td>
<td>11.0</td>
<td>9.91</td>
<td>9.86,(^{a}) 9.79(^{b})</td>
</tr>
<tr>
<td>(-A^{res}), kcal/mol</td>
<td>5.12</td>
<td>5.22</td>
<td>5.4,(^{c}) 5.93(^{b})</td>
</tr>
<tr>
<td>(-\mu^{res}), kcal/mol</td>
<td>4.54</td>
<td>2.70</td>
<td>—</td>
</tr>
<tr>
<td>(10^6\kappa), atm(^{-1})</td>
<td>26.8</td>
<td>58.9</td>
<td>18(^{a})</td>
</tr>
<tr>
<td>(p), atm</td>
<td>2670</td>
<td>7160</td>
<td>212.5(^{b})</td>
</tr>
</tbody>
</table>

\(^{a}\)NPT Monte Carlo simulation with \(p = 1\) atm and \(T = 25°C\). See Ref. 15. \(^{b}\)See Ref. 157. \(^{c}\)NVT Monte Carlo simulation with \(T = 25°C\) and \(\rho = 1\) g/cm³. See Ref. 88.

predicts a higher value for \(U^{res}\) and \(p\) seems to suggest that those illegal diagrams add an effective repulsion between the molecules.

### 8.5 Phase Behavior

For a pure fluid at phase equilibrium, the chemical potential of the liquid phase, \(\mu_l\), must be equal to the chemical potential of the vapor phase, \(\mu_v\), that is,

\[
\mu_l = \mu_v
\]  

(8.16)

Equation (8.16) can be rewritten in terms of the residual chemical potentials, \(\mu_l^{res}\) and \(\mu_v^{res}\), as follows

\[
k_B T \ln[\rho_l \Lambda(T)] + \mu_l^{res} = k_B T \ln[\rho_v \Lambda(T)] + \mu_v^{res}
\]  

(8.17)
Table 8.4: Predictions of the CSL-HNC and SSOZ-HNC Equations for MCY Water at 25°C and 0.997 g/cm³ and Comparison with Computer Simulations Values. The notation is the same as that in Figure 8.1.

<table>
<thead>
<tr>
<th></th>
<th>CSL-HNC</th>
<th>SSOZ-HNC</th>
<th>Simulations</th>
</tr>
</thead>
<tbody>
<tr>
<td>$-U^{res}$, kcal/mol</td>
<td>10.0</td>
<td>8.80</td>
<td>8.58,a 8.51b</td>
</tr>
<tr>
<td>$-A^{res}$, kcal/mol</td>
<td>3.62</td>
<td>3.74</td>
<td>4.31a</td>
</tr>
<tr>
<td>$-\mu^{res}$, kcal/mol</td>
<td>0.317</td>
<td>2.03</td>
<td>—</td>
</tr>
<tr>
<td>$10^6\kappa$, atm⁻¹</td>
<td>17.9</td>
<td>30.3</td>
<td>53b</td>
</tr>
<tr>
<td>$p$, atm</td>
<td>10400</td>
<td>14500</td>
<td>—</td>
</tr>
</tbody>
</table>

*a* NVT Monte Carlo simulation with $T = 25$°C and $p = 1$ g/cm³. See Ref. 88.  
*b* NVT Monte Carlo simulation with $T = 25$°C and $p = 0.997$ g/cm³. See Ref. 90.

or

$$\ln \rho_l + \beta \mu^{res}_l = \ln \rho_v + \beta \mu^{res}_v$$ (8.18)

where $\rho_l$ and $\rho_v$ are the densities of the liquid and vapor phases, respectively, and $\Lambda(T)$ is the internal partition function of the molecule, which is only a function of temperature.

At low densities, where $h^o_{OH}(r) \approx f_{OH}(r)$ (see Eq. (6.6)), one runs into problems with the numerical solution of the CSL equations. This is mainly a result of the presence of an extremely large peak in $f_{OH}(r)$ (see Figure 8-3) which makes finding its Fourier transform (and consequently $h^o_{OH}(r)$) extremely difficult. To circumvent this difficulty, I have used a virial expansion for the pressure, truncated at second order in the density, to describe the vapor branch of water. The pressure, $p$, and the
residual chemical potential, \( \mu_v^{**} \), are then given by

\[
p = k_B T \rho_v [1 + B(T) \rho_v]
\]

(8.19)

\[
\beta \mu_v^{**} = 2B(T) \rho_v
\]

(8.20)

where \( B(T) \) is the second virial coefficient, which is only a function of \( T \). Recall that for an ideal gas, \( B(T) = 0 \). The second virial coefficient can be computed using the following well-known statistical-mechanical relation\(^{159}\)

\[
B(T) = -\frac{1}{2V} \int dR_1 dR_2 [e^{-\beta u(R_1, R_2)} - 1]
\]

(8.21)

where \( R_1 \) and \( R_2 \) run over all the allowed positions and orientations of the molecules, \( u(R_1, R_2) \) is the interaction potential between the two molecules involved, and \( V \) is the total volume of the system.

The truncated virial expansion is most accurate at low densities. Accordingly, Eqs. (8.19) and (8.20) should be adequate for predicting \( p \) and \( \mu_v^{**} \) of the vapor branch far below the critical point, where the density of the coexisting vapor phase is low. However, as the critical point is approached and the density of the coexisting vapor phase increases, the truncated virial expansion will no longer accurately describe the vapor phase.

The predicted temperature dependence of the second virial coefficient of SPC water using Eq. (8.21) is shown in Figure 8-8, and compared to that of real water. As can be seen, the predicted second virial coefficient of SPC water is much more negative than that of real water. This is due to the fact that the SPC model represents an effective pair potential for water. Its parameters are optimized to reproduce the properties of the liquid state. The presence of many-body interactions in the bulk liquid makes the effective pair potential more attractive than the actual two-body potential. Therefore, \( B(T) \), which is a measure of the two-body interactions, for SPC water is more negative than that for real water.

In order to determine the point of phase coexistence at a particular temperature,
one must find the coexisting liquid and vapor densities for which the pressure and chemical potential of each phase are equal. For this purpose, I first compute the pressure and chemical potential of the vapor phase, using Eqs. (8.19) and (8.20), at several densities. The resulting pressure is then plotted as a function of the resulting chemical potential. As an example, in Figure 8-9, I plot the predicted pressure as a function of the predicted chemical potential for SPC water at $T = 25^\circ C$. The solid line is the prediction using Eqs. (8.19) and (8.20) for the vapor phase. The dashed line represents the ideal-gas prediction. Next, I compute the pressure and chemical potential of the liquid phase using the CSL-HNC and SSOZ-HNC equations. The dotted line in Figure 8-9 is the prediction of the CSL-HNC equations, and the dash-dotted line is the prediction of the SSOZ-HNC equation. Note that $(\partial p/\partial \mu)_T = \rho$, and consequently, the slopes of the lines corresponding to the liquid phase are much greater than the slopes of the lines corresponding to the vapor phase (see Figure 8-9).

The point at which the curve corresponding to the vapor phase intersects that corresponding to the liquid phase is the point of phase coexistence at the temperature
Figure 8-9: Predicted pressure versus chemical potential for SPC water at $T = 298.15$ K: (i) truncated virial expansion for the vapor phase (solid line), (ii) ideal-gas approximation for the vapor phase (dashed line), (iii) CSL-HNC equations for the liquid phase (dotted line), and (iv) SSOZ-HNC equation for the liquid phase (dash-dotted line).
of interest. The pressure at which the two curves intersect corresponds to the vapor pressure. The density of the liquid phase at which the two curves intersect corresponds to the density of the coexisting liquid phase, while the density of the vapor phase at which this occurs corresponds to the density of the coexisting vapor phase. Using this procedure, one can predict the $T - \rho$ coexistence curve and the vapor pressure versus temperature curve for water.

In Figure 8-10, I plot the vapor-liquid coexistence curve for SPC water. The open squares are the predictions of the CSL-HNC equations, the open triangles are the predictions of the SSOZ-HNC equation, the solid circles are the Monte Carlo simulations of de Pablo et al.,\textsuperscript{93} and the solid line represents the experimental data. Note that for the SPC model, de Pablo et al. compute\textsuperscript{93} that $T_c = 587$ K and $\rho_c = 0.27$ g/cm\textsuperscript{3}, which should be compared to the experimental values $T_c = 647.3$ K and $\rho_c = 0.32$ g/cm\textsuperscript{3}.

The SSOZ-HNC equation seems to capture the vapor branch of the coexistence curve better than the CSL-HNC equations, while the reverse is true for the liquid branch. At temperatures higher than about 400 K, the pressure-chemical potential vapor curve predicted by the truncated virial expansion (see Figure 8-9) does not intersect the pressure-chemical potential liquid curve predicted by either the CSL-HNC or SSOZ-HNC equations. Consequently, no predictions could be made for $T > 400$ K (see Figure 8-10).

The predicted vapor pressure of water as a function of temperature is shown in Figure 8-11. The solid line corresponds to the experimental data.\textsuperscript{1} The open squares are the predictions of the CSL-HNC equations, and the open triangles are the predictions of the SSOZ-HNC equation. The SSOZ-HNC equation predicts almost the same vapor pressure as that found experimentally, while the CSL-HNC equations predict higher vapor pressure values.
Figure 8-10: Predicted $T - \rho$ phase diagram of SPC water: (i) predictions of the CSL-HNC equations (open squares), (ii) predictions of the SSOZ-HNC equation (open triangles), (iii) results of Monte Carlo simulations of de Pablo et al.\textsuperscript{93} (solid circles), and (iv) experimental measurements\textsuperscript{1} (solid line).

8.6 Concluding Remarks

In this chapter, I have compared the ability of the CSL-HNC equations and the SSOZ-HNC equation to predict the structural and bulk thermodynamic properties of several different models of water. The only difference between these two equations is the presence of illegal diagrams in the SSOZ-HNC equation.

The prediction of the site-site correlation functions for water using the CSL-HNC equations was found to be in slightly better agreement with the computer simulation results than those of the SSOZ-HNC equation, especially for the oxygen-hydrogen pair correlation functions. In particular, the CSL-HNC equations appear to capture the tetrahedral structure of water, while the SSOZ-HNC equation does not. The addition of the zeroth-order bridge functions does not significantly alter the predictions of the CSL-HNC equations, except at large values of $r$. This is similar to what was found for the diatomic Lennard-Jones fluid (see Chapter 7).
I also computed several different thermodynamic properties of water using the CSL-HNC equations and the SSOZ-HNC equation. Both equations yielded similar results for the residual Helmholtz free energy. For the residual chemical potential, pressure, and isothermal compressibility, the CSL-HNC equations gave predictions which are in better agreement with the simulation results.

The phase behavior of water was also predicted using these integral equations. The vapor branch of the temperature-density coexistence curve is more accurately predicted by the SSOZ-HNC equation, while the liquid branch is better predicted by the CSL-HNC equations. The vapor pressure predictions of the SSOZ-HNC equation are in very good agreement with that found experimentally, while those of the CSL-HNC equations are somewhat higher.

In the next chapter, I will summarize the salient findings of this thesis, and propose directions for future research.
Chapter 9

Concluding Remarks

9.1 Summary of Salient Findings

Predicting the thermodynamic properties of fluids is of central importance to the field of chemical engineering. In this thesis, I have examined the use of integral equation theories to predict structural and bulk thermodynamic properties of several complex fluids which are described by interaction site potential models.

In Chapter 2, I presented a detailed discussion of a commonly used integral equation for interaction site fluids, known as the site-site Ornstein-Zernike (SSOZ) equation. Specifically, I discussed the approximate closure relations which complement the SSOZ equation, as well as presented formulae to calculate a variety of thermodynamic properties of the fluid.

In Chapter 3, the SSOZ equation was applied to several different potential models for water at ambient conditions. A comparison of the predictions of structural and bulk thermodynamic properties was made with results from computer simulations and experimental measurements. It was found that the SSOZ-HNC equation can capture reasonably well the short-ranged correlations in water. However, the distribution of water molecules in the second coordination shell and beyond, as predicted by the SSOZ-HNC equation, was found to deviate significantly from that predicted by computer simulations or deduced from experimental measurements. The predictions of the bulk thermodynamic properties of water, with the exception of the pressure,
were found to be reasonable.

In Chapter 4, the SSOZ equation, under a variety of different closure relations, was applied to n-alkanes at infinite dilution in water in order to compare the quantitative predictive capabilities of the various closures. The HNC closure, which is the only closure utilized to predict bulk thermodynamic properties of interaction site fluids prior to this thesis, was found to perform rather poorly. Specifically, it consistently underpredicted the magnitudes of both the solute partial molar volume and the solute-solvent interaction energy, grossly overpredicted the magnitude of the residual chemical potential, and gave the incorrect sign of the enthalpy of solution. On the other hand, the MaS and BPGG closures, which had not been utilized prior to this thesis in conjunction with the SSOZ equation, yielded reasonable predictions of the structural and bulk thermodynamic properties of the hydrocarbon-water systems examined. In particular, the SSOZ-BPGG equation predicted the temperature variation of the residual chemical potential over the relatively broad range 5 – 80°C in very good agreement with the experimental data.

The accuracy of the equivalent-site approximation (ESA) on the predictions of the structural and bulk thermodynamic properties of propane at infinite dilution in water was also tested. Note that of all the n-alkanes, propane poses the most severe challenge to the ESA. Interestingly, already for propane, the ESA yields predictions of bulk thermodynamic properties which are within 5% of those obtained using the rigorous calculations.

In addition, for flexible n-alkanes (4 ≤ n ≤ 7), the change in the chain conformations associated with transferring these molecules from vacuum to water at infinite dilution was predicted. Both the SSOZ-HNC and SSOZ-MaS equations predicted that the hydrocarbon chains become more collapsed when placed in water, which is what is expected from physical considerations. However, the SSOZ-HNC equation predicted a more severe collapse than that predicted by the SSOZ-MaS equation.

In Chapter 5, the SSOZ equation was applied to a surfactant-water model system, based on the Lennard-Jones interaction potential, and was found to yield some unphysical predictions. For HT surfactants in solution, where no self-assembled micel-
lar microstructures are expected to form, the predictions were found to be consistent with results of simulations performed on the same system. However, for H₂T₅ surfactants in a Lennard-Jones solvent, where micellar aggregates were observed to form by computer simulations, the SSOZ-PY equation yielded several unphysical results. In particular, the surfactant-surfactant site-site pair correlation functions were found to exhibit a large negative region at zero to low surfactant concentrations, and no solutions were found for a wide range of solution conditions. When the HNC closure was utilized, no solutions were found for the SSOZ-HNC equation except at very high temperatures. The unphysical behavior of the SSOZ equation, along with the large differences in the predictions of the SSOZ-PY and SSOZ-HNC equations, led to the conclusion that the SSOZ equation with a simple fluid closure has difficulties in modeling the behavior of self-assembling fluids.

The limitations of the SSOZ equation in the case of the surfactant-water model system, coupled to some of its other inherent limitations, led to the use of a new set of integral equations for interaction site fluids known as the Chandler-Silbey-Ladanyi (CSL) equations. The principal advantage of the CSL equations over the SSOZ equation is that their accuracy can, in principle, be systematically improved. In Chapter 6, the basic formalism behind the CSL equations was presented. In addition, formulae for various thermodynamic properties were developed in the context of the CSL equations, and connectivity and auxiliary site issues related to these equations were analyzed.

In Chapter 7, the CSL equations were applied to homonuclear and heteronuclear diatomic Lennard-Jones fluids to assess their range of validity and to compare their predictive accuracy with that of the SSOZ equation. For homonuclear molecules, the predictions of the CSL-HNC equations were found to be more accurate than those of the SSOZ-PY equation, when compared with computer simulation data, as the bond length increases or when the density decreases. The opposite was found to be the case for the SSOZ-PY equation. Temperature was not found to have a significant effect on the structural predictive capabilities of these equations.

A method for computing the low-order density bridge functions was also devel-
oped. In the homonuclear case, the zeroth-order bridge functions were found to have little effect on the predictions of the CSL equations. However, the addition of the first-order bridge functions resulted in a significant improvement in the predictive capabilities of the CSL equations.

For nonpolar heteronuclear diatomic Lennard-Jones molecules, the CSL-HNC equations were found to perform very well in predicting the correlation functions between the larger interaction sites, while for the correlations between the smaller interaction sites, the predictions were found to be less accurate. For polar diatomic molecules, the CSL-HNC equations seem to offer an improvement over the SSOZ-HNC equation. Here too, the CSL equations provide better predictions for the correlation functions between the larger interaction sites.

Finally, in Chapter 8, the CSL equations were applied to several different potential models for water to assess their predictive accuracy as compared to that of the SSOZ equation. The predictions of the site-site correlation functions for water using the CSL-HNC equations were found to be in slightly better agreement with the computer simulation results than those of the SSOZ-HNC equation. In particular, the CSL-HNC equations appear to capture the tetrahedral structure of water, while the SSOZ-HNC equation does not. The addition of the zeroth-order bridge functions does not significantly alter the predictions of the CSL-HNC equations. This is similar to what was found in Chapter 7 for the diatomic Lennard-Jones fluid.

Several different thermodynamic properties of water were also computed using the CSL-HNC and the SSOZ-HNC equations. Both equations yielded similar results for the residual Helmholtz free energy. For the residual chemical potential, pressure, and isothermal compressibility, the CSL-HNC equations gave predictions which were in better agreement with the simulation results than those of the SSOZ-HNC equation.

The phase behavior of water was also predicted using these integral equations. The vapor branch of the temperature-density coexistence curve was found to be more accurately predicted by the SSOZ-HNC equation, while the liquid branch was found to be better predicted by the CSL-HNC equations. The vapor pressure predictions of the SSOZ-HNC equation were found to be in very good agreement with those
measured experimentally, while those of the CSL-HNC equations were found to be somewhat higher.

In summary, the SSOZ equation seems to work fairly well, primarily at higher densities, and when repulsive interactions dominate, such as, for molecules composed of hard-sphere interaction sites. In addition, the SSOZ-PY, SSOZ-MaS, and SSOZ-BPGG equations work fairly well if only short-ranged interactions are present. On the other hand, the SSOZ-HNC and SSOZ-SMSA equations are more appropriate if long-range interactions are present. When the attractive interactions become extremely important in controlling the structure of the fluid, such as, in water or a self-assembling micellar system, the SSOZ equation with a simple fluid closure yields fairly poor and sometimes even unphysical predictions.

The CSL equations, on the other hand, work fairly well at low densities and for molecules having long bond lengths. The addition of low-order bridge functions will, in general, improve the predictive accuracy of the CSL equations. However, considerably more work is still needed in order to identify better approximations for the bridge functions, as well as to determine the full range of validity and applicability of the CSL equations.

9.2 Recommendations for Future Work

There are several directions in which this thesis can be extended. In what follows, I present a list of several interesting directions which could be pursued.

1. Monson and coworkers have developed\textsuperscript{136} a perturbation theory for interaction site fluids based on the CSL equations. To date, this perturbation theory has successfully predicted\textsuperscript{137, 138, 139} the structure, thermodynamics, and phase behavior of fluids composed of diatomic molecules. This perturbation theory could be extended to describe more complex fluids, including polymer melts and blends. Initial studies should focus on single-component polymer melts. The appropriate reference system would be a fluid consisting of hard-sphere chains. The thermodynamics of the reference system could be obtained using available
equations of state. The structure can be obtained by using the SSOZ-PY equation. A particularly interesting system to consider is a symmetric polymer blend. The dependence of the critical temperature, $T_c$, on the degree of polymerization, $N$, has been computed for this system using the SSOZ-MSA equation, which yields, $T_c \propto N^{1/2}$. This result is significantly different from the experimentally observed behavior, $T_c \propto N$, which is also predicted by both computer simulations and mean-field theory. It would be useful to determine the predicted behavior of $T_c$ with $N$ in the context of the CSL equations.

2. With the current available closures for the SSOZ equation, a non-trivial dielectric constant cannot be computed. Chandler et al. have shown that the CSL equations under certain constraints (local neutrality and connectivity) can provide nontrivial predictions for the dielectric constant. However, the current available closures for the CSL equations do not satisfy these constraints. Therefore, it appears important to develop new closures for the CSL equations which satisfy these constraints, so that reasonable predictions for the dielectric constant of interaction site fluids can be made.

3. Recall that the SSOZ equation with a simple fluid closure was found to be incapable of properly predicting the properties of a model surfactant-water system, in which spontaneous self-assembled microstructures form (see Chapter 5). In particular, the SSOZ equation yielded unphysical solutions, or even did not possess solutions, for the surfactant-surfactant pair correlation functions. Note that in these systems, surfactants were examined at low concentrations, where the SSOZ equation is known to perform poorly (see Chapter 7). However, the CSL equations were found to yield accurate predictions for systems at low densities (see Chapter 7). Therefore, it would be very interesting to utilize the CSL equations to predict the behavior of the surfactant-water model system in order to determine if they can predict the spontaneous formation of micellar aggregates.
4. Analytical solutions of the SSOZ-MSA equations have been obtained for hard dumbbell\textsuperscript{40, 41, 42, 43, 44, 45} and polar hard dumbbell\textsuperscript{46, 47} systems based on the method of Baxter factorization.\textsuperscript{164, 165} Analogous analytical solutions of the CSL equations with the MSA closure should also exist for these systems. Because analytical solutions offer more physical insight than numerical ones, it would be interesting to find these solutions and compare the predictions of the SSOZ-MSA and CSL-MSA equations.

5. As shown in this thesis, the treatment of the bridge functions plays a major role in the predictive accuracy of the CSL equations. Better approximations are required for the bridge functions. These can be obtained by systematically including bridge diagrams of successively higher-order in the density, or perhaps by some other method. The bridge functions of soft-sphere\textsuperscript{166} and Lennard-Jones\textsuperscript{167} fluids have been obtained through computer simulation methods. It would be interesting to determine the bridge functions of various interaction site fluids, such as diatomic soft-sphere and Lennard-Jones fluids, polymeric chains, and water, using computer simulations and compare the results with those obtained by the approximate methods.

9.3 Final Remarks

As a final note, it is important to put this thesis in perspective. Although both the SSOZ and CSL equations provide a useful description of the liquid phase for interaction site fluids, neither of them represents an "end all theory". That is, these equations are not derived from first principles and thus will never be able to provide an exact description of a real fluid. One must always keep in mind the basic assumptions which underly each of these equations. For example, they both assume that the system can be treated classically and that the interaction potential between molecules is pairwise decomposable. Although these assumptions can, in principle, be relaxed, the resulting theory is at this point computationally intractable (prohibitive).

Instead, the work presented in this thesis should be regarded as a progression in
a continuing process of increasing our understanding and predictive capability of the liquid state. There is always a tradeoff between the rigor of a theory and its predictive ability. In general, the closer a theory starts from first principles, the more difficult it becomes, computationally, to obtain predictions. However, as computers become faster and cheaper, this tradeoff will become less of a constraint and will allow the use of more fundamental equations.

For example, in the past, lattice theories were the most popular description of a fluid because of their relative conceptual and computational simplicity. However, it was known that these theories do not provide a fully accurate description of a fluid, although they do capture some of the essential underlying physics. As the theory of liquids progressed and as computers became more powerful, there was a move toward integral equation theories which dealt with off lattice fluids characterized by pairwise additive interaction potentials. Similarly, as computational resources become even greater, one should expect a move away from pairwise descriptions of the interaction potential toward a more accurate multibody description.

It is also important to realize that no practical theory will ever provide an exact description of the liquid state. Approximations must always be made in order to make the calculations involved in the theory tractable. One must also realize that although a theory is not completely rigorous, it can still be very useful. For the chemical engineer, the major issue is not whether a theory is exact, but instead whether it is accurate enough for the calculations at hand. For example, by correlating the parameters of the lattice theory of fluids (such as, surface areas, interaction energies, etc.) to properties of real molecules, fairly accurate semiempirical models have been developed. These models are still used today by many engineers, in spite of the fact that they represent a rather simplistic description of a fluid. In a similar manner, perhaps a semiempirical theory can be developed from the CSL equations.

In any case, this thesis represents an important step in the journey toward understanding the behavior of complex fluids which are relevant to the chemical engineer.
Appendix A

Derivation of Eq. (2.25)

If the bridge functions are approximated by the form \( b = b(t(r)) \), where \( t(r) = h(r) - c(r) \), then the last term on the right-hand side of Eq. (2.24) can be rewritten as

\[
\int_0^1 d\zeta' h_{\alpha M\alpha'M'}(r; \zeta') \frac{\partial b_{\alpha M\alpha'M'}(r; \zeta')}{\partial \zeta'}
= \int_0^1 d\zeta' h_{\alpha M\alpha'M'}(r; \zeta') \frac{\partial b_{\alpha M'\alpha'M'}(t_{\alpha M'\alpha'M'}(r; \zeta'))}{\partial t_{\alpha M'\alpha'M'}(r; \zeta')}
\]

(A.1)

If an integration path is chosen, such that, \( h(r; \zeta') = \zeta' h(r) \) for all solute-solvent pair correlation functions, one can write Eq. (A.1) as

\[
\int_0^1 d\zeta' h_{\alpha M\alpha'M'}(r; \zeta') \frac{\partial b_{\alpha M'\alpha'M'}(t_{\alpha M'\alpha'M'}(r; \zeta'))}{\partial t_{\alpha M'\alpha'M'}(r; \zeta')}
= \int_0^1 d\zeta' \zeta' h_{\alpha M\alpha'M'}(r) \frac{\partial b_{\alpha M'\alpha'M'}(t_{\alpha M'\alpha'M'}(r; \zeta'))}{\partial t_{\alpha M'\alpha'M'}(r; \zeta')}
\]

(A.2)

Because the solute is at infinite dilution in the solvent, the solvent-solvent pair correlation functions are independent of the solute-solvent coupling constant, \( \zeta' \). Choosing \( h_{uv}(r; \zeta') = \zeta' h_{uv}(r) \) implies that \( t_{uv}(r; \zeta') = \zeta' t_{uv}(r) \) for all sites \( u \) associated with the solute and all sites \( v \) associated with the solvent. This can be shown by writing
$t_{uv}(r)$ in terms of $h(r)$ in the context of the SSOZ equation, namely,

$$
\hat{t}_{uv}(k; \zeta') = \hat{h}_{uv}(k; \zeta') - \sum_{u'v'} \hat{w}_{u'v'}^{-1}(k) \hat{h}_{u'v'}(k; \zeta')[\hat{w}(k) - \rho \hat{h}(k)]_{u'v'}^{-1}
$$

(A.3)

where $u$ and $u'$ are sites associated with the solute and $v$ and $v'$ are sites associated with the solvent. If the molecule is rigid, the only factor which has a dependence on $\zeta'$ is $h_{u'v'}$. Therefore, as stated above, we find that $t_{uv}(r; \zeta') = \zeta' t_{uv}(r)$ for all sites $u$ associated with the solute and all sites $v$ associated with the solvent.

One can now express $\zeta'$ as

$$
\zeta' = \frac{t_{\alpha M\alpha'M'}(r; \zeta')}{t_{\alpha M\alpha'M'}(r)}
$$

(A.4)

Substituting Eq. (A.4) into Eq. (A.2), one obtains

$$
\int_0^1 d\zeta' \frac{h_{\alpha M\alpha'M'}(r; \zeta')}{t_{\alpha M\alpha'M'}(r)} \frac{\partial b_{\alpha M\alpha'M'}(r; \zeta')}{\partial \zeta'}
= \int_0^1 d\zeta' t_{\alpha M\alpha'M'}(r; \zeta') h_{\alpha M\alpha'M'}(r) \frac{\partial b_{\alpha M\alpha'M'}(t_{\alpha M\alpha'M'}(r; \zeta') \frac{\partial t_{\alpha M\alpha'M'}(r; \zeta')}}{\partial \zeta'}
= \frac{h_{\alpha M\alpha'M'}(r)}{t_{\alpha M\alpha'M'}(r)} \int_0^{t_{\alpha M\alpha'M'}(r)} dt' t' \frac{\partial b_{\alpha M\alpha'M'}(t')}{\partial t'}
$$

(A.5)

This completes the derivation of Eq. (2.25).
Appendix B

Coupling Constant Integrations in Eqs. (6.41) and (6.55)

In this Appendix, we provide an outline of the major steps involved in the analytical integration over the coupling constants in Eqs. (6.41) and (6.55).

Rewriting the integrands in Eqs. (6.41) and (6.55) in terms of the indirect correlation function, \( y_{\alpha\gamma}(r) = g_{\alpha\gamma}(\tau)/(1 + f_{\alpha\gamma}(\tau)) \), yields

\[
g_{\alpha\gamma}(r; \lambda) \frac{\partial u_{\alpha\gamma}(r; \lambda)}{\partial \lambda} = [1 + f_{\alpha\gamma}(r; \lambda)] y_{\alpha\gamma}(r; \lambda) \frac{\partial u_{\alpha\gamma}(r; \lambda)}{\partial \lambda} \\
= -\frac{1}{\beta} y_{\alpha\gamma}(r; \lambda) \frac{\partial f_{\alpha\gamma}(r; \lambda)}{\partial \lambda} \\
= -\frac{1}{\beta} \left\{ \frac{\partial}{\partial \lambda} \left[ y_{\alpha\gamma}(r; \lambda)(1 + f_{\alpha\gamma}(r; \lambda)) \right] \\
- [1 + f_{\alpha\gamma}(r; \lambda)] \frac{\partial y_{\alpha\gamma}(r; \lambda)}{\partial \lambda} \right\} \\
= -\frac{1}{\beta} \left\{ \frac{\partial h_{\alpha\gamma}(r; \lambda)}{\partial \lambda} - [1 + f_{\alpha\gamma}(r; \lambda)] \frac{\partial y_{\alpha\gamma}(r; \lambda)}{\partial \lambda} \right\}
\]

(B.1)

where the coupling constant, \( \lambda \), is either equal to \( \zeta \) or \( \zeta' \) depending on whether one integrates Eq. (6.41) or Eq. (6.55), respectively.

From the closure relations, Eqs. (6.25)–(6.28), one finds that the indirect correla-
tion function, \( y_{\alpha \gamma}(r) \), can be written as follows

\[
y_{\alpha \gamma}(r; \lambda) = e^{w_{\alpha \gamma}(r; \lambda)} \left\{ [1 + w_{\alpha \gamma}^{l}(r; \lambda)][1 + w_{\alpha \gamma}^{s}(r; \lambda)] + w_{\alpha \gamma}^{b}(r; \lambda) \right\}
\]  

(B.2)

Taking the derivative of Eq. (B.2) with respect to the coupling constant, \( \lambda \), yields

\[
\frac{\partial y_{\alpha \gamma}(r; \lambda)}{\partial \lambda} = y_{\alpha \gamma}(r) \frac{\partial w_{\alpha \gamma}^{o}(r; \lambda)}{\partial \lambda} + e^{w_{\alpha \gamma}(r; \lambda)} \left\{ \frac{\partial w_{\alpha \gamma}^{l}(r; \lambda)}{\partial \lambda} [1 + w_{\alpha \gamma}^{s}(r; \lambda)] \\
+ [1 + w_{\alpha \gamma}^{l}(r; \lambda)] \frac{\partial w_{\alpha \gamma}^{s}(r; \lambda)}{\partial \lambda} + \frac{\partial w_{\alpha \gamma}^{b}(r; \lambda)}{\partial \lambda} \right\}
\]

(B.3)

Multiplying both sides of Eq. (B.3) by \([1 + f_{\alpha \gamma}(r; \lambda)]\) yields

\[
[1 + f_{\alpha \gamma}(r; \lambda)] \frac{\partial y_{\alpha \gamma}(r; \lambda)}{\partial \lambda} = [1 + h_{\alpha \gamma}(r; \lambda)] \frac{\partial w_{\alpha \gamma}^{o}(r; \lambda)}{\partial \lambda} + [1 + h_{\alpha \gamma}^{o}(r; \lambda)] \frac{\partial w_{\alpha \gamma}^{l}(r; \lambda)}{\partial \lambda} [1 + w_{\alpha \gamma}^{s}(r; \lambda)] \\
+ [1 + w_{\alpha \gamma}^{l}(r; \lambda)] \frac{\partial w_{\alpha \gamma}^{s}(r; \lambda)}{\partial \lambda} + w_{\alpha \gamma}^{b}(r; \lambda)
\]

\[
= [1 + h_{\alpha \gamma}(r; \lambda)] \frac{\partial w_{\alpha \gamma}^{o}(r; \lambda)}{\partial \lambda} + [1 + h_{\alpha \gamma}^{o}(r; \lambda) + h_{\alpha \gamma}^{s}(r; \lambda)] \frac{\partial w_{\alpha \gamma}^{l}(r; \lambda)}{\partial \lambda} \\
+ [1 + h_{\alpha \gamma}^{o}(r; \lambda) + h_{\alpha \gamma}^{l}(r; \lambda)] \frac{\partial w_{\alpha \gamma}^{s}(r; \lambda)}{\partial \lambda} + [1 + h_{\alpha \gamma}(r; \lambda)] \frac{\partial w_{\alpha \gamma}^{b}(r; \lambda)}{\partial \lambda}
\]

(B.4)

Substituting in Eq. (B.4) the expressions for \( w_{\alpha \gamma}^{i} \) (i=0, l, r, or b) given in Eqs. (6.29)–(6.32), multiplying both sides by \( \rho^{2} \), and summing over all indices \( \alpha \) and \( \gamma \), yields

\[
\rho^{2} \sum_{\alpha \gamma} [1 + f_{\alpha \gamma}(r; \lambda)] \frac{\partial y_{\alpha \gamma}(r; \lambda)}{\partial \lambda} \\
= \frac{\partial}{\partial \lambda} \left\{ -\rho^{2} \sum_{\alpha \gamma} [c_{\alpha \gamma}^{o}(r; \lambda) + c_{\alpha \gamma}^{l}(r; \lambda) + c_{\alpha \gamma}^{s}(r; \lambda) + c_{\alpha \gamma}^{b}(r; \lambda)] \\
+ \rho^{2} \sum_{\alpha \gamma} [b_{\alpha \gamma}^{o}(r; \lambda) + b_{\alpha \gamma}^{l}(r; \lambda) + b_{\alpha \gamma}^{s}(r; \lambda) + b_{\alpha \gamma}^{b}(r; \lambda)] \\
+ \rho^{2} \sum_{\alpha \gamma} h_{\alpha \gamma}(r; \lambda) + \frac{1}{2} Tr[H(r; \lambda)\bar{p}]^{2} \\
- Tr[H(r; \lambda)\bar{p} \frac{\partial C(r; \lambda)}{\partial \lambda} \bar{p}] + Tr[H(r; \lambda)\bar{p} \frac{\partial B(r; \lambda)}{\partial \lambda} \bar{p}] \right\}
\]

(B.5)
Summing over all sites $\alpha$ and $\gamma$ in Eq. (B.1), multiplying the result by $\rho^2$, substituting Eq. (B.5), and integrating over the coupling constant, $\lambda$, from 0 to 1, yields

$$
\beta \rho^2 \sum_{\alpha, \gamma} \int_0^1 d\lambda d^3 r g_{\alpha \gamma}(r; \lambda) \frac{\partial u_{\alpha \gamma}(r; \lambda)}{\partial \lambda} 
= -\rho^2 \sum_{\alpha, \gamma} \int d^3 r [c_{\alpha \gamma}^\alpha(r) + c_{\alpha \gamma}^\gamma(r) + c_{\alpha \gamma}^\delta(r) + c_{\alpha \gamma}^\beta(r)] 
+ \rho^2 \sum_{\alpha, \gamma} \int d^3 r [b_{\alpha \gamma}^\alpha(r) + b_{\alpha \gamma}^\gamma(r) + b_{\alpha \gamma}^\delta(r) + b_{\alpha \gamma}^\beta(r)] + \frac{1}{2} \int d^3 r Tr[H(r)\bar{\rho}]^2 
- \int_0^1 d\lambda \int \frac{d^3 k}{(2\pi)^3} Tr[\hat{H}(k; \lambda)\bar{\rho} \frac{\partial \hat{H}(k; \lambda)}{\partial \lambda} \bar{\rho}] 
+ \int_0^1 d\lambda \int \frac{d^3 k}{(2\pi)^3} Tr[\hat{H}(k; \lambda)\bar{\rho} \frac{\partial \hat{B}(k; \lambda)}{\partial \lambda} \bar{\rho}] 
= -\rho^2 \sum_{\alpha, \gamma} \int d^3 r [h_{\alpha \gamma}^\alpha(r) + h_{\alpha \gamma}^\gamma(r) + h_{\alpha \gamma}^\delta(r) + h_{\alpha \gamma}^\beta(r)] 
+ \rho^2 \sum_{\alpha, \gamma} \int d^3 r [w_{\alpha \gamma}^\alpha(r) + w_{\alpha \gamma}^\gamma(r) + w_{\alpha \gamma}^\delta(r) + w_{\alpha \gamma}^\beta(r)] 
+ \int d^3 r \left\{ Tr[W(r)\bar{\rho}H(r)\bar{\rho}] - \frac{1}{2} Tr[H(r)\bar{\rho}]^2 + Tr[C(r)\rho H(r)\bar{\rho}] \right\} 
- \int_0^1 d\lambda \int d^3 r Tr[B(r; \lambda)\bar{\rho} \frac{\partial H(r; \lambda)}{\partial \lambda} \bar{\rho}] 
- \int_0^1 d\lambda \int \frac{d^3 k}{(2\pi)^3} Tr[\hat{H}(k; \lambda)\bar{\rho} \frac{\partial \hat{C}(k; \lambda)}{\partial \lambda} \bar{\rho}] 
$$

(B.6)

The only coupling constant integrations left are contained in the last two terms of Eq. (B.6). The $\lambda$-integration in the second to last term of Eq. (B.6) involves the bridge functions, and therefore, its value is specific to the particular closure under consideration and will not be modified further. The $\lambda$-integration in the last term of Eq. (B.6) can be manipulated so that it depends only on the correlation functions at full coupling. From this point on, the derivations of the residual Helmholtz free energy and the residual chemical potential differ. The evaluation of this integral will be given separately for $A^{\alpha \beta}$ in Appendix B1, and for $\mu^{\alpha \beta}$ in Appendix B2.
B.1 Integral for the Residual Helmholtz Free Energy

The CSL equations given in Eq. (6.20) can be rewritten as follows

\[ p \hat{H}(k) = -[\bar{p} + p \hat{S}(k)\bar{p}] + \left\{ 1 - [\bar{p} + p \hat{S}(k)\bar{p}]\hat{C}(k) \right\}^{-1} [\bar{p} + p \hat{S}(k)\bar{p}] \]  

(B.7)

Substituting Eq. (B.7) in the last term of Eq. (B.6) yields

\[
\int_0^1 d\zeta \text{Tr}[\hat{H}(k; \zeta)\bar{p} \frac{\partial \hat{C}(k; \zeta)}{\partial \zeta} \bar{p}]
\]

\[
= \int_0^1 d\zeta \left\{ -\text{Tr}[(\bar{p} + p \hat{S}(k)\bar{p}) \frac{\partial \hat{C}(k; \zeta)}{\partial \lambda} \bar{p}] 
+ \text{Tr}[(\bar{p} + p \hat{S}(k)\bar{p}) \hat{C}(k)]^{-1} (\bar{p} + p \hat{S}(k)\bar{p}) \frac{\partial \hat{C}(k; \zeta)}{\partial \lambda} \right\}
\]

\[
= -\text{Tr}[(\bar{p} + p \hat{S}(k)\bar{p}) \hat{C}(k)] - \text{Tr} \ln[1 - (\bar{p} \cdot \bar{p} \hat{S}(k)\bar{p})\hat{C}(k)]
\]  

(B.8)

Substituting Eq. (B.8) in Eq. (B.6), and subsequently using the resulting expression in Eq. (6.41), yields Eq. (6.42)

B.2 Integral for the Residual Chemical Potential

Defining a matrix, \( \chi \), as

\[ \hat{\chi}(k) = \bar{p} + p \hat{S}(k)\bar{p} + p \hat{H}(k)\bar{p} \]  

(B.9)

it is possible to rewrite Eq. (6.20) as follows

\[ \hat{H}(k)\bar{p} = [\hat{C}(k) + \hat{S}(k)](\bar{p} + p \hat{S}(k)\bar{p} + \bar{p} \hat{H}(k)\bar{p}) - \hat{S}(k)\bar{p} \]

\[ = \hat{C}(k)\hat{\chi}(k) + \hat{S}(k)\bar{p} \hat{S}(k)\bar{p} + \bar{p} \hat{S}(k)\bar{p} \hat{H}(k) \]
\[ \frac{1}{2} \left\{ [1 - \bar{p}\hat{S}(k)]^{-1}\hat{C}(k)\hat{\chi}(k) \right\} \] (B.10)

Note that the functions, \( \chi \) and \( S \), are independent of the solute-solvent coupling constant. Using Eq. (B.10) in the last term of Eq. (B.6) yields

\[
\int_0^1 d\zeta' Tr \left[ \hat{H}(k; \zeta')\bar{p} \frac{\partial \hat{C}(k; \zeta')}{\partial \zeta'} \right]
\]

\[
= \int_0^1 d\zeta' Tr \left\{ [1 - \bar{p}\hat{S}(k)]^{-1}\hat{C}(k; \zeta')\hat{\chi}(k) \frac{\partial \hat{C}(k; \zeta')}{\partial \zeta'} \bar{p} \right\}
\]

\[
= \frac{1}{2} Tr \left\{ [1 - \bar{p}\hat{S}(k)]^{-1}\hat{C}(k)\hat{\chi}(k)\hat{C}(k)\bar{p} \right\}
\]

\[
= \frac{1}{2} Tr \left[ \hat{H}(k)\bar{p}\hat{C}(k)\bar{p} \right]
\] (B.11)

Substituting Eq. (B.11) in Eq. (B.6), and subsequently using the resulting expression in Eq. (6.55), yields Eq. (6.56).
Appendix C

Numerical Methods

C.1 Introduction

The SSOZ and CSL equations with their associated closure relations result in a set of coupled nonlinear integral equations which must be solved in order to obtain the correlation functions of a fluid. For a system with \( n \) distinct interaction sites, there are \( n(n + 1)/2 \) coupled integral equations for the SSOZ equation, and \( n(2n + 1) \) coupled integral equations for the CSL equations. These equations are nonlinear and as a result no analytical solutions are available. Therefore, one must employ numerical methods to solve them.

The first step in obtaining a numerical solution to these equations is to convert the integral equations into a set of coupled nonlinear algebraic equations

\[
R(\Gamma) = 0 \quad \text{(C.1)}
\]

where \( R \) and \( \Gamma \) are both vectors. These equations can be solved by several methods. Two of the most common include the direct substitution\(^{149}\) (or Picard) method, and the Newton-Raphson\(^{149}\) method.

The Picard method has an advantage over the Newton-Raphson method in that it is less computationally intensive. To apply the Picard method, Eq. (C.1) is written
in the form
\[ \Gamma = R'(\Gamma) \] (C.2)

One must then make an initial guess for the vector \( \Gamma \), which I will denote as \( \Gamma^{(0)} \). To determine successive values of \( \Gamma \), the following formula is used
\[ \Gamma^{(i+1)} = \alpha \Gamma^{(i)} + (1 - \alpha)R'(\Gamma^{(i)}) \] (C.3)

where \( \Gamma^{(i)} \) is the \( i \)th approximation to \( \Gamma \), and \( \alpha \) is an arbitrary parameter with a value between 0 and 1. This procedure is continued until \( \Gamma^{(i)} \) satisfies Eq. (C.2). The convergence of this procedure depends on the precise form of Eq. (C.3), the value of \( \alpha \), and the initial guess used for \( \Gamma \). In general, however, the Picard method is not always stable. That is, it does not always converge to a solution and even when it does converge, it does so very slowly. In terms of the SSOZ and CSL equations, the Picard method is too inefficient to be useful.

The Newton-Raphson method has an advantage over the Picard method in that is is much more stable. It uses the following iterative procedure
\[ \Gamma^{(i+1)} = \Gamma^{(i)} - J^{-1}(\Gamma^{(i)})R(\Gamma^{(i)}) \] (C.4)

where \( J \) is the Jacobian which is given by
\[ J_{ij}(\Gamma) = \frac{\partial R_i(\Gamma)}{\partial \Gamma_j} \] (C.5)

This iterative procedure is repeated until \( \Gamma^{(i)} \) satisfies Eq. (C.1). Although the Newton-Raphson method is more robust than the Picard method, it requires the inversion of a very large matrix, which is computationally expensive. In the case of differential equations, this matrix is sparse, that is, many of its elements are always equal to zero, and efficient algorithms for inverting the Jacobian can be constructed to take advantage of this fact. For integral equations, however, every matrix element is nonzero. This severely restricts the size of the systems which can be studied. In
terms of the SSOZ and CSL equations, this means that the Newton-Raphson method is too prohibitively expensive to employ. For the reasons discussed above, a new solution method is needed.

In the next section, I will describe a hybrid method, known as the Gillan method, which has been applied successfully to solve integral equations in the case of simple fluids.

C.2 Gillan Method

The Gillan\textsuperscript{168} method combines the best of both the Picard and Newton-Raphson methods. In this method, the function $\Gamma$ is divided into a coarse contribution and a fine contribution. By applying the Newton-Raphson method to the coarse part of the solution and the Picard method to the fine part, the Gillan method is able to be fairly stable while remaining computationally tractable.

The first step in the Gillan method is to discretize the function $\tilde{\Gamma}(k)$ so that one is no longer solving for the entire function but rather only for the value of the function $\tilde{\Gamma}(k_i)$ at various grid points $k_i$, where $i = 1, N$. The next step is to choose how to divide $\Gamma$ into a coarse contribution and a fine contribution. Labik et al.\textsuperscript{121} suggested using the first $M$ grid points as the coarse contribution of the function $\Gamma$, and the remaining $N - M$ points as the fine contribution. This choice is reasonable since the small values of $k$ are associated with the slowly varying portions of $\Gamma$, and is the one which I have actually utilized in my calculations.

A flow diagram of the Gillan method is given in Figure C-1. One begins with an initial guess for $\Gamma$. From this, the residual, $R$, and the Jacobian, $J$, are computed. From these, the Newton-Raphson method is applied to determine $\Gamma$ at the first $M$ grid points. Once this has converged, the Picard method is used to determine $\Gamma$ at the remaining grid points. This process is repeated until it has converged to a self-consistent solution for $\Gamma$.

The remainder of this Appendix is organized as follows. In Section C.3, I will present formulae for the residual, $R$, and the Jacobian, $J$, for the SSOZ equation. In
Figure C-1: Flow diagram of the Gillan method.
Section C.4, I will present similar formulae for the CSL equations. Finally, in Section C.5, I will provide a brief description of calculations involving the Fourier transforms.

C.3 The SSOZ Equation

C.3.1 Equivalent Sites

The number of equations which need to be solved can be reduced by taking into account the presence of equivalent sites. Two sites are equivalent if they have the same interaction potentials and the same correlation functions. I will now rearrange the SSOZ equation to explicitly show the presence of equivalent sites.

Let a Greek index represent a particular type of site, and a lower case Latin index represent a particular site of a certain type. The SSOZ equation (see Eq. (2.13)) can then be written as

\[ \hat{h}_{\alpha\gamma\beta}(k) = \sum_{\sigma\tau\tau'} \left[ \hat{w}_{\alpha\alpha\sigma\tau}(k) \hat{c}_{\sigma\tau\tau'}(k) \hat{\omega}_{\tau\tau'\gamma\beta}(k) + \hat{w}_{\alpha\alpha\sigma\tau}(k) \hat{\rho}_{\tau\tau'} \hat{h}_{\tau\tau'\gamma}(k) \right] \]  

(C.6)

Because the Latin indices refer to equivalent sites, the correlation functions should be independent of them. That is, \( h_{\alpha\alpha\beta}(r) = h_{\alpha\gamma}(r) \) and \( c_{\alpha\alpha\beta}(r) = c_{\alpha\gamma}(r) \) for all \( a \) and \( b \). Also, note that \( \rho_{\alpha\alpha} = \rho_{\alpha} \). Taking these facts into account, Eq. (C.6) can be rewritten as follows

\[ \hat{h}_{\alpha\gamma}(k) = \sum_{\sigma\tau\tau'} \left[ \hat{w}_{\alpha\alpha\sigma\tau}(k) \hat{c}_{\sigma\tau\tau'}(k) \hat{\omega}_{\tau\tau'\gamma}(k) + \hat{w}_{\alpha\alpha\sigma\tau}(k) \hat{\rho}_{\tau\tau'} \hat{h}_{\tau\tau'\gamma}(k) \right] \]  

(C.7)

If one defines \( \hat{w}_{\alpha\gamma}(k) = \sum_{ab} \hat{w}_{\alpha\alpha\beta}(k) \), and sums over \( a \) and \( b \) on both sides of Eq. (C.7), one obtains

\[ n_{\alpha} \hat{h}_{\alpha\gamma}(k)n_{\gamma} = \sum_{\sigma\tau} \left[ \hat{w}_{\alpha\sigma}(k) \hat{c}_{\sigma\tau}(k) \hat{\omega}_{\tau\gamma}(k) + \hat{w}_{\alpha\sigma}(k) \hat{\rho}_{\sigma\tau} n_{\tau} \hat{h}_{\tau\tau'\gamma}(k) n_{\gamma} \right], \]  

(C.8)

where \( n_{\alpha} \) is the number of sites of type \( \alpha \) in the system. This equation is rewritten
below in matrix form in momentum \((k)\) space

\[
\hat{h}(k) = n^{-1}\hat{\omega}(k)\hat{c}(k)[1 - \rho\hat{\omega}(k)\hat{c}(k)]^{-1}\hat{\omega}(k)n^{-1}
\]

Note that this equation only involves distinct interaction sites and not equivalent sites.

**C.3.2 Development of the Residual**

The SSOZ equation (see Eq. (C.9)) can be written as

\[
\dot{i}(k) = n^{-1}\hat{\omega}(k)\hat{c}(k)[1 - \rho\hat{\omega}(k)\hat{c}(k)]^{-1}\hat{\omega}(k)n^{-1} - \dot{c}(k)
\]

where \(\dot{i}(k) = \hat{h}(k) - \dot{c}(k)\) is the chain function.

It is more convenient to work with a new set of functions, \(\Gamma\) and \(\Theta\), which are defined by the following equations

\[
\tilde{\Gamma}(k) = k\tilde{\dot{c}}(k)
\]

\[
\tilde{\Theta}(k) = k\tilde{\dot{c}}(k)
\]

where \(\tilde{\cdot}\) denotes the sine Fourier transform of a function (see Eq. (C.104)). Note that it follows from Eqs. (C.98) and (C.100) that

\[
\Gamma(r) = rt(r)
\]

\[
\Theta(r) = rc(r)
\]

The residual, \(R\), is defined by the following equation

\[
R(k) = k\dot{\Gamma}(k) - n^{-1}\hat{\omega}(k)k^2\hat{c}(k)[k - \rho\hat{\omega}(k)\hat{c}(k)]^{-1}\hat{\omega}(k)n^{-1} + k\dot{c}(k)
\]

\[
= \tilde{\Gamma}'(k) - n^{-1}\hat{\omega}(k)k\tilde{\Theta}(k)[k - \rho\hat{\omega}(k)\tilde{\Theta}(k)]^{-1}\hat{\omega}(k)n^{-1} + \tilde{\Theta}(k)
\]

The function, \(\Theta\), can be computed from \(\Gamma\) through the closure relation. The
The hypernetted-chain closure is given by

\[ c_{\alpha\gamma}(r) = \exp[-\beta u_{\alpha\gamma}(r) + t_{\alpha\gamma}(r)] - t_{\alpha\gamma}(r) - 1 \]  

(C.17)

\[ \Theta_{\alpha\gamma}(r) = r \exp[-\beta u_{\alpha\gamma}(r) + \Gamma_{\alpha\gamma}(r)/r] - \Gamma_{\alpha\gamma}(r) - r \]  

(C.18)

and the Percus-Yevick closure is given by

\[ c_{\alpha\gamma}(r) = \exp[-\beta u_{\alpha\gamma}(r)][1 + t_{\alpha\gamma}(r)] - t_{\alpha\gamma}(r) - 1 \]  

(C.19)

\[ \Theta_{\alpha\gamma}(r) = \exp[-\beta u_{\alpha\gamma}(r)][r + \Gamma_{\alpha\gamma}(r)] - \Gamma_{\alpha\gamma}(r) - r \]  

(C.20)

Given a guess for \( \Gamma \), one can compute \( \Theta \) from one of the above closure relations. With this, one can then compute the residual, \( R \), by utilizing Eq. (C.18). Note that if we use the correct \( \Gamma \), then \( R_{\alpha\gamma}(k) = 0 \).

### C.3.3 Development of the Jacobian

In this section, I develop an expression for the Jacobian. To begin, I evaluate \( \delta \dot{\Theta}_{\alpha\gamma}(k)/\delta \Gamma_{\alpha'\gamma'}(k') \)

\[
\frac{\delta \dot{\Theta}_{\alpha\gamma}(k)}{\delta \Gamma_{\alpha'\gamma'}(k')} = \int_0^\infty dx \frac{\delta \dot{\Theta}_{\alpha\gamma}(k)}{\delta \Theta_{\alpha\gamma}(x)} \frac{\partial \Theta_{\alpha\gamma}(x)}{\partial \Gamma_{\alpha'\gamma'}(x)} \frac{\delta \Gamma_{\alpha'\gamma'}(x)}{\delta \Gamma_{\alpha\gamma}(k')}
\]

\[
= \int_0^\infty dx [4\pi \sin kx] \frac{\partial \Theta_{\alpha\gamma}(x)}{\partial \Gamma_{\alpha\gamma}(x)} \frac{\delta \Gamma_{\alpha'\gamma'}(x)}{\delta \Gamma_{\alpha\gamma}(k')} \frac{1}{2\pi^2 \sin k'x}
\]

\[
= \frac{1}{\pi} \int_0^\infty dx \cos(k-k')x \frac{\partial \Theta_{\alpha\gamma}(x)}{\partial \Gamma_{\alpha\gamma}(x)} \delta_{\alpha\gamma,\alpha'\gamma'}
\]

\[
- \frac{1}{\pi} \int_0^\infty dx \cos(k+k')x \frac{\delta \Theta_{\alpha\gamma}(x)}{\delta \Gamma_{\alpha\gamma}(x)} \delta_{\alpha\gamma,\alpha'\gamma'}
\]

\[
= [\Phi_{\alpha\gamma}(k-k') - \Phi_{\alpha\gamma}(k+k')] \delta_{\alpha\gamma,\alpha'\gamma'}
\]

\[
= F_{\alpha\gamma}(k,k') \delta_{\alpha\gamma,\alpha'\gamma'}
\]  

(C.21)

where

\[
\Phi_{\alpha\gamma}(k) = \frac{1}{\pi} \int_0^\infty dx \cos kx \frac{\partial \Theta_{\alpha\gamma}(x)}{\partial \Gamma_{\alpha'\gamma'}(x)}
\]  

(C.22)
and

\[ F_{\gamma}(k, k') = \Phi_{\gamma}(k - k') - \Phi_{\gamma}(k + k') \quad (C.23) \]

The expression, \( \partial \Theta_{\gamma}(r)/\partial \Gamma_{\gamma}(r) \), can be determined through the closure relation.

For the HNC closure,

\[ \frac{\partial \Theta_{\gamma}(r)}{\partial \Gamma_{\gamma}(r)} = \exp[-\beta u_{\gamma}(r) + \Gamma_{\gamma}(r)] - 1 \quad (C.24) \]

and for the PY closure,

\[ \frac{\partial \Theta_{\gamma}(r)}{\partial \Gamma_{\gamma}(r)} = \exp[-\beta u_{\gamma}(r)] - 1 \quad (C.25) \]

I will now derive an expression for the Jacobian. In what follows, summation over repeated indices is implied. Specifically,

\[ J_{\gamma,\gamma'}(k, k') = \frac{\delta R_{\gamma}(k)}{\delta \Gamma_{\gamma'}(k')} = \delta_{\gamma,\gamma'} \delta(k - k') - n_{\gamma}^{-1} \hat{w}_{\gamma}(k) \frac{\delta \tilde{\Theta}_{\gamma}(k)}{\delta \Gamma_{\gamma'}(k')} [k - \rho \hat{w}(k) \tilde{\Theta}(k)]^{-1} \hat{w}_{\gamma}(k) n_{\gamma}^{-1} \]

\[ - n_{\gamma}^{-1} \hat{w}_{\gamma}(k) \frac{\delta \tilde{\Theta}_{\gamma}(k)}{\delta \Gamma_{\gamma'}(k')} [k - \rho \hat{w}(k) \tilde{\Theta}(k)]^{-1} \rho \hat{w}_{\gamma}(k) \]

\[ \times \frac{\delta \tilde{\Theta}_{\gamma'}(k)}{\delta \Gamma_{\gamma'}(k')} [k - \rho \hat{w}(k) \tilde{\Theta}(k)]^{-1} \hat{w}_{\gamma}(k) n_{\gamma}^{-1} \]

\[ + \frac{\delta \tilde{\Theta}_{\gamma}(k)}{\delta \Gamma_{\gamma'}(k')} \]

\[ = \delta_{\gamma,\gamma'} \delta(k - k') - n_{\gamma}^{-1} k^2 \frac{\delta \tilde{\Theta}_{\gamma}(k)}{\delta \Gamma_{\gamma'}(k')} [k - \rho \hat{w}(k) \tilde{\Theta}(k)]^{-1} \hat{w}_{\gamma}(k) n_{\gamma}^{-1} \]

\[ + \frac{\delta \tilde{\Theta}_{\gamma'}(k)}{\delta \Gamma_{\gamma'}(k')} \]

\[ = \delta_{\gamma,\gamma'} \delta(k - k') - n_{\gamma}^{-2} \hat{w}_{\gamma}(k) \frac{\delta \tilde{\Theta}_{\gamma}(k)}{\delta \Gamma_{\gamma'}(k')} [k - \rho \hat{w}(k) \tilde{\Theta}(k)]^{-1} \hat{w}_{\gamma}(k) n_{\gamma}^{-1} \]

\[ + F_{\gamma}(k, k') \delta_{\gamma,\gamma'} \]

212
where

\[ \chi(k) = [k - \rho \dot{\omega}(k) \tilde{\Theta}(k)]^{-1} \dot{\omega}(k) \]  

(C.27)

and

\[ \epsilon_{\alpha\gamma,\alpha'\gamma'} = \epsilon_{\alpha\alpha'} \delta_{\gamma\gamma'} + \epsilon_{\alpha\gamma'} \delta_{\gamma\alpha'} (1 - \delta_{\alpha'\gamma'}) \]  

(C.28)

Given the function, \( \tilde{\Gamma}(k) \), one can compute the Jacobian using Eq. (C.26).

### C.3.4 Long-Ranged Correlations

When dealing with polar fluids, one must deal with the fact the direct correlation function, \( c_\gamma \), is long-ranged. For a simple fluid closure, the direct correlation function will have the following long-range decay

\[ c_\gamma(r) \sim \frac{\beta q_{\alpha} q_\gamma}{r}, \quad \text{as } r \to \infty \]  

(C.29)

This implies that the low-\( k \) behavior of \( \hat{c}_\alpha\gamma(k) \) is given by

\[ \hat{c}_\alpha\gamma(k) \sim -\frac{4\pi q_{\alpha} q_\gamma}{k^2}, \quad \text{as } k \to 0 \]  

(C.30)

Note that \( \hat{c}_\alpha\gamma(k) \) diverges for small \( k \). The Fourier transforms are performed numerically on a finite interval. Therefore, in order to obtain accurate results, it is necessary to remove the divergent portion of a function, and numerically transform the resulting short-ranged function. I define the short-ranged portion of the direct correlation function in accord with Ng.\textsuperscript{154} This function, denoted by \( c_{\alpha\gamma}^*(r) \), is given by

\[ c_{\alpha\gamma}^*(r) = c_{\alpha\gamma}(r) - \psi_{\alpha\gamma}(r) \]  

(C.31)
where the function, $\psi$, is given by

$$
\psi_{\alpha\gamma}(r) = -\frac{\beta q_\alpha q_\gamma}{r}
$$
(C.32)

$$
\dot{\psi}_{\alpha\gamma}(k) = -\frac{4\pi\beta q_\alpha q_\gamma}{k^2} \exp \left( -\frac{k^2}{4\alpha^2} \right)
$$
(C.33)

where $\alpha$ is an arbitrary parameter, which is typically chosen to be 1 Å.

Accordingly, the following functions are also short-ranged

$$
\Theta^*(r) = \Theta(r) - r\psi(r)
$$
(C.34)

$$
\tilde{\Theta}^*(k) = \tilde{\Theta}(k) - k\dot{\psi}(k)
$$
(C.35)

and

$$
\Gamma^*(r) = \Gamma(r) + r\psi(r)
$$
(C.36)

$$
\tilde{\Gamma}^*(k) = \tilde{\Gamma}(k) + k\dot{\psi}(k)
$$
(C.37)

where $\Theta^*$ and $\Gamma^*$ denote the short-ranged contributions to $\Theta$ and $\Gamma$, respectively.

In order to find the Fourier transform of $\Theta$ ($\Gamma$), one numerically computes the Fourier transform of $\Theta^*$ ($\Gamma^*$) and then adds (subtracts) $k\dot{\psi}(k)$ to (from) the result.

### C.4 The CSL Equations

In this section, I present expressions for the residual, $R$, and Jacobian, $J$, for the CSL equations. Throughout this section, I will denote the $h$-component bonds as

$$
H_{ab}^{AB}
$$
(C.38)

where the lower indices refer to specific interaction sites. The upper indices refer to the various $h$-component bonds, and can take on a value of either $o$, which means no $s$-vertices intersect that site, or a value of $s$, which means an $s$-vertex intersects that site. These "super" matrices are related to the $h$-component bonds by the following
Because of the symmetry of the \( h \)-component bonds, the following relations hold
\[
H_{\alpha\gamma}^{AB} = (H_{\beta\alpha}^{BA})^T = H_{ba}^{BA} \quad (C.43)
\]

Similar relations also apply for the direct correlation functions.

**C.4.1 Equivalent Sites**

For the CSL equations, the number of equations which need to be solved can be reduced by taking into account the presence of equivalent sites. In this section, a Greek index will represent a particular type of interaction site, and a lower case Latin index will denote a particular site among sites which are equivalent. Using this notation, the CSL equations (see Eq. (6.20)) can be written as

\[
\hat{H}_{\alpha\alpha\gamma\beta}^{AB}(k) = \hat{C}_{\alpha\alpha\gamma\beta}^{AB}(k) + \sum_{\sigma\tau\sigma\tau T} [\hat{C}_{\alpha\alpha\sigma\tau}^{AS}(k) + \hat{S}_{\alpha\alpha\sigma\tau}^{ST}(k)] \rho_{\sigma\tau\sigma\tau T}^{ST}
\times [\hat{H}_{\tau\tau\gamma\beta}^{TB}(k) + \hat{S}_{\tau\tau\gamma\beta}^{TB}(k)]
\]

\[
= \hat{C}_{\alpha\alpha\gamma\beta}^{AB}(k) + \sum_{\sigma\tau\sigma\tau T} \left[ \hat{C}_{\alpha\alpha\sigma\tau}^{AS}(k) \rho_{\sigma\tau\sigma\tau T}^{ST} \hat{H}_{\tau\tau\gamma\beta}^{TB}(k) + \hat{C}_{\alpha\alpha\sigma\tau}^{AS}(k) \rho_{\sigma\tau\sigma\tau T}^{ST} \hat{S}_{\tau\tau\gamma\beta}^{TB}(k) \right]
+ \hat{S}_{\alpha\alpha\sigma\tau}^{AS}(k) \rho_{\sigma\tau\sigma\tau T}^{ST} \hat{H}_{\tau\tau\gamma\beta}^{TB}(k) \quad (C.44)
\]

where I have used that fact that \( \sum_{ST} \hat{S}_{\alpha\sigma}^{AS}(k) \rho_{\sigma\tau}^{ST} \hat{S}_{\tau\gamma}^{TB}(k) = 0 \). The correlation functions are independent of the lower-case Latin indices because they refer to equivalent sites. This implies that, \( H_{\alpha\alpha\gamma\beta}^{AB} = H_{\alpha\gamma}^{AB} \) and \( C_{\alpha\alpha\gamma\beta}^{AB} = C_{\alpha\gamma}^{AB} \), for all \( a \) and \( b \). Using these
facts, one can rewrite Eq. (C.44) as

\[
\hat{H}^{AB}_{\alpha \gamma}(k) = \hat{C}^{AB}_{\alpha \gamma}(k) + \sum_{\sigma \sigma' \tau \tau'} \left[ \hat{C}^{AS}_{\alpha \sigma}(k) \hat{\rho}^{ST}_{\sigma \sigma'} \hat{H}^{TB}_{\tau \gamma}(k) + \hat{\epsilon}^{AS}_{\alpha \sigma}(k) \hat{\rho}^{ST}_{\sigma \sigma'} \hat{S}^{TB}_{\tau \gamma}(k) \right] + \hat{S}^{AS}_{\alpha \sigma \tau}(k) \hat{\rho}^{ST}_{\sigma \sigma'} \hat{H}^{TB}_{\tau \gamma}(k)
\]

(C.45)

Summing over \(a\) and \(b\) on both sides of Eq. (C.45), and using the fact that the density matrix is given by \(\hat{\rho}^{AB}_{\alpha \gamma \beta} = \rho_{\alpha \delta} \delta_{\alpha \beta} (1 - \delta_{A A} \delta_{B B})\), yields

\[
n_\alpha \hat{H}^{AB}_{\alpha \gamma}(k) n_\gamma = n_\alpha \hat{C}^{AB}_{\alpha \gamma}(k) n_\gamma + \sum_{\sigma \sigma' \tau \tau'} \left[ n_\alpha \hat{C}^{AS}_{\alpha \sigma}(k) \hat{\rho}^{ST}_{\sigma \sigma'} \hat{H}^{TB}_{\tau \gamma}(k) n_\gamma \right. \\
+ n_\alpha \hat{\epsilon}^{AS}_{\alpha \sigma}(k) \hat{\rho}^{ST}_{\sigma \sigma'} \hat{S}^{TB}_{\tau \gamma}(k) \\
+ \left. \sum_{\sigma} \hat{S}^{AS}_{\alpha \sigma \tau}(k) \hat{\rho}^{ST}_{\sigma \sigma'} \hat{H}^{TB}_{\tau \gamma}(k) n_\gamma \right]
\]

(C.46)

\[
\hat{H}^{AB}_{\alpha \gamma}(k) = \hat{C}^{AB}_{\alpha \gamma}(k) + \sum_{\sigma \sigma' \tau \tau'} \left[ \hat{C}^{AS}_{\alpha \sigma}(k) n_\sigma \rho \delta_{\sigma \tau} (1 - \delta_{S S} \delta_{T T}) \hat{H}^{TB}_{\tau \gamma}(k) \\
+ \hat{\epsilon}^{AS}_{\alpha \sigma}(k) n_\sigma \rho \delta_{\sigma \tau} (1 - \delta_{S S} \delta_{T T}) \hat{S}^{TB}_{\tau \gamma}(k) \right] \\
+ \frac{1}{n_\alpha n_\sigma} \sum_{\sigma} \hat{S}^{AS}_{\alpha \sigma \tau}(k) n_\sigma \rho \delta_{\sigma \tau} (1 - \delta_{S S} \delta_{T T}) \hat{H}^{TB}_{\tau \gamma}(k) \\
+ \frac{1}{n_\alpha n_\sigma} \sum_{\sigma} \hat{S}^{AS}_{\alpha \sigma \tau}(k) \hat{\rho}^{ST}_{\sigma \sigma'} \hat{S}^{TB}_{\tau \gamma}(k) \right]
\]

(C.47)

where, once again, I have used the fact that \(\sum_{\sigma \sigma' \tau \tau'} \hat{S}^{AS}_{\alpha \sigma \tau}(k) \hat{\rho}^{ST}_{\sigma \sigma'} \hat{S}^{TB}_{\tau \gamma}(k) = 0\), and have defined \(\hat{\rho}^{AB}_{\alpha \gamma}\) as

\[
\hat{\rho}^{AB}_{\alpha \gamma} = n_\alpha \rho \delta_{\alpha \gamma} (1 - \delta_{A A} \delta_{B B})
\]

(C.48)
Defining $\hat{S}_{\alpha\gamma}^{AB}(k)$ as

$$\hat{S}_{\alpha\gamma}^{AB}(k) = \frac{1}{n_\alpha n_\gamma} \sum_{ab} S_{aa'\gamma b}^{AB}$$

(C.49)

and substituting this into Eq. (C.47), one finds

$$\hat{H}_{\alpha\gamma}^{AB}(k) = \hat{C}_{\alpha\gamma}^{AB}(k) + \sum_{\sigma S T} [\hat{C}_{\alpha\sigma}^{AS}(k)\hat{\rho}_{\sigma\alpha}^{ST} \hat{H}_{\tau\tau}^{TB}(k)$$

$$+ \hat{\dot{C}}_{\alpha\sigma}(k)\hat{\rho}_{\sigma\alpha}^{ST} \hat{S}_{\tau\tau}^{TB}(k) + \hat{S}_{\alpha\sigma}^{AS}(k)\hat{\rho}_{\sigma\alpha}^{ST} \hat{H}_{\tau\tau}^{TB}(k)$$

$$+ \hat{\dot{S}}_{\alpha\sigma}^{AS}(k)\hat{\rho}_{\sigma\alpha}^{ST} \hat{S}_{\tau\tau}^{TB}(k)]$$

$$= \hat{C}_{\alpha\gamma}^{AB}(k) + \sum_{\sigma S T} [\hat{\dot{C}}_{\alpha\sigma}(k) + \hat{\dot{S}}_{\alpha\sigma}^{AS}(k)]\rho_{\sigma\alpha}^{ST} [\hat{H}_{\tau\tau}^{TB}(k) + \hat{S}_{\tau\tau}^{TB}(k)]$$

(C.50)

Accordingly, the CSL equations for a system with equivalent sites reduce to those for a system without equivalent sites by using the modified definitions of $\hat{\rho}$ and $S$ given in Eqs. (C.48) and (C.49).

**C.4.2 Development of the Residual**

The CSL equations (see Eq. (C.50)) can be written as

$$\hat{T}(k) = [\hat{\dot{C}}(k) + \hat{\dot{S}}(k)]\hat{\rho}[\hat{\dot{C}}(k) + \hat{\dot{S}}(k)][1 - \hat{\rho}[\hat{\dot{C}}(k) + \hat{\dot{S}}(k)]]^{-1}$$

(C.51)

where $\hat{T}(k) = \hat{H}(k) - \hat{C}(k)$ is the chain function.

Again, it is more convenient to work with the functions, $\Gamma$ and $\Theta$, which are defined as

$$\tilde{\Gamma}(k) = k\hat{T}(k)$$

(C.52)

$$\tilde{\Theta}(k) = k\hat{\dot{C}}(k)$$

(C.53)
Note that it follows from Eqs. (C.98) and (C.100) that

\[ \Gamma(r) = rT(r) \]  
\[ \Theta(r) = rC(r) \]  

(C.54)  
(C.55)

The residual is defined by

\[
R(k) = k\hat{T}(k) - k[\hat{C}(k) + \hat{S}(k)]\overline{\rho}[\hat{C}(k) + \hat{S}(k)] \\
\times \{1 - \overline{\rho}[\hat{C}(k) + \hat{S}(k)]\}^{-1} 
\]

(C.56)

\[
= \hat{\Gamma}(k) - [\hat{\Theta}(k) + k\hat{S}(k)]\overline{\rho}[\hat{\Theta}(k) + k\hat{S}(k)] \\
\times \{k - \overline{\rho}[\hat{\Theta}(k) + k\hat{S}(k)]\}^{-1} 
\]

(C.57)

The dependence of \( \Theta \) on \( \Gamma \) is given by the closure relation. The HNC closure (see Eqs. (6.33)-(6.36)) can be written as

\[
c_{\alpha\gamma}(r) = \exp[-\beta u_{\alpha\gamma}(r) + \tau_{\alpha\gamma}(r)] - 1 - \tau_{\alpha\gamma}(r) 
\]

(C.58)

\[
c_{l\alpha\gamma}(r) = \exp[-\beta u_{\alpha\gamma}(r) + \tau_{\alpha\gamma}(r)][\tau_{\alpha\gamma}(r) - \tau_{\alpha\gamma}(r)] 
\]

(C.59)

\[
c_{r\alpha\gamma}(r) = \exp[-\beta u_{\alpha\gamma}(r) + \tau_{\alpha\gamma}(r)][\tau_{\alpha\gamma}(r) - \tau_{\alpha\gamma}(r)] 
\]

(C.60)

\[
c_{b\alpha\gamma}(r) = \exp[-\beta u_{\alpha\gamma}(r) + \tau_{\alpha\gamma}(r)][\tau_{\alpha\gamma}(r) + \tau_{\alpha\gamma}(r)] - \tau_{\alpha\gamma}(r) 
\]

(C.61)

This implies that

\[
\Theta_{\alpha\gamma}(r) = r \exp[-\beta u_{\alpha\gamma}(r) + \Gamma_{\alpha\gamma}(r)/r] - r - \Gamma_{\alpha\gamma}(r) 
\]

(C.62)

\[
\Theta_{l\alpha\gamma}(r) = \exp[-\beta u_{\alpha\gamma}(r) + \Gamma_{\alpha\gamma}(r)/r]\Gamma_{\alpha\gamma}(r) - \Gamma_{\alpha\gamma}(r) 
\]

(C.63)

\[
\Theta_{r\alpha\gamma}(r) = \exp[-\beta u_{\alpha\gamma}(r) + \Gamma_{\alpha\gamma}(r)/r]\Gamma_{\alpha\gamma}(r) - \Gamma_{\alpha\gamma}(r) 
\]

(C.64)

\[
\Theta_{b\alpha\gamma}(r) = \exp[-\beta u_{\alpha\gamma}(r) + \Gamma_{\alpha\gamma}(r)/r][\Gamma_{\alpha\gamma}(r)\Gamma_{\alpha\gamma}(r)/r + \Gamma_{\alpha\gamma}(r)] \\
- \Gamma_{\alpha\gamma}(r) 
\]

(C.65)

Given the function \( \Gamma \), one can then compute the residual, \( R \), by first computing \( \Theta \) from Eqs. (C.62)-(C.62), and then using Eq. (C.51).
C.4.3 Development of the Jacobian

In this section, I derive the Jacobian for the CSL equations. To begin, I first compute 
\[ \frac{\delta \tilde{\Theta}_{\alpha\gamma}^{AB}(k)}{\delta \Gamma_{\alpha'\gamma'}^{A'B'}(k')} \]. Specifically,

\[ \frac{\delta \tilde{\Theta}_{\alpha\gamma}^{AB}(k)}{\delta \Gamma_{\alpha'\gamma'}^{A'B'}(k')} = \int_0^\infty dx \frac{\delta \tilde{\Theta}_{\alpha\gamma}^{AB}(k)}{\delta \Theta_{\alpha\gamma}^{AB}(x)} \frac{\partial \Theta_{\alpha\gamma}^{AB}(x)}{\partial \Gamma_{\alpha'\gamma'}^{A'B'}(x)} \delta_{\alpha'\gamma'}^{A'B'}(x) \]

\[ = \int_0^\infty dx [\frac{\delta \Theta_{\alpha\gamma}^{AB}(x)}{\delta \Gamma_{\alpha'\gamma'}^{A'B'}(x)}] \frac{1}{2\pi^2} \sin k'x \]

\[ = \frac{1}{\pi} \int_0^\infty dx \cos(k - k')x \frac{\delta \Theta_{\alpha\gamma}^{AB}(x)}{\partial \Gamma_{\alpha'\gamma'}^{A'B'}(x)} \]

\[ = \frac{1}{\pi} \int_0^\infty dx \cos(k + k')x \frac{\delta \Theta_{\alpha\gamma}^{AB}(x)}{\partial \Gamma_{\alpha'\gamma'}^{A'B'}(x)} \]

\[ = [\Phi_{\alpha\gamma}^{A'B'}(k - k') - \Phi_{\alpha\gamma}^{A'B'}(k + k')] \delta_{\alpha'\gamma'}^{A'B'}(k, k') \]

\[ = F_{\alpha\gamma,\alpha'\gamma'}^{A'B'}(k, k') \] (C.66)

where \( \Phi \) is given by

\[ \Phi_{\alpha\gamma,\alpha'\gamma'}^{A'B'}(k) = \frac{1}{\pi} \int_0^\infty dx \cos kx \frac{\partial \Theta_{\alpha\gamma}^{AB}(x)}{\partial \Gamma_{\alpha'\gamma'}^{A'B'}(x)} \] (C.67)

The elements of, \( \frac{\partial \Theta_{\alpha\gamma}^{AB}(r)}{\partial \Gamma_{\alpha'\gamma'}^{A'B'}(r)} \), are shown below for the HNC closure

\[ \frac{\partial \Theta_{\alpha\gamma}^{oo}(r)}{\partial \Gamma_{\alpha'\gamma'}^{oo}(r)} = \{\exp[-\beta u_{\alpha\gamma}(r) + \Gamma_{\alpha\gamma}(r)/r] - 1\} \delta_{\alpha'\gamma'}^{A'B'} \] (C.68)

\[ \frac{\partial \Theta_{\alpha\gamma}^{oo}(r)}{\partial \Gamma_{\alpha'\gamma'}^{oo}(r)} = 0 \] (C.69)

\[ \frac{\partial \Theta_{\alpha\gamma}^{oo}(r)}{\partial \Gamma_{\alpha'\gamma'}^{oo}(r)} = 0 \] (C.70)

\[ \frac{\partial \Theta_{\alpha\gamma}^{oo}(r)}{\partial \Gamma_{\alpha'\gamma'}^{oo}(r)} = 0 \] (C.71)

\[ \frac{\partial \Theta_{\alpha\gamma}^{oo}(r)}{\partial \Gamma_{\alpha'\gamma'}^{oo}(r)} = \exp[-\beta u_{\alpha\gamma}(r) + \Gamma_{\alpha\gamma}(r)/r] \Gamma_{\alpha\gamma}(r) \delta_{\alpha'\gamma'}^{A'B'} \] (C.72)

\[ \frac{\partial \Theta_{\alpha\gamma}^{oo}(r)}{\partial \Gamma_{\alpha'\gamma'}^{oo}(r)} = \{\exp[-\beta u_{\alpha\gamma}(r) + \Gamma_{\alpha\gamma}(r)/r] - 1\} \delta_{\alpha'\gamma'}^{A'B'} \] (C.73)

\[ \frac{\partial \Theta_{\alpha\gamma}^{oo}(r)}{\partial \Gamma_{\alpha'\gamma'}^{oo}(r)} = \{\exp[-\beta u_{\alpha\gamma}(r) + \Gamma_{\alpha\gamma}(r)/r] - 1\} \delta_{\alpha'\gamma'}^{A'B'} \] (C.74)

219
\[ \frac{\partial \Theta_{\alpha\gamma}^0(r)}{\partial \Gamma_{\alpha\gamma}^0(r)} = 0 \quad (C.75) \]
\[ \frac{\partial \Theta_{\alpha\gamma}^0(r)}{\partial \Gamma_{\alpha\gamma}^0(r)} = \exp[-\beta u_{\alpha\gamma}(r) + \Gamma_{\alpha\gamma}^0(r)/r] \delta_{\alpha\gamma,\alpha'\gamma'} \quad (C.76) \]
\[ \frac{\partial \Theta_{\alpha\gamma}^0(r)}{\partial \Gamma_{\alpha\gamma}^0(r)} = \left\{ \exp[-\beta u_{\alpha\gamma}(r) + \Gamma_{\alpha\gamma}^0(r)/r] - 1 \right\} \delta_{\alpha\gamma,\alpha'\gamma'} \quad (C.77) \]
\[ \frac{\partial \Theta_{\alpha\gamma}^0(r)}{\partial \Gamma_{\alpha\gamma}^0(r)} = \left\{ \exp[-\beta u_{\alpha\gamma}(r) + \Gamma_{\alpha\gamma}^0(r)/r] - 1 \right\} \delta_{\alpha\gamma,\alpha'\gamma'} \quad (C.78) \]
\[ \frac{\partial \Theta_{\alpha\gamma}^0(r)}{\partial \Gamma_{\alpha\gamma}^0(r)} = \exp[-\beta u_{\alpha\gamma}(r) + \Gamma_{\alpha\gamma}^0(r)/r] \quad (C.79) \]
\[ \frac{\partial \Theta_{\alpha\gamma}^0(r)}{\partial \Gamma_{\alpha\gamma}^0(r)} = \exp[-\beta u_{\alpha\gamma}(r) + \Gamma_{\alpha\gamma}^0(r)/r] \quad (C.80) \]
\[ \frac{\partial \Theta_{\alpha\gamma}^0(r)}{\partial \Gamma_{\alpha\gamma}^0(r)} = \exp[-\beta u_{\alpha\gamma}(r) + \Gamma_{\alpha\gamma}^0(r)/r] \quad (C.81) \]
\[ \frac{\partial \Theta_{\alpha\gamma}^0(r)}{\partial \Gamma_{\alpha\gamma}^0(r)} = \exp[-\beta u_{\alpha\gamma}(r) + \Gamma_{\alpha\gamma}^0(r)/r] \quad (C.82) \]
\[ \frac{\partial \Theta_{\alpha\gamma}^0(r)}{\partial \Gamma_{\alpha\gamma}^0(r)} = \exp[-\beta u_{\alpha\gamma}(r) + \Gamma_{\alpha\gamma}^0(r)/r] \quad (C.83) \]

Next, I derive an expression for the Jacobian. Note that in what follows, summation over repeated indices is implied. Specifically,

\[ J_{\alpha\gamma,\alpha'^\prime \gamma'}^{AB, A'B'} (k, k') = \delta_{\alpha\gamma,\alpha'^\prime \gamma'} \delta(k - k') \]
\[ = \delta_{\alpha\gamma,\alpha'^\prime \gamma'} \delta(k - k') \]
\[ -\frac{\delta \hat{\Theta}_{\alpha\gamma}^{AB}(k)}{\delta \hat{T}_{\alpha'^\prime \gamma'}^{A'B'}(k')} \rho_{\sigma\tau}^{ST}[\hat{\Theta}(k) + k\hat{S}(k)]_{\tau\mu}^{TM} \]
\[ \times \left\{ [k - \sigma[\hat{\Theta}(k) + k\hat{S}(k)][-1]_{\mu\gamma}^{MB} \right\} \]
\[ -[\hat{\Theta}(k) + k\hat{S}(k)]_{\alpha\sigma}^{AS} \rho_{\sigma\tau}^{ST} \frac{\delta \hat{T}_{\mu\tau}^{TM}(k)}{\delta \hat{T}_{\alpha'^\prime \gamma'}^{A'B'}(k')} \]
\[ \times \left\{ [k - \sigma[\hat{\Theta}(k) + k\hat{S}(k)][-1]_{\mu\gamma}^{MB} \right\} \]
\[ -[\hat{\Theta}(k) + k\hat{S}(k)]_{\alpha\sigma}^{AS} \rho_{\sigma\tau}^{ST} [\hat{\Theta}(k) + k\hat{S}(k)]_{\tau\mu}^{TM} \]
\[ \times \left\{ [k - \sigma[\hat{\Theta}(k) + k\hat{S}(k)][-1]_{\mu\gamma}^{MN} \right\} \]

220
\[ \chi(k) = \{ k - \bar{\rho} \hat{\Theta}(k) + k \hat{S}(k) \}^{-1} \] (C.85)

where

\[ \chi(k) = \{ k - \bar{\rho} \hat{\Theta}(k) + k \hat{S}(k) \}^{-1} \] (C.85)

and

\[ \delta^{AB,A'B'}_{\alpha\gamma,\alpha'\gamma'} = \delta_{\alpha\alpha'} \delta_{A A'} \delta_{\gamma \gamma'} \delta_{B B'} + \delta_{\alpha\gamma} \delta_{A B'} \delta_{\gamma \alpha'} \delta_{B A'} (1 - \delta_{\alpha\gamma} \delta_{A B}) \] (C.86)

C.4.4 Long-Range Correlations

For polar fluids, \( c^o \) becomes long-ranged, and behaves asymptotically as\(^{124}\)

\[ c^o_{\alpha\gamma}(r) \longrightarrow - \frac{\beta q_{\alpha} q_{\gamma}}{r}, \quad \text{as } r \rightarrow \infty \] (C.87)

The other direct correlation component bonds, \( c^l, c^s, \) and \( c^b, \) are short ranged,\(^{124}\) that is,

\[ c^{lo}_{\alpha\gamma}(r) = c^o_{\alpha\gamma}(r) - \varphi_{\alpha\gamma}(r) \] (C.88)
where the function, $\psi$, is given by

$$\psi_{\alpha\gamma}(r) = -\frac{\beta q_\alpha q_\gamma}{r}$$  \hspace{1cm} (C.89)

$$\hat{\psi}_{\alpha\gamma}(k) = -\frac{4\pi\beta q_\alpha q_\gamma}{k^2} \exp\left(-\frac{k^2}{4\alpha^2}\right)$$  \hspace{1cm} (C.90)

where $c_{\alpha\gamma}^\circ$ is the short-ranged contribution to $c_{\alpha\gamma}^\circ$, and $\alpha$ is an arbitrary parameter, which is typically chosen to be 1 Å.

Accordingly, the following functions are also short-ranged

$$\Theta^{\star,\circ}(r) = \Theta^\circ(r) - r\psi(r)$$  \hspace{1cm} (C.91)

$$\tilde{\Theta}^{\star,\circ}(k) = \tilde{\Theta}^\circ(k) - k\hat{\psi}(k)$$  \hspace{1cm} (C.92)

and

$$\Gamma^{\star,\circ}(r) = \Gamma^\circ(r) + r\psi(r)$$  \hspace{1cm} (C.93)

$$\tilde{\Gamma}^{\star,\circ}(k) = \tilde{\Gamma}^\circ(k) + k\hat{\psi}(k)$$  \hspace{1cm} (C.94)

where $\Theta^{\star,\circ}$ and $\Gamma^{\star,\circ}$ are the short-ranged contributions to $\Theta$ and $\Gamma$, respectively.

In order to find the Fourier transform of $\Theta^\circ$ ($\Gamma^\circ$), one numerically computes the Fourier transform of $\Theta^{\star,\circ}$ ($\Gamma^{\star,\circ}$), and then adds (subtracts) $k\hat{\psi}(k)$ to the result.

### C.5 Fourier Transforms

In this section, I discuss some properties of Fourier transforms. The three-dimensional Fourier transform of a function, $f$, is defined as

$$\hat{f}(k) = \int d^3r e^{ik\cdot r} f(r)$$  \hspace{1cm} (C.95)

and the inverse of this transformation is given by

$$f(r) = \int \frac{d^3k}{(2\pi)^3} e^{-ik\cdot r} \hat{f}(k)$$  \hspace{1cm} (C.96)
Because the systems of interest in this thesis are isotropic, all functions depend only on the magnitude of \( r \). Therefore, the Fourier transform reduces to

\[
\hat{f}(k) = \frac{4\pi}{k} \int_0^\infty dr \sin kr f(r) \tag{C.97}
\]

and its inverse reduces to

\[
f(r) = \frac{1}{2\pi^2 r} \int_0^\infty dk k \sin kr \hat{f}(k) \tag{C.98}
\]

One transform which I have used extensively in this thesis, and which is closely related to the Fourier transform, is the Fourier sine transform, defined by

\[
\tilde{f}(k) = 4\int_0^\infty dr \sin kr f(r) \tag{C.99}
\]

and the associated inverse transform is given by

\[
f(r) = \frac{1}{2\pi^2} \int_0^\infty dk \sin kr \tilde{f}(k) \tag{C.100}
\]

In order to perform the sine transform numerically, I first approximate it by

\[
\tilde{f}(k_j) = 4\pi \int_0^\infty dr \sin kj r f(r) \\
\approx 4\pi \sum_{i=0}^{N-1} \Delta r \sin[(j\Delta k)(i\Delta r)]f(r_i) \\
\approx 4\pi \Delta r \sum_{i=0}^{N-1} \sin \pi ij f(r_i) \tag{C.101}
\]

where

\[
r_i = i\Delta r \tag{C.102}
\]

\[
k_i = i\Delta k \tag{C.103}
\]
Similarly, the inverse sine transform is approximated by

\[
f(r_j) = \frac{1}{2\pi^2} \int_0^\infty dk \sin kr \hat{f}(k)
\]

\[
\approx \frac{1}{2\pi^2} \sum_{i=0}^{N-1} \Delta k \sin[(i\Delta k)(j\Delta r)] \hat{f}(k_i)
\]

\[
\approx \frac{\Delta k}{2\pi^2} \sum_{i=0}^{N-1} \sin \pi ij \tilde{f}(k_i)
\]  \hfill (C.104)

The sums which appear in Eqs. (C.104) and (C.104) are performed using the Fast Fourier Transform (FFT) method. Using the FFT method requires that the spacing in \( r \) space be related to the spacing in \( k \) space by

\[
\Delta r \Delta k = \frac{\pi}{N}
\]  \hfill (C.105)

where \( N \) is the number of grid points.
Bibliography


